PEROXY COMPOUNDS OF TRANSITION METALS

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I. Introduction

It has been appreciated for at least 140 years that characteristic color reactions may occur when hydrogen peroxide is added to solutions of transition metal derivatives, and solid peroxy compounds of transition metals have been known for more than 100 years. These derivatives, besides having an intrinsic interest of their own, are of considerable and growing importance in relation to the catalysis of oxidations involving hydrogen peroxide or oxygen gas, the catalytic decomposition of hydrogen peroxide itself, and the storage and use of oxygen in biological systems; so we have sought to present a review of what is at present known of transition metal peroxides. We have included less than half of the references we have studied; we hope to have covered most of what is known about those peroxides that have been isolated as solid compounds, though the material is presented in a critical manner; some general principles of transition metal peroxide chemistry that have emerged are mentioned at the end of the article. We have considered the transition series as including scandium, the rare earths, the actinides, and the copper group, but the zinc group peroxides have been omitted. Regarding applications of transition metal peroxides to analysis, and their use as intermediates in catalytic oxidation or decomposition, we have done no more than to include brief summaries and to give a number of further references; these topics demand (and in some cases have been given) reviews to themselves.

Nowadays, when it is sometimes considered safe to ignore work published before 1945, it is chastening to realize how large a proportion of the most convincing work dealing with transition metal peroxides was completed before 1914. It is clear that the broad range of physical and chemical methods available to the modern chemist should be able to extend and deepen our knowledge of these compounds, and we hope that this review may help to stimulate studies of this kind.

II. Detection and Estimation of Peroxide in Transition Metal Compounds

It is not always easy to prove that a particular compound contains peroxide oxygen, or to discover the amount of peroxide oxygen present; the only ultimate criterion is X-ray crystallography. In most cases chemical tests, coupled with elemental analysis, are capable of showing conclusively whether peroxide is present or not, but in some compounds, notably those in which other, readily oxidized groups are present as well as peroxide, chemical methods may not be very reliable. In the chemistry of "main group" peroxides, a distinction has been drawn between "bound" (or "true") peroxide and "H_2O_2 adducts" (or "false" peroxide); in transition metal derivatives, the former class are "complex" peroxides, while "ionic" peroxides behave in aqueous solution as do the H_2O_2 adducts. Attempts have been made to devise chemical tests to distinguish between these two classes; since such a distinction must depend on the resistance of the complex peroxide to hydrolysis, it is bound to be to that extent unreliable.

A. PHYSICAL METHODS

The only reliable method of determining peroxy groups in solids is that of X-ray crystallography. Few structures of transition metal peroxides have been determined and, of these, few have R values low enough to provide unequivocal proof that the structures are correct in detail.[1] Recent

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[1] The R values used in this chapter in connection with crystallographic work represent the function

$$\frac{\Sigma\,\big|\,|F_{obs}| - |F_{cacl}|\,\big|}{\Sigma\,|F_{obs}|}$$

this is a measure of the agreement between observed and predicted diffraction patterns. Ideally, this factor should be no larger than the experimental errors, which with normal photographic methods are of the order of 10–15%.

studies (*137*, *181*, *182*, *551*) have shown that the infrared spectra of many transition metal peroxides contain strong absorption in the range 800–900 cm^{-1}, which has been assigned to stretching modes involving the peroxy group.

B. Chemical Methods

In a number of the simpler transition metal peroxides, the peroxide oxygen has been determined by measuring the amount of O_2 evolved on thermal decomposition. Where there is no other oxidizable group present, and where the transition metal does not change its oxidation state on thermal decomposition of the peroxide, half a molecule of O_2 is evolved to each peroxy group decomposed, the remaining oxygen atom remaining as a metal–oxygen system. This method is useful and reliable, provided the compound in question decomposes cleanly and simply (*58*, *59*, *304*, *504*).

Acidified potassium permanganate solution is generally used in the determination of H_2O_2 (*10*), and its use in the analysis of transition metal peroxides seems to be accurate and reliable, so long as the necessary precautions are taken, particularly with respect to other redox systems that may be present. Cerium(IV) has been used similarly (*181*, *551*). Both of these reagents give a measure of the total peroxide content.

Acidified potassium iodide has been used in the presence of catalytic amounts of manganese(II) or magnesium ions to analyze peroxy compounds (*343*), but H_2O_2 gives no iodine with neutral potassium iodide solution (*72*); it has been claimed that bound peroxide liberates iodine quantitatively under these conditions, and the distinction has been made the basis of a method designed to determine bound peroxide. Riesenfeld (*449*) believed that addition of concentrated neutral potassium iodide solution to a true peroxycarbonate produces iodine immediately, while with H_2O_2 adducts of carbonates, only O_2 is evolved (presumably from decomposition of the H_2O_2). Subsequent discussion has shown that this view was oversimplified, and that the effects of pH and of the degree and rate of hydrolysis had not been considered (*297*, *306*, *362*, *443*, *530*, *531*). The use of a phosphate buffer to maintain pH 7.5–8 was proposed by Liebhafski (*311*); under these conditions, the distinction between "true" and "false" peroxides seemed clearer, and the modified test was used to investigate a number of transition metal peroxides (*492*), though some of the results bear little relation to the structures of the compounds studied (as determined by other and more reliable methods). Other studies, however (*245*, *453*), suggested that the test is only valid at pH 7; more recent and more exhaustive investigation of peroxycarbonates, using the Riesenfeld-Liebhafski test, have shown that its reliability is in doubt (*384*), while we have found that with such well-characterized systems as the tetraperoxychromate(V) anion, $[Cr(O_2)_4]^{-3}$, or the μ-peroxodicobalt cations the test either does not work at all or gives wildly varying and inconsistent results (*101*). The use of the test in transition metal compounds is further complicated by the range of possible redox reactions of the metal itself with iodide ion or with iodine; all in all, while in some cases the test has proved useful, its reliability even in qualitative analysis is questionable.

Potentiometric titration, using sodium hypochlorite and potassium ferricyanide, of the H_2O_2 liberated from peroxy compounds on hydrolysis in alkaline solution has been used to estimate the amount of "active" oxygen in these compounds (*452, 453*). The use of acetone extraction at 0°C has been suggested (*581*), but this method is limited in scope, and has received little attention.

III. Some Physical Constants of H_2O_2 and Related Species

Pure hydrogen peroxide is a pale blue, syrupy, endothermic liquid. Its dielectric constant and proton dissociation constant indicate that the liquid is a good ionizing solvent, somewhat more dissociated than water. The redox potentials in acid and in base are summarized as follows:

Acid $$\overbrace{O_2 \underset{+0.693}{\text{————}} H_2O_2 \underset{+1.76}{\text{————}} H_2O}^{+1.229}$$

Base $$\overbrace{O_2 \underset{-0.084}{\text{————}} HO_2^- \underset{+0.87}{\text{————}} OH^-}^{+0.38}$$

These figures show that hydrogen peroxide tends to act as an oxidizing or a reducing agent; the oxidizing power, i.e., the tendency to form water or OH^-, decreases with increasing pH, whereas the potential for oxidation of hydrogen peroxide, or the reducing power, increases with increasing pH. Other physical properties are set out in Table I.

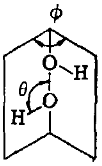
IV. Scandium and the Lanthanides

Peroxy derivatives of scandium, lanthanum, praseodymium, and neodymium have been obtained at temperatures below 0° by treating a suspension of the metal hydroxide with H_2O_2, or by adding alkali to a solution containing the metal cation and H_2O_2 (*70, 71, 96, 361, 497*). The compounds of scandium and lanthanum contain peroxide and the metal in the molar ratio 1:1 (as determined using potassium permanganate), even after treatment with 90% H_2O_2, though it was suggested that the initial product with praseodymium was a triperoxide that subsequently decomposed (*353*). Elaborate phase studies (*328–330*) indicate the formation of compounds

TABLE I

SOME PHYSICAL CONSTANTS OF H_2O_2 AND RELATED SPECIES

A. Distances and angles



Species	r(O—O) (Å)	r(O—H) (Å)	θ	ϕ	Phase	Reference
H_2O_2	1.47 ± 0.02	—	—	—	Vapor[a]	*(166)*
	1.475 ± 0.004	0.96 ± 0.01	94.8 ± 2°	119.8 ± 3°	Vapor[b]	*(433)*
	1.49 ± 0.02	—	96°52′	93°51′	Solid[c]	*(1)*
F_2O_2	1.217	1.575 (O—F)	109°30′	87°30′	Vapor[d]	*(233)*

Species	r(O—O) (Å)	Systems	Phase	Reference
$O_2^{=}$	1.49 ± 0.04	MO_2(M = Sr, Ba, Zn, Cd)	Solid	*(2, 146)*
		M_2O_2(M = Li, Na, K, Rb, Cs)		*(222, 529)*
	1.48	$CaO_2 \cdot 8H_2O$		*(209)*
O_2^-	1.31 ± 0.03	β-NaO_2		*(595)*
	1.28 ± 0.02	α-KO_2		*(3)*
O_2	1.2107 ± 0.0001	Oxygen gas	Vapor	*(366)*
O_2^+	1.1227 ± 0.0001		Vapor	*(218)*
	1.17 ± 0.17	$(O_2)PtF_6$	Solid	*(26)*

B. Vibrational properties: point group C_2

Mode, approximate description, and symmetry class	Frequency (cm^{-1})	Reference	Force constants (dyne/cm × 10^{-5})	Reference
ν_1 (O—H) stretch *a*	3599.2	*(433)*	(O—H) stretch, 7.28	*(164)*
ν_2 (O—H) bend *a*	1380	*(433)*	(O—O) stretch, 3.84	
ν_3 (O—O) stretch *a*	890	*(163)*	(OOH) bend, 0.89	
ν_4 Torsion *a*	314	*(94)*	(HO—OH) bend, 0.11	
ν_5 (O—H) stretch *b*	3607.9	*(433)*		
ν_6 (O—H) bend *b*	1266	*(163)*		

[a] Electron diffraction.

[b] Infrared.

[c] X-ray.

[d] Microwave.

C. Some thermodynamic properties

For H_2O_2, heat of formation $\Delta H_f{}^\circ = -32.52$ kcal/mole at 25°C (*464*)
$\Delta G^\circ = -25.24$ kcal/mole at 25°C (*464*)

Bond dissociation energies

Bond	Species	Energy (kcal/mole)	Reference
(O—O)	H_2O_2	47.8	(*312*)
(O—H)	H_2O_2	90.0	(*145*)
(O—H)	OH	101.5	(*25*)
(O=O)	O_2	117.96	(*116*)

D. Other properties

Dipole moment $\mu = 2.13$ D in dioxane (*314*)
Dielectric constant $\epsilon = 84.9$ at 0°C (*187*)
Conductivity $\lambda = 4.0 \times 10^{-7}$ ohm cm^{-1} (*467*)
Molar diamagnetic susceptibility $\chi_m = -17 \times 10^{-6}$ cgsu/mole at 10°C (*486*)
Polarizability $\alpha = 2.3 \times 10^{24}$ cc/molecule at 25°C (*162*)
Barrier to internal rotation = 3.5 kcal/mole (*165*)
Proton dissociation constant $K = 2.24 \times 10^{-12}$ at 25°C (*133*)

of lanthanum, praseodymium, and neodymium that are formulated as $M_2O_4 \cdot 2H_2O$ (at 0°) or $M_2O_4 \cdot H_2O$ (at $-20°$), though the analytical data presented are not entirely convincing, and none of these substances was obtained pure; the molar ratio (peroxide:metal) seems to be 1:2, though evidence was also obtained for the formation of a 1:1 peroxide of neodymium, formulated as Nd_2O_5 (*328*). These solids are not very stable thermally, losing oxygen slowly at room temperature and rapidly at 100°; they cannot be dehydrated without loss of peroxide oxygen. With dilute acids they give O_2, and with concentrated sulfuric acid ozone is evolved. Little else is known of their properties; it is assumed that the metals are all in the +3 state.

Under the same conditions, cerium forms an apparently definite compound formulated as $CeO_3 \cdot 2H_2O$, in which the metal is in the +4 state and the ratio (peroxide:metal) is 1:1 (*303*, *327*, *408*, *409*, *489*); there is some evidence that an unstable cerium(III) peroxide is formed as an intermediate in the reaction between cerium(III) hydroxide and H_2O_2 (*303*). The heat of formation of the substance, often described as $Ce(O_2H)(OH)_3$, has been measured; the compound loses O_2 rapidly at 60–80°, and with dilute acids gives O_2 and Ce(III).

Phase studies indicate the formation of $Ce(O)(O_2) \cdot H_2O$, $Ce(O)(O_2)$, and $Ce(O_2)_2$ at low temperatures, though no anhydrous solids seem to have been isolated (*327*); the diperoxy derivative is extremely unstable.

In the presence of citrate, cerium(IV) forms a soluble complex with H_2O_2; the species is colored and contains two peroxy groups to each cerium atom (*14, 539*).

V. Titanium

The appearance of an orange color when H_2O_2 is added to an acid solution of Ti(IV) was noted as long ago as 1870: in the ninety-odd years since then, remarkably little has been established for certain about peroxy compounds of titanium. As several studies have made clear, the color of an aqueous solution of Ti(IV) in H_2O_2 depends on the pH, being orange in acid solutions, yellow in solutions of about pH 8, and colorless in strongly alkaline solutions. Several solid peroxy derivatives have been isolated, but there is little agreement about their formulas and structures.

A. Reactions at High pH

A spectrophotometric investigation of solutions containing Ti(IV), H_2O_2, sulfate, and potassium carbonate indicates that at pH greater than 10, a colorless species containing two peroxy groups per titanium atom is formed; this is given the formula $[Ti(O_2)_2(OH)_2]^{-2}$ (*370*). Different spectrophotometric studies (*11, 13*) indicate that under these conditions the complex formed contains peroxide and titanium in the ratio 1:1; at pH 10–13, the species is formulated as $[Ti(O)(O_2)(OH)_2]^{-2}$, though at pH 14 the species formed is given the structure $[Ti(O)(O_2)_2]^{-2}$.

Solid tetraperoxytitanates of formulas $M_4{}^ITi(O_2)_4{\cdot}6H_2O$ have been obtained by adding ice-cold solutions of H_2O_2 and alkali metal hydroxide to peroxytitanium hydrate (see below) (*489*).[1a] These compounds seem to be genuine complex peroxides, and not orthotitanates with H_2O_2 of crystallization (*238*), as had been suggested (*492*) on the basis of their behavior in the Riesenfeld-Liebhafski test. These tetraperoxytitanates are decomposed by aqueous acid to peroxytitanium hydrate. At the same time, the differently hydrated compounds $M_4{}^ITi(O_2)_4{\cdot}2.4H_2O$ (where M is Na or K) behave in solution as if they should be represented by the formulas $M_4TiO_6{\cdot}2H_2O_2$, the criterion being again the Reisenfeld-Liebhafski test (*32*); in view of the spectrophotometric study mentioned above (*370*) it seems likely that, while tetraperoxytitanates may exist in the solid state, the species present in alkaline solution probably contains no more than two peroxy groups per titanium atom.

[1a] The compounds described (*355*) as $K_4TiO_9{\cdot}10H_2O$ and as $(Na_2O_2)_4Ti_2O_7{\cdot}10H_2O$ have been shown (*238*) to be tetraperoxytitanates.

The yellow solid obtained by the reaction of ammonium hydroxide and ammonium fluoride with peroxytitanium hydrate, or by the decomposition of $(NH_4)_3TiF_6$ in air followed by dissolution of the resulting solid and saturation of the solution with ammonium fluoride, contains the $[Ti(O_2)F_5]^{-3}$ ion (*400, 401, 404*). When dissolved in a cold aqueous solution of potassium chloride this ion decomposes to the tetrafluoroanion $[Ti(O_2)F_4]^{-2}$, which may also be obtained by the action of H_2O_2 on K_2TiF_6. Attempts to repeat the preparation of the $[Ti(O_2)F_4]^{-2}$ ion (*489*) have failed.

X-ray examination of the solid $(NH_4)_3[Ti(O_2)F_5]$ showed that it is isomorphous with $(NH_4)_3ZrF_7$ (*397*); calculations from the observed intensities indicate that the ion belongs to the asymmetric group O_h^5—Fm3m. This is an interesting example of seven-coordination which is rare in transition metal complexes and might well repay closer attention to determine the exact orientation of the peroxy group.

B. REACTIONS IN NEUTRAL SOLUTION

The several spectrophotometric studies made of the reaction between Ti(IV) and H_2O_2 in neutral solution for once agree in formulating the yellow species present as containing one peroxy group for each titanium atom (*11, 13, 370, 469*). A shift in the ultraviolet absorption maximum as the concentration of titanium increased was taken as showing that the species is polymeric (*434*), but the observation derives from a wrongly prepared starting material (*309*); there is no evidence to suggest that the species present in solution is not a monomer.

By the addition of alcohol to a solution of titanyl sulfate containing hydrogen peroxide and adjusted to pH 8.6 with potassium carbonate, a yellow solid of formula $TiO_3 \cdot 2H_2O$ has been obtained (*11, 13, 309*). Similar solids are precipitated by the addition of excess of base to an acid solution of Ti(IV) containing H_2O_2 (*398, 399*), and from the reaction between H_2O_2 and alkaline solutions of Ti(IV) (*565*); the material, which has strong oxidizing properties, has been called peroxytitanium hydrate. Analysis has established the presence of one peroxy group to each titanium atom (*309, 356, 358, 398, 399, 434, 465, 489, 493, 505, 565*), but there has been some discussion as to the number of molecules of water of crystallization; the most generally accepted number is two (*489, 505*), but the formula $TiO_3 \cdot H_2O$ has received some support (*140, 256, 277, 456*). It seems clear that the peroxy group is not present as H_2O_2 of crystallization, but in view of the uncertainty of formula it is not surprising that the relative arrangement of peroxy group and titanium atom is not known. The compound passed through cation- and anion-exchange columns and so is uncharged (*370*).

Peroxytitanium hydrate reacts with alkali and H_2O_2 to give tetraperoxytitanates, from which it may be obtained on hydrolysis (*238, 489, 492*). It may also be obtained by hydrolysis of complex peroxytitanyl sulfate (*438, 487, 493*) and perchlorate (*238*), and has been produced by ultraviolet and γ-radiolysis of solutions of Ti(IV) (*16*), presumably through intermediate formation of H_2O_2.

The compound described by Billy (*51–53*) as $Ti_2O_5 \cdot nH_2O$ was almost certainly a mixture of $TiO_3 \cdot aq$ and $TiO_2 \cdot aq$. An attempt to rationalize the triangular peroxytitanyl group by the reaction

$$(\pi\text{-}C_5H_5)_2TiCl_2 + H_2O_2 \rightarrow (\pi\text{-}C_5H_5)_2Ti(O_2)$$

has failed (*102*). There was no reaction with alkali metal peroxides; and the reaction with 10% H_2O_2 at 0°C was very vigorous—the only recoverable product was TiO_2.

C. Reactions in Acid Solution

The reaction between Ti(IV) and H_2O_2 in acid solution, giving a red color, has been extensively studied because of its importance in analysis; even now, however, there is much uncertainty as to what the colored species may be. Spectrophotometric studies indicate that it contains one peroxy group to each titanium atom, but this is where general agreement ends.

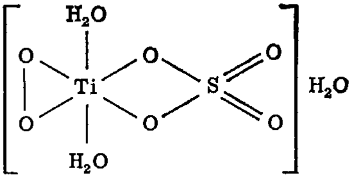
In sulfuric acid solutions, it was originally suggested on the basis of transport studies that the colored complex is anionic, perhaps $[Ti(O_2)(SO_4)_2]^=$ (*489*); the analogous titanium peroxyoxalate anion $[Ti(O_2)(C_2O_4)_2]^=$ is formed by the reaction between H_2O_2 and the titanyl oxalate anion $[Ti(O)(C_2O_4)_2]^=$ (*345, 438*). Hydrolysis of the sulfate complex gives peroxytitanium hydrate (*51, 438, 487, 493*). On the other hand, it has often been claimed that the ultraviolet absorption is unaffected, save in intensity, by changing the anion present (*13, 156, 238, 370, 479*) (though this has been contested) (*386*); because of this, and on the strength of dialytic experiments (*238*), the colored species has been formulated as a cation.

The species present at pH < 3 has been described as $[Ti(O_2) \cdot 3H_2O]^{+2}$ (*370*), as $[Ti(H_2O_2)]^{+4}$ (*13*), and as $[Ti(OH)_2 \cdot H_2O_2]^{+2}$ (*555*); at pH between 3 and 6 the various formulas $[Ti(O_2)OH \cdot 2H_2O]^+$ (*370*) $[Ti(O_2H)]^{+3}$ and $[Ti(O_2)]^{+2}$ (*13*) have been proposed, though it is hard to understand how the details of some of these structures could have been determined spectrophotometrically from the evidence presented. The addition of alcohol to solutions containing potassium sulfate, Ti(IV), sulfuric acid, and H_2O_2 leads to the precipitation of red solids of formulas $K_2SO_4 \cdot Ti(O_2)SO_4 \cdot 3H_2O$ (from solutions of pH < 3) or $4K_2SO_4 \cdot Ti(O_2)OH \cdot SO_4 \cdot 2H_2O$ (from solutions of 3 < pH < 6 (*51, 348, 370, 489, 493*); these compounds are usually supposed to contain the peroxytitanium cation, and the peroxytitanium species are held on cation-exchange resins (*370*), though it is perhaps worth noting that the former could well contain the anion $[Ti(O_2)(SO_4)_2]^{-2}$. Various measurements have been made of the dissociation constant of the red complex; these have been interpreted on the basis of equations such as

$$Ti(O)SO_4 + H_2O_2 \rightleftharpoons Ti(O_2)SO_4 + H_2O$$

The results are wildly divergent (*13, 47, 156, 217, 479*).

If an excess of H_2O_2 is added to a solution of titanyl sulfate in concentrated sulfuric acid, a dark red amorphous solid is obtained when the solution is evaporated to dryness (*sic*). This solid analyzes as $Ti(O_2)SO_4{\cdot}3H_2O$; it gives a positive Riesenfeld-Liebhafski test and is freely soluble in both water and alcohol, though hydrolysis occurs in dilute (*sic*) aqueous solution. The complex shows only feeble cathodic migration when the solution in dilute sulfuric acid is electrolyzed, and so appears to be a nonelectrolyte; molecular weight determinations in aqueous acid solution indicate only 28% dissociation from the value for a monomer (*sic*), though the significance of this measurement is open to question since there is the possibility of some hydrolysis. These observations (*387*), coupled with somewhat inconclusive infrared spectroscopy (*254, 255*) and differential thermal analysis and with some differences between the ultraviolet spectra of this species and that formed in perchloric acid, which is formulated (*386*) as $Ti(O_2)(ClO_4)_2$, have been used by Patel to propose the structure given below for the sulfato compound



He has proposed similar structures for compounds obtained from solutions of Ti(IV), H_2O_2, and certain dibasic organic acids such as oxalic (*253, 254, 278, 279, 385*), malonic (*252, 253, 254, 257, 385*), and maleic (*252, 253, 254, 385*). Similar preparative and analytical methods have been employed, and the oxalato species is probably the best characterized of these derivatives.

Thermal studies (*253*) indicating that the oxalate derivative is more stable than the malonate or the maleate compounds have been taken to imply that the five-membered ring of the oxalate derivative is under minimal strain, while the appearance of two bands in the infrared spectra of these compounds (*385*), which have been assigned rather tenuously to vibrations of the peroxy group, has been taken as showing that the O—O bond in these compounds is bent (whatever that may mean). The possible effects of crystal field splitting seem to have been ignored.

These conflicting observations seem to be almost impossible to interpret without the help of X-ray crystallography. At the same time if a cation were formed at all, it would be expected to be formed in concentrated sulfuric acid solution, unless dehydration greatly reduced the basic properties of the system; furthermore, it is hard to see why a compound obtained from so strongly dehydrating a solvent should have one molecule of uncoordinated water of crystallization.

The action of H_2O_2 upon Ti(IV) salts in phosphoric and acetic acids (*134*) and upon complex chlorides and pyrophosphates of Ti(IV) (*348*) has been shown to give peroxycomplexes, though the structures advanced for these are very doubtful. The addition of H_2O_2 to a solution of Ti(IV) and EDTA in perchloric acid has been shown to form the ion $[Ti(H_2O_2)(OH)_2(EDTA^{4-})]^{-2}$; such solutions are pale yellow in color (*555*). The same spectrophotometric study has been used to evaluate various equilibria in this system and the $Ti(IV)/H_2O_2$ system. Addition of a large excess of EDTA to these solutions precipitates a solid complex which is electrically neutral and which has been formulated as $[Ti(O_2H)(EDTA^{3-})]$.

VI. Zirconium

Reaction of a Zr(IV) salt in acid or alkaline solution with H_2O_2 produces a white precipitate which has been formulated as $ZrO_3 \cdot nH_2O$, where n varies between 3 and 5 (*18, 19, 20, 96*). These compounds contain one peroxy group per zirconium atom.

The reaction of Zr(IV) salts with an excess of H_2O_2 results in a peroxidic hydrolysis (*212, 409*); the final product is represented by the formula $ZrO_3 \cdot 2H_2O$, or perhaps $Zr(OH)_3O_2H$. The possible reactions are described by the equations:

$$(i)\quad Zr(IV) + 4H_2O_2 \rightarrow Zr(O_2H)_4 \xrightarrow{H_2O} Zr(OH)_3(O_2H) + 3H_2O_2$$

$$(ii)\quad Zr(OH)_4 + H_2O_2 \rightarrow Zr(OH)_3(O_2H) + H_2O$$

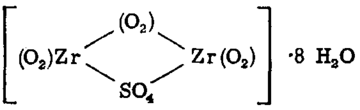
$$(iii)\quad ZrO_2 \cdot 2H_2O + H_2O_2 \rightarrow ZrO_3 \cdot 2H_2O$$

$$(iv)\quad Zr(OH)_4 + O \rightarrow Zr(OH)_3 \cdot O_2H$$

The application of phase diagrams and thermogravimetric analysis to the reaction between H_2O_2 and zirconium(IV) hydroxide in the range 0° to $-20°C$ has shown (*325, 326*) that the primary product is $ZrO_3 \cdot 2H_2O$, which may then undergo successive dehydration to give ZrO_3 (though the anhydrous compound was not isolated). The peroxyzirconium hydrate is said to be obtained by the reaction of hydrated zirconia ($ZrO_2 \cdot 2H_2O$) with NaOCl.

The reaction of $ZrO_3 \cdot 2H_2O$ with ice-cold alkali metal hydroxide in the presence of excess H_2O_2 produces a white solid (*408*, *489*), which contains the tetraperoxyzirconate ion, $[Zr(O_2)_4]^{-4}$; a close physical study of the production of the reaction between Zr(IV) and alkaline H_2O_2 has shown (*230*) that the appearance and composition of the product depends upon the conditions of its formation. The compound may be the salt of an isopoly acid formed by the condensation of more highly peroxidized units; the presence of peroxy groups of three different levels of stability is indicated, and the polyacid is shown to contain hydroxyl groups and either 3 or 5 zirconium atoms in its basic unit. In solutions of pH 12–14 in the presence of an excess of H_2O_2, analysis suggests that the zirconium is present as the anionic $[Zr(O)(O_2)_2]^{-2}$ (*12*); studies using the ultraviolet absorption maxima at 465 mμ and 255 mμ have shown that, as the pH of such solutions decreases, anionic complexes in which the ratio of Zr(IV) to peroxide has the values 1:1 and 2:1 are formed. There appears to be no evidence as to whether these species are monomeric or condensed polyacid derivatives.

The reaction of H_2O_2 with ice-cold aqueous solution of zirconium(IV) sulfate produces a white solid of formula $Zr_2O_6SO_4 \cdot 8H_2O$ (*489*, *538*). It is suggested that this is a basic peroxosulfate of structure



but there is no physical evidence to support this. The formation of this compound has been proposed as a method of separating zirconium from hafnium.

A complex peroxosulfatozirconate, analogous to that of titanium mentioned above, is formed when H_2O_2 is added to an ice-cold mixture of Zr(IV), potassium sulfate, and sulfuric acid (*489*). As previously, the formulation of this $[Zr(O_2)(SO_4)_2]^{-2}$ ion is not supported by any physical evidence.

Spectrophotometric studies have shown (*15*, *382*) that zirconium does not form a peroxy species in concentrated acid solution. The product obtained by refluxing ZrO_2Cl_2 with urea and H_2O_2, of composition H_3ZrO_4, has found some application as a stationary phase oxidant in chromatography (*155*); peroxyzirconium hydrate has found application in analysis (*158*) and in the production of high purity zirconia (*561*).

VII. Hafnium

Little is known about the peroxide chemistry of hafnium. The addition of ice-cold H_2O_2 to hafnium sulfate produces a white insoluble precipitate of composition $HfO_3 \cdot 2H_2O$ (*220, 489*) for which, by analogy with other elements, the structure denoted by $Hf(OH)_3O_2H$ has been proposed.

Peroxyhafnium hydrate is insoluble in cold alkaline H_2O_2, in contrast to its zirconium analog; this prevents the formation of the anionic tetraperoxyhafnate $[Hf(O_2)_4]^{-4}$. However, the complex peroxysulfate hafnate anion $[Hf(O_2)(SO_4)_2]^{-2}$ is formed in a manner exactly similar to the analogous titanium and zirconium complexes (*489*).

VIII. Vanadium

A. VANADIUM PENTOXIDE–WATER SYSTEM

Any discussion of the vanadium–H_2O_2 system should be prefaced by a short description of the vanadium pentoxide–water system. It has been shown (*465*) by means of potentiometry and absorption spectra that vanadium(IV) exists as VO^{2+} in the acidity range $2.95\,M \geqslant [H^+] \geqslant 0.002\,M$. Similarly (*301, 466*) V(V) exists as VO_2^+ in the acidity range $2.9\,M \geqslant [H^+] \geqslant 0.05\,M$; this formulation is preferred to $V(OH)_4^+$. The hydrolysis of the VO_2^+ ion by acid was studied with various total concentrations of vanadium in perchlorate media of different ionic strength. In the range $3 < pH < 8$ the assembled data are consistent with the existence of $(V(O)_2)_{10}(OH)_{14}^{-4}$ over the biggest range of Z (the number of OH groups per VO_2^+ group) (*509*), so that initially hydrolysis occurs according to

$$10V(O)_2^+ + 14H_2O \rightleftharpoons (V(O)_2)_{10}(OH)_{14}^{-4} + 14H^+$$

Conductometric and potentiometric titrations of vanadic acid (*321*), obtained by passing orthovanadate through an ion-exchange column, give support to its formulation as a decavanadate species. On the grounds of simplicity and from X-ray crystallography of isopolyvanadates (*131*), it is suggested that $H_2V_{10}O_{28}^{-4}$ is hydrolyzed successively to $HV_{10}O_{28}^{-5}$ and $V_{10}O_{28}^{-6}$; the hydrolysis constants are summarized below for $1\,M$ perchlorate solutions.

$$10VO_2^+ + 8H_2O \rightleftharpoons H_2V_{10}O_{28} + 14H^+ \ (\ln k_{14,10} = -6.82 \pm 0.17)$$
$$H_2V_{10}O_{28}^{-4} \rightleftharpoons HV_{10}O_{28}^{-5} + H^+ \ (\ln k_{15,10} = -3.6 \pm 0.3)$$
$$HV_{10}O_{28}^{-5} \rightleftharpoons V_{10}O_{28}^{-6} + H^+ \ (\ln k_{16,10} = -5.8 \pm 0.1)$$

Further investigation (*172, 243, 246–248, 350, 378, 415*) using a variety of techniques has confirmed these results and shown that the conclusions are also correct for the concentration range $1.05 \times 10^{-3} > [V^V] > 1.05 \times 10^{-4}$ at an ionic strength of 3.0. As the pH of vanadium(V) solution increases beyond 6.5, a depolymerization occurs and the metavanadate ion species is formed. The exact nature of the metavanadate ion is still not satisfactorily elucidated. On the one hand Jahr (*242, 243, 246*) and

Glemser (*172*), as a result of cryoscopic studies, suggest that the metavanadate ion is tetrameric, $V_4O_{12}^{-4} \equiv (VO_3^-)_4$; on the other hand, Thilo (*481*) maintains the hypothesis of a trimer, $V_3O_9^{-3} \equiv (VO_3^-)_3$, on the basis of spectrophotometry. Thilo resolves this contradiction by suggesting that the polymerization number (n_v) is dependent on pH to such an extent that, unless the pH and concentration of metavanadate solutions are varied very considerably, the value $n \approx 4$ will inevitably result from the presence of small amounts of decavanadate in the solution, and the data he presents on the effect of small amounts of decavanadate on the observed value of n_v are certainly impressive.

A further increase in pH leads successively to the formation of pyrovanadate and orthovanadate. In pyrovanadate solutions the dimer $V_2O_7^{-4}$ is in equilibrium with the monomeric form HVO_4^{-2}, the latter predominating in all but the most vanadium-rich solutions. In strong alkali, the orthovanadate ion VO_4^{-3} exists at all concentrations. The over-all picture of the vanadate system may be represented as follows (*494*):

$$\begin{array}{ll}
(\mathrm{pH} \geq 13) & 2VO_4^{-3} + 2H^+ \rightleftharpoons 2HVO_4^{-2} \rightleftharpoons V_2O_7^{=} + H_2O \\
(\mathrm{pH} \geq 8.4) & 3V_2O_7^{-4} + 6H^+ \rightleftharpoons 2V_3O_9^{-3} + 3H_2O \\
(8 > \mathrm{pH} > 3) & 10V_3O_9^{-3} + 12H^+ \rightleftharpoons 3V_{10}O_{28}^{-6} + 6H_2O \\
 & V_{10}O_{28}^{-6} + H^+ \rightleftharpoons HV_{10}O_{28}^{-5} \xrightarrow{H^+} H_2V_{10}O_{28}^{-4} \\
(\mathrm{pH} < 3) & H_2V_{10}O_{28}^{-4} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O
\end{array}$$

Two further points are worth attention; the first is the description (*172*) of the transient red color observed when an orthovanadate solution is acidified. On the basis of a linear relation between extinction coefficient and n_v, this has been formulated as dodecavanadate, $V_{12}O_{33}^{-6}$, a conclusion which is supported by the R_f value from paper chromatography. Readjusting the data to fit the trimetavanadate hypothesis, we may visualize the formation of this ion in the following terms

$$12V_3O_9^{-3} + 18H^+ \rightleftharpoons 3V_{12}O_{33}^{-6} + 9H_2O$$
$$5V_{12}O_{33}^{-6} + 3H_2O \rightleftharpoons 6V_{10}O_{28}^{-6} + 6H^+$$

This red dodecavanadate is the same as the octavanadate of Jander and Jahr (*249*). The second point is the observation (*481*) that monomeric vanadate and metavanadic acid exist in very dilute solutions of vanadates; in such dilute solutions ($< 10^{-4}$ *M*) the predominant equilibria with changing pH are

$$\begin{array}{ll}
(\mathrm{pH} \sim 13) & VO_4^{-3} + H^+ \rightleftharpoons HVO_4^{-2} \\
(\mathrm{pH} \sim 8.4) & HVO_4^{-2} + H^+ \rightleftharpoons VO_3^- + H_2O \\
(\mathrm{pH} = 4.5) & VO_3^- + H^+ \rightleftharpoons HVO_3^- \\
(\mathrm{pH} = 3.7) & HVO_3 + H^+ \rightleftharpoons VO_2^+ + H_2O
\end{array}$$

In summary, the degree of condensation in the vanadium–water system is determined by two factors:

(*i*) The concentration of free hydrogen ion.
(*ii*) The concentration of vanadium.

Linked with these two, the ionic strength of the medium is obviously very important. It is reasonable to suppose that these same factors will affect the vanadium–H_2O_2 system and that for complete understanding of this system the same extensive variation of conditions will be necessary.

B. 4:1 PEROXYVANADATES: $V(O_2)_4^{-3} \equiv VO_8^{-3}$

The reaction of concentrated alkali hydroxide with concentrated solutions of V_2O_5 in H_2O_2 at temperatures below 0°C gives blue solutions which contain the ion VO_8^{3-}. These salts, which can be precipitated by the addition of alcohol, can also be obtained by the addition of a large excess of H_2O_2 to a cold concentrated orthovanadate solution (*239, 351*). Reaction with permanganate shows these compounds to be tetraperoxy derivatives, and this has been confirmed by spectrophotometric studies (*91, 239*). Various other products of formulas such as $M_3^IVO_6 \cdot 2.5H_2O$, $M_3^IVO_7$, $M_4^IV_2O_{12}$, and $M_6^IH_2V_2O_{16}$ have been obtained by this preparative reaction (*42, 43, 351, 359*), but it appears that these substances are mixtures of the tetraperoxy salt with decomposition products such as the $[HVO_2(O_2)_2]^{-2}$ ion (*137, 239*).

The salts are stable only at low temperatures, the stability decreasing with increasing cation size (*239*). The potassium salt, which is isomorphous with $K_3[Cr(O_2)_4]$, has a magnetic moment of 0.6 B.M., consistent with the presence of vanadium(V), and the infrared spectra of the potassium and ammonium salts contain bands in the region 800–900 cm^{-1} that have been assigned to vibrations of the peroxy group (*137*). It has been suggested (*268*) from spectrophotometric studies that in solution there is a hydrolytic equilibrium, involving hydroxyl ions and hydrogen peroxide, between the tetraperoxy species and a diperoxy anion as follows:

$$HVO_2(O_2)_2^{-2} + OH^- + 2H_2O_2 \rightleftharpoons V(O_2)_4^{-4} + 3H_2O$$

This explains the need for a high concentration of H_2O_2 to stabilize the blue tetraperoxy species. The reaction with acid potassium iodide has been used to confirm the formulation of a tetraperoxy species (*239*).

C. 3:1 PEROXYVANADATES: $V(O)(O_2)_3^{-3} \equiv VO_7^{-3}$; $HV(O)(O_2)_3^{-2} \equiv HVO_7^{-2}$

Cryoscopic titration of concentrated pyrovanadate solutions with excess concentrated H_2O_2 indicates the existence in solution of the yellow ion

$[HV(O)(O_2)_3]^{-2}$, which contains three peroxy groups per vanadium atom (*91*). This ion is stable only in the presence of excess H_2O_2, otherwise hydrolyzing to a diperoxy species:

$$HV(O)(O_2)_3^{-2} + H_2O \rightleftharpoons HV(O)_2(O_2)_2^{-2} + H_2O_2$$

Similar results are obtained for the orthovanadate–H_2O_2 system.

Spectrophotometric titration of the acid triperoxy species with base has been shown to produce the tetraperoxy anion $V(O_2)_4^{-3}$ so long as the base is not present in excess:

$$H_2O_2 + HV(O)(O_2)_3^{-2} + OH^- \rightleftharpoons V(O_2)_4^{-3} + 2H_2O$$

It is suggested that any slight excess of base causes the destruction of the tetraperoxy species and the formation of the yellow triperoxy anion $V(O)(O_2)_3^{-3}$:

$$V(O_2)_4^{-3} + OH^- \rightleftharpoons V(O)(O_2)_3^{-3} + HO_2^-$$

which is stable at room temperature. An acid-base equilibrium exists between the two triperoxy anions

$$HV(O)(O_2)_3^{-2} + OH^- \rightleftharpoons V(O)(O_2)_3^{-3} + H_2O$$

The spectra of the two ions in the region 400–450 mμ are very similar.

D. 2:1 Peroxyvanadates:

$[V(O)(O_2)_2]^- \equiv VO_5^-$; $[V(O)_2(O_2)_2]^{-3} \equiv VO_6^{-3}$;
$[HV(O)_2(O_2)_2]^{-2} \equiv HVO_6^{-2}$; $[H_2V(O)_2(O_2)_2]^- \equiv H_2VO_6^-$;
$[HV_2(O)_3(O_2)_4]^{-3} \equiv HV_2O_{11}^{-3}$; $[V_2(O)_3(O_2)_4]^{-4} \equiv V_2O_{11}^{-4}$

The yellow color produced by addition of H_2O_2 to a dilute solution of a metavanadate has been shown to be due to a diperoxy anion by cryoscopy and spectrophotometry (*91*) as well as by thermochemical studies (*410*); the same anion is apparently produced when an excess of H_2O_2 is added to vanadium pentoxide (*363*, *364*), though decomposition to the red monoperoxy cation takes place in the absence of excess of H_2O_2. There is some controversy, however, as to how the anion should be formulated. Potentiometric titration of lithium hydroxide against vanadium pentoxide dissolved in H_2O_2 (*239*) indicates that a tribasic anion, $[V(O)_2(O_2)_2]^{-3}$, is formed, while the addition of alkali hydroxide to solutions of vanadium pentoxide in H_2O_2 has led to the formation of yellow crystalline solids of formulas $M^IH_2V(O)(O_2)_2$. On the other hand, the cryoscopic and spectrophotometric studies have been interpreted in terms of the monobasic anion $[V(O)(O_2)_2]^-$. This apparent contradiction can be resolved if the monobasic anion is formulated with one molecule of water: $[(H_2O)V(O)(O_2)_2]^-$; this might well lose the two protons associated with the water molecule at high pH. In accordance with this view, the yellow anion $[HV(O)_2(O_2)_2]^=$ is formed in the titration of solutions of pyrovanadates with H_2O_2 (*91*) and by the decomposition of ammonium tetraperoxyvanadate (*38*).

The equilibrium between the tribasic anion, the red monoperoxy cation, and H_2O_2 has been studied by dialysis (*239*) and by spectrophotometry (*269, 270*); dilute acid is necessary to stabilize the anion. A spectrophotometric study of the thermal decomposition of the "peroxyvanadium complex" formed by the action of H_2O_2 on an acid solution of a vanadate has also shown that the red peroxy cation is in equilibrium with a yellow diperoxy anion, though in this case the anion was not identified; various kinetic parameters were evaluated for the system (*112*). Orthovanadate may be formed as an intermediate in the decomposition of the diperoxy species of isopolyvanadate (*235, 237*).

At least two dimeric peroxyvanadate anions have been identified. Cryoscopic titration of an alkaline solution of a metavanadate with H_2O_2 indicates (*91*) the formation of the anion $[HV_2(O)_3(O_2)_4]^{-3}$, formally derived by condensation of $[V(O)(O_2)_2]^-$ and $[HV(O)_2(O_2)_2]^{-2}$; this confirms earlier observations (*33*) on a compound previously described (*359*) as containing the anion $V_6O_{26}^{-8}$. Compounds that are supposed to contain the ion $[V_2(O)_3(O_2)_4]^{-4}$ have been prepared by the action of aqueous ammonia on a solution of a metavanadate in H_2O_2 (*359*), by the action of H_2O_2 on a complex oxyfluoride of vanadium (*352*), and by the action of H_2O_2 on a melt of V_2O_5 and potassium hydroxide (*183*). The formulation of the potassium salt was supported by differential thermal analysis and by X-ray studies, but it should be noted that when sodium hydroxide was used the product was sodium tetraperoxyvanadate. It has been suggested that the species described as $[V_2(O)_3(O_2)_4]^{-4}$ and $[HV(O)_2(O_2)_2]^=$ are really the same (*91*).

The salts described as containing the anions $[V(O)_2(O_2)]^-$ (*480*) and $[V_2(O)_4(O_2)_3]^{-4}$ (*38, 45, 46*) may have been partly decomposed samples of diperoxyvanadates (*91*).

E. 1:1 PEROXYVANADATES: $V(O)(O_2)^+ \equiv VO_3^+$

The addition of H_2O_2 to V_2O_5 (*24, 87, 239, 363, 365, 411, 574*), to an acid solution of a metavanadate (*91, 112, 469, 515*), to a vanadium(V) salt in weakly acid solution (*270*), and to a decavanadate (*321*) produces a red color which has been shown by transport (*363, 365*), cryoscopic (*91, 515*), dialytic (*239*), spectrophotometric (*91, 112, 270, 321, 469, 515*), conductometric (*270, 321*), and pH (*270, 321*) studies to arise from the monomeric monoperoxyvanadate cation $V(O)(O_2)^+$. The red color is stable in moderately acid media; in excess acid, condensation to isopolyvanadate occurs, with subsequent production of V_2O_5 and VO_2^+; in strong acid, particularly if the solution is heated, the red cation is reduced to vanadium(IV), VO^{+2} (*112, 270, 469*). In excess H_2O_2 the red cation is converted to the yellow peroxy anion $V(O)(O_2)_2^-$ (*91, 112, 239, 270, 321*). Spectrophotometric studies (*321*) have shown that the red cation has $\lambda_{max} = 560$ mμ, at which point the pH is 2.30. It has been suggested that the vanadate-catalyzed oxidation of iodide by acid–H_2O_2 involves the formation of an intermediate monoperoxyvanadium species, $V(O_2)OH$ (*425*). A study of the reduction of acid solutions of $V(O)(O_2)^+$ by γ-radiation has shown that the absence of H_2O_2 and $V(O)(O_2)^+$ when vanadium(V) is reduced by γ-radiation of acid solutions is due to reduction of these by ·OH, either of H_2O_2 before peroxidation of VO_2^+ can occur, or of $V(O)(O_2)^+$ as soon as it is formed (*138, 418*). A spectrophotometric study has been made (*112*) of the thermal decomposition of the red-yellow "pervanadium complex" and the kinetics of the process elucidated. The 1:1:1 complex formed between ammonium vanadate, pyridine-2,6-dicarboxylic acid, and H_2O_2 (*211*) has been obtained as a pure solid (*210*) and the structure of the anion has been proposed as $[V(O)(O_2)\cdot C_5H_3N(COO)_2\cdot H_2O]^-$, but this suggestion awaits the application of physical methods for confirmation. Solutions of V_2O_5 in H_2O_2 have been used as oxidizing agents in organic chemistry (*545–547, 553, 554*).

Figure 1 shows the interrelation of the vanadium(V)–water and the vanadium(V)–H_2O_2 systems. We may make the following general observations:

(1) The number of peroxy groups per vanadium atom increases with alkalinity.

(2) Increasing acidity increases polymerization and decreases the number of peroxy groups per vanadium atom.

(3) Increasing the concentration of H_2O_2 decreases the degree of polymerization.

We may also make the more specific observations as follows:

(1) The 2:1 species $V(O)(O_2)_2^-$ has acidic properties, thus explaining the observed decrease in pH when H_2O_2 is added to a metavanadate; in the presence of excess of metavanadate, polymerization will occur due to the acidity of the medium. With increasing alkalinity this diperoxy anion is converted to the 3:1 species $HV(O)(O_2)_3^{-2}$ and $V(O)(O_2)_3^{-3}$ successively.

(2) The 2:1 species $HV_2(O)_3(O_2)_4^{-3}$ is favored by high concentrations of vanadium and is converted to the 3:1 species $HV(O)(O_2)_3^{-2}$ by high concentrations of H_2O_2.

(3) The 4:1 species $V(O_2)_4^{-3}$ is favored by alkaline media of high ionic strength, rich in H_2O_2. Under such conditions H_2O_2 functions as an acid; thus any excess of base causes all the H_2O_2 to be involved in the formation of HO_2^-, and consequently the 3:1 species $V(O)(O_2)_3^{-3}$ is formed.

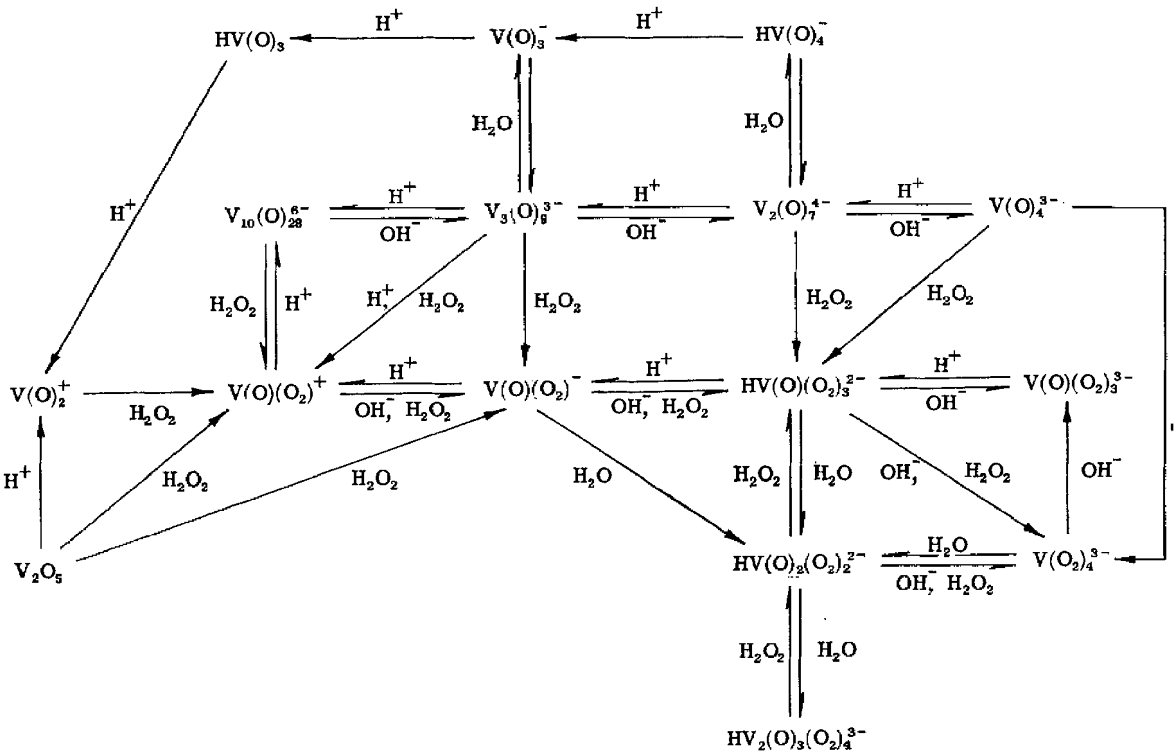


Fig. 1. Diagram showing the relationships between vanadium (V) oxy and peroxy compounds in aqueous solution.

(4) Comparison of the pK values of the transformations

$$VO(O_2)^- \rightleftharpoons HVO_2(O_2)_2^{-2} \qquad (pK = 7.15)$$
$$V_3O_9^{-3} \rightleftharpoons V_2O_7^{-4} \qquad (pK \sim 8.5)$$

and the dissociation constants

$$HVO(O_2)_3^{-2} \rightleftharpoons VO(O_2)_3^{-3} \qquad (K = 1.1 \times 10^{-12})$$
$$HVO_4^{-2} \rightleftharpoons VO_4^{-3} \qquad (K = 3.15 \times 10^{-14})$$

shows that the peroxy species are more acidic and less polymerized than the simple vanadates.

IX. Niobium and Tantalum

A. 4:1 PEROXY SPECIES: $M(O_2)_4^{-3} \equiv MO_8^{-3}$

The addition of ethanol to a solution containing H_2O_2 together with the metal pentoxide M_2O_5 (M = Nb, Ta) and an excess of an alkali metal hydroxide precipitates a white crystalline solid which contains the $M(O_2)_4^{-3}$ anion (*21, 137, 182, 184, 360, 508*). Salts of this anion are stable in air and dissolve in water without decomposition, although the tantalum derivatives are much less soluble and, in general terms, much more stable than their niobium analogs (*360*). The salts previously described (*360*) as containing the $Nb_2(O)_3(O_2)_4^{-4}$ ion have been shown to be tetraperoxyniobates (*21*).

Hydrolysis of the tetraperoxy salts with dilute acid gives the monoperoxy anions $MO_2(O_2)^-$ (*360*). The tetraperoxy anions are isomorphous and isostructural with the tetraperoxy species of chromium (*57*); their salts are diamagnetic and conductivity measurements confirm the presence of a 3:1 electrolyte (*137*). Measurements of the infrared (*137, 182*) and Raman spectra (*182*) show the presence of strong absorption in the region 810–820 cm^{-1} which is assigned to ν (O-O). The compounds have been investigated by differential thermal analysis and by quantitative X-ray phase analysis (*184*).

B. 1:1 PEROXY SPECIES: $M(O)_2(O_2)^- \equiv MO_4^-$

The reaction of the tetraperoxy anions $M(O_2)_4^{-3}$, either as solids or in solution, with dilute acids affords a gelatinous precipitate of the monoperoxy anion $M(O)_2(O_2)^-$ (*21, 184, 360, 508*). The niobium compound is light yellow and the tantalum compound is white: both are insoluble in water and are decomposed by hot dilute acid (*184*). The free monoperoxy acid $HMO_2(O_2)$ is formed when an aqueous solution of M_2O_5 is warmed with H_2O_2 (*21, 360*).

The reaction of H_2O_2 with metaniobates gives salts of the corresponding monoperoxy compound, $M^INb(O)_2(O_2)$, although it appears that some of these may contain hydrogen peroxide of crystallization, particularly when obtained by using high concentrations of H_2O_2. These salts are not particularly stable at 0°C (*185*).

A spectroscopic study (*4, 5*) has shown by the method of continuous variations that a 1:1 peroxyniobate species having $\lambda_{max} = 256$ mμ is formed in solutions of Nb_2O_5 in a large excess of H_2O_2 which contain less than 40% sulfuric acid. Increasing the acid concentration produces a diperoxy species. The 1:2 species described by earlier workers (*479*) has been shown to be the same as the 1:1 species.

C. Other Peroxyniobate Species

A spectrophotometric study (*4, 5*) of the species existing in solutions of Nb_2O_5 in H_2O_2 in which the acid concentration is varied over a wide range has shown that three complexes are formed. The first (I), having $\lambda_{max} = 365$ mμ in 100% H_2SO_4, is destroyed by the addition of less than 2% sulfur trioxide and exists throughout the range 50–100% H_2SO_4. The second (II), whose absorption maximum is inaccessible, is important at acid concentrations of less than 60%. The third species (III) has an absorption maximum at 256 mμ and is important at acid concentrations less than 40%. The H_2O_2:Nb ratios of these three complexes were determined to be:

I	3:2
II	2:1
III	1:1

A study (*6*) of the condensation equilibrium between I and II shows that its acid dependence is due to the additional equilibrium between H_2O_2 and its conjugate acid $H_3O_2^+$ which is not dissociated in strong mineral acids.

These results represent one of the few exceptions to the general rule that the number of peroxy groups per metal atom decreases with increasing acidity.

No comparable study has been made of the $Ta(V)/H^+/H_2O_2$ system.

X. Chromium

The peroxides of chromium are probably better known and better characterized than those of any other transition element. Four different series of derivatives are known, formed under different conditions of pH, and solid members of each series have been prepared: they have the formulas $M_3^I[Cr(O_2)_4]$, $M^IHCr(O)_2(O_2)_2$, $BCr(O)(O_2)_2$ (where B is a nitrogen base), and $D_3Cr(O_2)_2$ (where D is a nitrogen base or cyanide ion). In addition to these, other peroxychromium compounds have been described, but are less well characterized. In the account that follows, the series are considered in turn, after which an attempt is made to discuss the relationships between them.

A. THE RED TETRAPEROXYCHROMATES(V)

When an alkaline solution of a chromate is treated with H_2O_2, it turns from yellow to deep red-brown; if the system is kept at 0°, dark brown crystals slowly precipitate (*450*). Analysis shows that the alkali metal derivatives have the formulas $M_3^ICrO_8$, while the amount of O_2 evolved on decomposition in acid or alkaline solution, together with the reaction with potassium permanganate, indicates the presence of four peroxy groups (*441*, *442*). Acid salts of this series have not been prepared; the triammonium salt $(NH_4)_3[Cr(O_2)_4]$ is formed from solutions that are only weakly ammoniacal, provided enough H_2O_2 is present, though triamminodiperoxychromium(IV) is formed as well (*446*) if this condition is not fulfilled.

These red salts are relatively stable to heat, and may be kept for some months at room temperature without decomposition. The potassium salt decomposes relatively slowly even at 170° (*450*), but pure samples explode at 178° and the explosion temperature is apparently lowered by the presence of impurity. The sodium and ammonium salts are less stable (*450*).

The formula $M_3^I[Cr(O_2)_4]$ implies the presence of chromium(V), and in accordance with this the potassium salt has a paramagnetic susceptibility at 20° of 1.80 B.M. (*280*, *541*, *542*), while electron resonance spectra

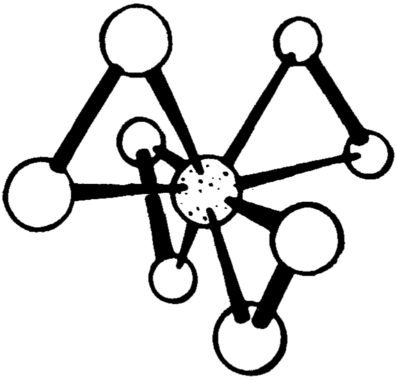


FIG. 2. The tetraperoxychromate(V) ion (*232*, *522a*, *523*). The structural parameters from a least-squares refinement (*524*) of earlier (*523*) experimental data are: $r(Cr—O_a)$, 1.846 ± 0.022; $r(Cr—O_b)$, 1.944 ± 0.024; $r(O_a—O_b)$, 1.405 ± 0.039A; $\angle O_aCrO_a = 86.8 \pm 1.4°$; $\angle O_bCrO_b = 173.7 \pm 2.5°$; three-dimensional analysis, $R = 0.1$. A different (*522a*) least-squares refinement gives parameters that differ insignificantly from these, but the value for $r(O_a—O_b)$, 1.472 ± 0.025A, is worth noting. Circle, O; dotted circle, Cr.

have been obtained from the powder (*147*, *232*, *319*, *524*) (with $g_{\|} = 1.936 \pm 0.002$, $g_{\perp} = 1.983 \pm 0.002$) (*524*) and from aqueous and alkaline solutions (*103*). A recalculation (*524*) of data from an X-ray study of a single crystal of the potassium salt (*523*), which is isomorphous with the analogous derivatives of niobium and tantalum (*57*), shows that the chromium atom is surrounded by four equivalent peroxy groups, in an arrangement that could be described as a distorted dodecahedron of oxygen atoms (see Fig. 2); the two Cr—O distances are significantly different. Molecular orbital calculations have been made using parameters derived from the *g* values (*524*); the unpaired electron is assigned to a B_1 orbital of chromium. The O—O distance of 1.40 Å is rather less than the 1.49 Å found in alkali metal peroxides (*2*), perhaps because electrons that in the free peroxide ion are in antibonding π orbitals are partly delocalized in the complex into orbitals of chromium.[2] The crystal field parameter Δ has been calculated from two weak ultraviolet bands (which may be due to crystal field transitions) as ~35,000 cm^{-1} (*524*), while the infrared spectrum of the potassium salt has been recorded (*137*, *181*) (see Table II).[3]

TABLE II

INFRARED FREQUENCIES ASSOCIATED WITH THE PEROXY GROUPS IN SOME PEROXYCHROMIUM COMPOUNDS[a]

	Frequency (cm^{-1})	
Compound	Reference (*181*)	Reference (*137*)
$(NH_3)_3Cr(O_2)_2$	865s	891s
$En\cdot Cr(O_2)_2\cdot 3H_2O$	—	880s
$K_3[Cr(O_2)_4]$	875s	975w, 875s, 675m[b]
$(NH_4)_3[Cr(O_2)_4]$	—	970w, 870s, 665m[b]
$NH_4[HCr(O)_2(O_2)_2]\cdot H_2O$	980*s, 932s	980s, 937s
$K[HCr(O)_2(O_2)_2]$	984*m, 924*s, 876s	—
$Tl[HCr(O)_2(O_2)_2]$	970*w, 920*s, 870s	—
$Cr(O)(O_2)_2$ (in ethyl acetate)	940*s, 864s	—
$Py\cdot Cr(O)(O_2)_2$	937*s, 875m	950w, 942w, 934
$Bipy\cdot Cr(O)(O_2)_2$	922*s, 890m	947m, 925m
1,10-phen$\cdot Cr(O)(O_2)_2$	—	945m, 925s, 910w

[a] All spectra save that of $Cr(O)(O_2)_2$ in ethyl acetate were recorded as nujol mulls; the bands marked with asterisks were assigned to (Cr═O) modes, making a distinction that in these systems may be artificial; s = strong, m = medium, w = weak intensity.

[b] May be due to carbonate impurity.

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[2] A different least-squares refinement of the same data (*522a*) gives a value for the O—O distance of 1.472 ± 0.025 Å, not significantly different from that in the $O_2^{=}$ ion.

[3] There are differences in detail in the reported ultraviolet spectra and electron resonance *g* values (*319*, *524*), which may arise from differences in experimental conditions.

The red tetraperoxychromates(V) are slightly soluble in water and the solutions are stable for some days, particularly in the presence of free alkali (*450*). Freezing point measurements confirm that the potassium salt gives four particles in solution (*442*), while the molar conductivity is 252 $ohm^{-1}mol^{-1}cm^2$ at infinite dilution (*442*) (see also *137*).

The course of decomposition in aqueous solution depends on the pH. In neutral or alkaline solution, chromate and oxygen are formed according to the equation (*442, 450*):

$$2H_2O + 4Cr(O_2)_4^{-3} = 4CrO_4^{=} + 4OH^- + 7O_2$$

The decomposition is first order. In acid solution, Cr(III) is produced according to the limiting equation:

$$2Cr(O_2)_4^{-3} + 12H^+ = 2Cr^{+3} + 6H_2O + 5O_2$$

Under these conditions, the decomposition is second order (*59*). In practice, some chromate is always formed at the same time, the amount decreasing as the acidity rises (*442, 450*). The blue hydrated chromium pentoxide or the violet salts of diperoxychromic acid (see below) are formed as intermediates in this reaction: if an aqueous paste of ammonium tetraperoxychromate(V) is acidified, the violet $(NH_4)[Cr(O)_2(O_2)_2H]$ is precipitated (*447*), while the amount of ether-extracted chromium pentoxide produced by the addition of various acids to cooled solutions of the tetraperoxychromates(V) varies with the strength of the acid (*448*). In the absence of water the sodium and potassium salts do not react with ethereal solutions of hydrogen chloride; decomposition, which is very slow, gives chromate. If a few drops of water are added, however, the solution turns an intense blue (*448*). When heated with an excess of ammonia solution, ammonium tetraperoxychromate(V) gives triamminodiperoxychromium(IV).

Several other red peroxychromates have been reported, with complex formulas (such as $Li_8Cr_2O_{15}$ or $Mg_2K_2Cr_2O_{15}$) that imply the presence of $Cr—O_2—Cr$ bridges (*37, 39–41, 44*). In at least one case, magnetic measurements have shown that the compound really contains the tetraperoxychromate(V) ion (*460*); it seems very likely that this is true of all of them, the odd formulas arising from slight decomposition or from side reactions in the course of analysis.

B. DERIVATIVES OF BLUE CHROMIUM(VI) PENTOXIDE

The blue substance formed when hydrogen peroxide is added to an acid solution of a chromate, though very unstable in water, can be extracted with ether (*24*) or other oxygen-containing organic solvents in which it is much more stable (*186*). The ethereal solution reacts with electron-pair donors such as pyridine (*575*), aniline (*575*), quinoline (*577*), or 1,10-phenanthroline (*130*), and solid compounds of formulas $BCrO_5$ (B = base) have been obtained from the reaction mixtures by evaporating the excess solvent. The pyridine derivative was given the structure $PyCr(O)(O_2)_2$ on the basis of its reactions with dilute sulfuric acid, with silver(I) oxide, and with neutral potassium permanganate (of which four equivalents were consumed per mole of pyridine complex) (*490*):

$$8H^+ + 2PyCr(O)(O_2)_2 = 2Cr^{+3} + 3H_2O + 7/2O_2 + 2PyH^+$$
$$PyCr(O)(O_2)_2 + Ag_2O = Ag_2CrO_4 + Py + O_2$$

This structure implies that the chromium atom is in the (formal) +6 state, and that the compound is a molecular donor-acceptor complex; in keeping with this, the molecular weight in benzene is that of a monomer (*442*, *575*), the conductivity in dimethylformamide is very small (*137*), while the small (and probably temperature-independent) paramagnetic susceptibility [μ = 0.4–0.8B.M. (*137*, *181*, *280*)] is consistent with the presence of Cr(VI). Moreover, careful analysis of the 1,10-phenanthroline derivative gave the hydrogen content expected for the adduct rather than for a salt, while there is no band in the infrared spectrum of the pyridine complex that is likely to be associated with a N^+—H stretching mode (*130*). Physicochemical studies of the preparative reaction in a variety of solvents (*130*, *456*, *468*, *469*) confirm that the formation of CrO_5 involves two molecules of H_2O_2 to each chromate ion, with an equilibrium constant for formation of 5.4×10^7 at 10° in water of pH ~1.5 (*130*); the conclusion from an earlier spectrophotometric study (*168*) that the blue compound was the monoperoxy acid $HCr(O)_3(O_2)$ has since been abandoned (*171*). Two X-ray studies of

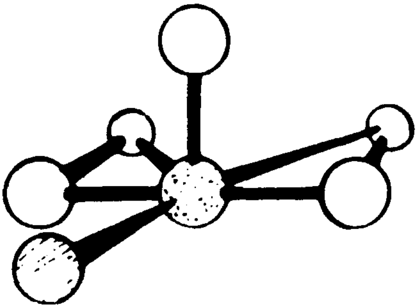

FIG. 3. Coordination around the chromium atom in pyridinechromium pentoxide (*392*, *522*). A recent least-squares refinement of the three-dimensional analysis (*522*) gives the following structural parameters: $r(Cr—O_1)$, 1.794 ± 0.014; $r(Cr—O_2)$, 1.825 ± 0.014; $r(Cr—O_3)$, 1.796 ± 0.014; $r(Cr—O_4)$, 1.844 ± 0.014; $r(Cr—O_5)$ (chromyl oxygen), 1.576 ± 0.018; $r(Cr—N)$, 2.047 ± 0.013; $r(O_1—O_2)$, 1.407 ± 0.016; $r(O_3—O_4)$, 1.400 ± 0.016A; $\angle O_1CrO_2$ = 45.7 ± 0.7°. In this determination the *R* value for the refined determination is 0.11. Circle, O; dotted circle, Cr; lined circle, N.

the pyridine complex confirm this view. The chromium atom, the two peroxy groups, and the nitrogen atom of the pyridine molecule are all nearly coplanar, while the fifth oxygen lies above the chromium atom (*392, 522*) (see Fig. 3).

The blue pentoxide has never been isolated. Attempts to prepare it directly from chromyl chloride and H_2O_2 gave an equilibrium mixture that retained some chromyl chloride and from which no definite compound was isolated (*488*):

$$Cr(O)_2Cl_2 + 2H_2O_2 = Cr(O)(O_2)_2 + H_2O + 2HCl$$

From a solution of the pentoxide in dimethyl ether, an etherate has been obtained by careful evaporation of the excess solvent at −50° (*488*); the crystals, which were originally mistaken for the free acid $H_3Cr(O_2)_4$ (*448*), exploded if allowed to warm to −30°. By analogy with the etherate, it seems likely that in water the species present should be written $H_2O{\cdot}Cr(O)(O_2)_2$ or $H_2Cr(O)_2(O_2)_2$. Aqueous solutions decompose rapidly to Cr(III) and O_2 at $pH < 4$ (*55*); as the pH rises, the amount of Cr(VI) formed in the decomposition increases (*55, 444, 516*). When the ethereal solution is treated with less than the calculated amount of ethereal ammonia, alcoholic potassium hydroxide (*440, 576*), or concentrated aqueous potassium cyanide (*578*), the violet salts of diperoxychromic acid, $M^IHCr(O)_2(O_2)_2$, are precipitated; ammonium tetraperoxychromate has been obtained from ethereal chromium pentoxide and saturated aqueous ammonia (*442*) and, with an excess of aqueous ammonia (*575*), triamminodiperoxychromium(IV) is formed. Aqueous potassium hydroxide, aqueous or alcoholic sodium hydroxide (*576*), or aqueous sodium carbonate (*439*) decomposes the ethereal solution to chromate, while solid sodium acetate reacts to give a purple substance that is probably $Na[Cr(O)_2(O_2)_2H]$ (*388*). With organic nitrogen bases, either adducts or salts of diperoxychromic acid are formed: aniline (*575*), quinoline (*577*), pyridine (*575*), dipyridyl (*137*), 1,10-phenanthroline (*130*), and probably strychnine (*24*) give adducts, while tetramethylammonium hydroxide, trimethylamine, and piperidine give what appear to be salts (*577*). All these reactions imply, as was suggested many years ago (*10*), that in aqueous solution the blue pentoxide is the parent acid of the violet salts, and that in water it can act as either a protonic or a Lewis acid:

$$Cr(O)(O_2)_2 + H_2O \rightleftharpoons H_2OCr(O)(O_2)_2 \rightleftharpoons H^+ + [Cr(O)_2(O_2)H]^-$$

The rise in pH on formation of chromium pentoxide in aqueous solution (*55*) implies that its formation involves removal of protons

$$CrO_4^= + 2H_2O_2 + 2H^+ = H_2O{\cdot}Cr(O)(O_2)_2 + 2H_2O$$

and that if it is a protonic acid it must be a weak one. No thorough study seems to have been made of the competing reactions of salt and adduct formation; on the basis outlined above, it seems likely that the stronger bases would give adducts rather than salts.

The reaction between alkali metals and ethereal solutions of chromium pentoxide gives purple-red solids that have been formulated as $M_2Cr_2O_8$, but which are probably diperoxychromates (*81*) (see below). The reaction between chromium pentoxide and such compounds as nitrophenols led to little or no hydroxylation (*219*).

The adducts with amines are rather more stable than the etherates, though the pyridine derivative explodes when heated to 70° or when treated with concentrated sulfuric acid (*442*).[3a] The suggestion that it exists in stereoisomeric forms (*445*) has not apparently been pursued. The adducts with bidentate ligands seem to be rather more thermally stable than those with monodentate bases (*130*, *137*); this raises an interesting question of structure. In the pyridine derivative, the chromium atom is in a sense six-coordinated, but the ligands form a pentagonal pyramid, so that there is what might be called a vacant coordination position axial to the unique oxygen atom (see Fig. 3). In the adducts of bidentate diamines, this position might well be filled. There is little direct evidence, however, for such a structural difference. The ultraviolet spectrum of the 1,10-phenanthroline derivative is rather different, it is true, from that of the pyridine compound; it shows, in place of the two peaks at ~5800 and 7000 Å ($\epsilon \sim 500$), two bands of about this intensity but at ~6300 and ~8300 Å. The infrared bands assigned to modes of the peroxy groups in the spectra of the two compounds in the NaCl region, however, are at very similar frequencies (*137*).

The decomposition of chromium pentoxide has been the subject of some unconvincing kinetic studies. One series of experiments has led to the conclusion that the rate of decomposition in aqueous solution, like the rate of formation, is independent of the concentration of H_2O_2, is first order in chromium pentoxide, and at a given concentration of H_2O_2 and of dichromate is first order in sulfuric acid (*176*). In organic solvents, the decomposition is unimolecular with rate constants at 10° and 20° of 0.002125 and 0.005273 sec^{-1}, respectively (*414*).

In papers (*414*, *419–424*) in which many details appear to conflict with other published work, it has been proposed that the blue compound decomposes to give chromium(III) chromate, though it seems to be generally agreed (*55*, *444*, *516*) that the amount of Cr(III) formed depends on the pH of the solution. On the basis of some low analytical results, it is proposed that the blue compound should be described as chromium(III) perchromate,

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[3a] The pyridine adduct, when dry, has been known to explode violently at room temperature.

$Cr_2^{III}(Cr_2^{VI}O_{10})_3$, while the pyridine adduct is regarded as containing a complex chromium(III)-pyridine cation. It must be admitted that the numerical results obtained by Schwarz and Giese (*490*) in their analysis of the pyridine complex are not very impressive, but this is a reflection of the instability of the compound rather than an indication that the formula is more complicated. The suggested structure is not consistent with the results of the X-ray studies (*392*, *522*) and the ethereal solution gave no electron resonance spectrum (*123*) such as would be expected for a derivative of chromium(III). Finally, evidence is presented (*421*, *423*) to show that Cr(III) is an intermediate in the formation of the blue compound. The reader is referred to the original papers to form his own judgment.

C. THE VIOLET DIPEROXYCHROMATES(VI)

These salts, which have been given a number of different formulas (see Subsection E), are obtained either by the action of H_2O_2 on weakly acidic solutions of alkali metal chromates (*450*) or by treating an ethereal solution of chromium pentoxide with less than the calculated amounts of ethereal ammonia, alcoholic potassium hydroxide, or aqueous potassium cyanide (*576*). The salts are soluble in water; the ammonium salt dissolves in alcohol, though not in other organic solvents; the aqueous solutions are conducting, (*137*, *181*, *450*) and the molar conductivity of a solution of the ammonium salt has been given as 67 (at 5°) (*137*) and as 111 ohm^{-1} mol^{-1} cm^2 (*181*). The instability of these solids makes analysis difficult; the composition was long believed to be represented by the formula M^ICrO_6, usually with one molecule of water of crystallization (*491*), but careful analysis of the anhydrous potassium salt has shown that it contains one hydrogen atom per molecule (*181*) and the presence of —OH— groups is confirmed by the infrared spectrum (*181*). Treatment with potassium permanganate, ceric sulfate, or silver(I) oxide shows that there are two peroxy groups to each chromium atom; it was also established that the number of peroxy groups per chromium was the same in the violet salts and in chromium pentoxide (*181*). Since physicochemical studies (*456*, *468*, *469*) of the reaction between H_2O_2 and chromate in neutral solution had already indicated this conclusion, and since the salts show the small (and probably temperature-independent) paramagnetism ($\mu \sim 0.6$ B.M.) associated with Cr(VI) (*137*), the structural formula $M^I[Cr(O)_2(O_2)_2H]$ seems well established for these compounds. It is probable that the peroxy groups are laterally coordinated to chromium; since no acid salts of tetraperoxychromic(V) acid have been obtained, the proton seems most likely, as Griffith (*181*) concluded on other grounds, to be associated with one of the Cr—O groups. Until recently, the anion has been described as a dimer, $[Cr_2(O)_4(O_2)_4]^=$, because it was not realized that an atom of hydrogen was present in the anion; the correctness of the monomeric formulation has been confirmed by cryoscopic measurements (*181*). It is remarkable that no authentic derivative of the fully substituted acid has been described, though the brick-red solids of formulas K_2CrO_6 (*59*) and $CaCrO_6$ (*68*) could be such compounds (see below). Aqueous solutions of the violet salts are neutral to litmus; the relatively low conductivity suggests that the proton in the anion is not particularly mobile.

The violet salts are all extremely unstable, exploding when struck or warmed, "*z.B. mit dem Hand*". They decompose in water or in the solid state to give oxygen and chromic acid or chromate (*576*). The aqueous solutions give unstable precipitates with soluble salts of lead, barium, or silver(I), while solutions of iron(III) turn green (*576*). The action of alkali leads to the formation of some of the red tetraperoxychromate(V), with some decomposition to chromate and oxygen (*450*); with acid, chromium pentoxide hydrate is produced (*225*), while the main product of reaction with aqueous ammonia is triamminodiperoxychromium(IV) (*447*).

D. DERIVATIVES OF DIPEROXYCHROMIUM(IV)

When a tetraperoxychromate(V) (*450*), a diperoxychromate(VI) (*450*), or an ethereal solution of chromium pentoxide (*575*) is treated with an excess of aqueous ammonia, a brown-red crystalline solid is formed, of composition $Cr(O_2)_2{\cdot}3NH_3$; the same substance has been obtained by direct reaction of ammonium dichromate, aqueous ammonia, and H_2O_2 (*226*). In water, in which it is slightly soluble, its molecular weight (determined cryoscopically) is roughly the same as its formula weight (*442*) and the solution is almost nonconducting (*137*), while the ammonia content is unaffected by treatment with acetic acid (*226*); evidently the compound is not an ammonium salt. Five electron equivalents of iodine are liberated per formula weight on treatment with potassium iodide (*575*), while reaction with potassium permanganate gives a net consumption of three electron equivalents of oxidizing power per mole (*130*); these observations can be explained if the substance is a diperoxy derivative of chromium(IV):

$$(NH_3)_3Cr(O_2)_2 + 8H^+ + 5I^- = (NH_3)_3Cr(OH_2)_3^{+3} + 5/2I_2 + H_2O$$

$$3(NH_3)_3Cr(O_2)_2 + 10H_2O = 2(NH_3)_3Cr(OH_2)_3^{+3} + 3NH_4^+ + CrO_4^{=} + 6O_2 + 5H^+ + 12e^-$$

$$CrO_4^{=} + 8H^+ + 3e^- = Cr^{+3} + 4H_2O$$

In agreement with this view, the paramagnetic moment of the compound is 2.8 B.M., consistent with the presence of the two unpaired electrons associated with chromium(IV) (*49*, *137*). In the crystal (*320*), the chromium atom may be described as seven-coordinated (see, however, Section XXIV) with a roughly T-shaped arrangement of nitrogen atoms round it; the peroxy groups lie with the O—O axes in the plane of the downstroke of the T, so that they and one nitrogen atom form an irregular plane pentagon around the chromium atom (see Fig. 4). The O—O distance of 1.31 Å is some 0.18 Å less than in the peroxide ion (*2*), so the compound was described as a superoxide of Cr(II); since the infrared frequencies probably associated with vibrations of the peroxy group are very similar in this and in other peroxychromium compounds, the short O—O distance is surprising (*181*).[4] The compound is polymorphic, and two forms (*226*, *446*) were described wrongly as isomers; its ultraviolet spectrum has been recorded (*506*).

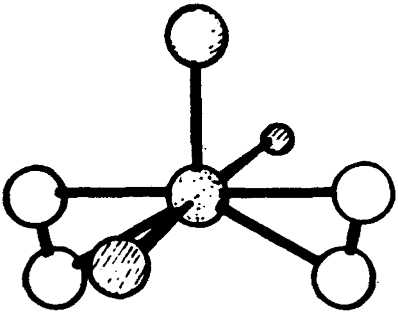

FIG. 4. The arrangement of the heavy atoms in triamminodiperoxychromium(IV). In the orthorhombic form, the structural parameters are: $r(Cr—O_1)$, 1.891 ± 0.020; $r(Cr—O_2)$, 1.879 ± 0.021; $r(Cr—O_3)$, 1.858 ± 0.020; $r(Cr—O_4)$, 1.867 ± 0.019; $r(Cr—N_1)$, 2.147 ± 0.025; $r(Cr—N_2)$, 2.084 ± 0.020; $r(Cr—N_3)$, 2.110 ± 0.022; $r(O_1—O_2)$, 1.414 ± 0.026; $r(O_3—O_4)$, 1.424 ± 0.024A. $\angle O_1CrO_2 = 44.0°$, $\angle O_3CrO_4 = 45.0°$, both ±0.8°; three-dimensional analysis, $R = 0.11$ (*522b*). A two-dimensional analysis of the monoclinic form (*320*) indicates that the atomic arrangement is the same, but the structural parameters are less precise, even when refined by a least-squares analysis (*522a,b*). Circle, O; dotted circle, Cr; lined circle, N.

Analogous derivatives of ethylenediamine, en·$Cr(O_2)_2·2H_2O$, and of hexamethylenetetramine, $C_6H_{12}N_4·Cr(O_2)_2$, have been made by treating solutions of the appropriate amine and chromic acid with 30% H_2O_2 (*223*); their structures have not been determined.

Triamminodiperoxychromium(IV) is a relatively stable compound, which when dry may be kept at room temperature for months without decomposition (*442*), though it explodes when ground up or when heated with a flame (*226*). The products of decomposition include ammonia, chromium(VI), and chromium(III) possibly as hexammine chromium(III) chromate (*442*). It is insoluble in alcohol and in ether, but gives a violet-

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[4] A least-squares refinement of the data (*522c*) indicates that the limits of error of this value are ~0.1 Å; a more precise study of the orthorhombic form (see Fig. 4) gives O—O distances of 1.41–1.42 ± 0.025 Å (*522b*).

red solution in water, which decomposes on heating, giving off oxygen (*575*). Treatment with acid induces decomposition to chromium(III), chromium(VI), and oxygen, the speed of decomposition depending on the strength of the acid; in dilute acid, most of the peroxy oxygen is evolved as O_2 (*442*), while with acid and ether some chromium pentoxide may be extracted (*226*, *575*). With concentrated hydrochloric acid, the main chromium-containing product is aquotriamminechlorochromium(III) chloride (*567*, *569*); with concentrated sulfuric acid the compound explodes (*226*), and when warmed with alkali it decomposes to give chromate (*575*).

The reaction with potassium cyanide solution at 60° leads to the formation of a compound of formula $CrO_4 \cdot 3KCN$ (*578*). This compound probably contains the complex anion $[Cr(O_2)_2(CN)_3]^{-3}$, at least in the solid state[5]; it gives about six electron equivalents of iodine with potassium iodide, as against a calculated five for the above formula (*578*). It is fairly stable at room temperature, though exploding at 115°C[5a]; it is soluble in water, giving a brown solution that slowly decomposes with evolution of oxygen. When the aqueous solution is treated with sulfuric acid, the brown color turns a deep violet, and the colored component can be extracted with ether; the ethereal extract contained a cyanoperoxy derivative of chromium, but no definite compound was isolated (*578*). Wiede suggested that the violet species was the free acid $H_3[Cr(O_2)_2(CN)_3]$, but offered no evidence for this view (*578*).

When an aqueous solution of potassium tricyanodiperoxychromium(IV) is heated with dilute sulfuric acid, O_2 and hydrogen cyanide are evolved, leaving chromium(III). The aqueous solution of the peroxycyanide gives unstable precipitates with soluble salts of silver(I), thallium(I), lead(II), or copper(II); the formation of a brown rather than a white precipitate with silver(I) implies that the solution contains little cyanide ion (*578*).

When a mixture of potassium cyanide and chromic acid in appropriate concentrations is treated with 30% H_2O_2, a pentacyanide derivative, of formula $Cr(O_2)_2 \cdot 5KCN \cdot 5H_2O$, is formed (*440*). This compound, which is dark red, is hygroscopic, and dissolves in water to give a conducting solution; some rather unsatisfactory cryoscopic measurements suggest that ten particles are formed in solution:

$$K_5[Cr(O_2)_2(CN)_5] \rightleftharpoons 5K^+ + [Cr(O_2)_2CN]^- + 4CN^-$$

though dissociation to two cyanide ions and the complex $[Cr(O_2)_2(CN)_3]^{-3}$, giving eight particles, seems more reasonable if the tricyano complex exists

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[5] This has been confirmed by X-ray crystallography (*522c*); refinement of the structure is not complete, but with $R = 0.125$, $r(O—O) = 1.445–1.446 \pm 0.016$, and $r(C{\equiv}N) = 1.133$ Å.

[5a] Griffith, however, found that the compound is dangerously explosive at room temperature (*182a*).

in solutions of the tricyanide derivative. The aqueous solution, which is alkaline, gives the reactions of cyanide ion; with concentrated ammonia it forms the dark red solid $K_2[Cr(O_2)_2(CN)_2NH_3]$, which is also hygroscopic; the solution of this in water is conducting, and cryoscopic measurements are consistent with dissociation according to the equation (*440*):

$$K_2[Cr(O_2)_2(CN)_2NH_3] \rightleftharpoons 2K^+ + [Cr(O_2)_2(CN)_2NH_3]^-$$

E. OTHER PEROXYCHROMIUM COMPOUNDS

$(NH_4)_2CrO_6$. Attempts to repeat the preparation of this compound, described in two different communications (*224, 379*), have led either to the formation of $NH_4[Cr(O)_2(O_2)_2H]$, or to a mixture of ammonium tetraperoxychromate(V) and ammonium chromate (*181*).

$K_2CrO_{10}\cdot nH_2O$, K_2CrO_6 (60). The dark violet compound described as K_2CrO_{10} was made by treating 60% H_2O_2, cooled by solid CO_2, with a saturated solution of potassium chromate and adding a large excess of cooled ethanol. The compound was extremely unstable at room temperature; its formula was deduced from the ratio of O_2 evolved to potassium chromate formed on decomposition with (finally) gentle warming; it should apparently be written $K_2[Cr(O_2)_5]$. Such a formula implies the presence of Cr(VI) with a coordination number of 5 (see Section XXIV); perhaps some of the peroxide was present as H_2O_2. The compound dissolves in water, with evolution of oxygen; when dispersed on a watchglass at room temperature, it decomposes to form the stabler solid K_2CrO_6, formulated as $K_2[Cr(O)_2(O_2)_2]$. The former compound sounds in some ways like $K[Cr(O)_2(O_2)_2H]$, but in the absence of physical data no further conclusions can be drawn. The existence of these two compounds was deduced from catalytic studies.

$CaCrO_6\cdot nH_2O$, $CaCrO_5\cdot nH_2O$. If 55% H_2O_2 is added to freshly prepared calcium chromate at $-80°$ and the resulting solution treated with an excess of alcohol, a brick-red compound is formed of formula $CaCrO_6\cdot nH_2O$; it decomposes at room temperature to the stabler $CaCrO_5\cdot nH_2O$, which itself gives calcium chromate on prolonged standing (*68*). The former compound apparently contains two peroxy groups per mole, and so might well be a disubstituted salt of diperoxychromic acid, $H_2[Cr(O)_2(O_2)_2]$, but it is not clear if either of these substances is a definite compound. Analogous derivatives of sodium (*66a*), cobalt (*396*), and nickel (*67*) have been obtained; all were prepared as a result of kinetic studies.

$M^IH_2CrO_7$, $M^ICrO_5\cdot H_2O_2$, $M_2{}^ICr_2O_{11}$. These are all formulas applied to the violet salts of diperoxychromic acid.

$Ca_3Cr_2O_{12}\cdot 12H_2O$ (431). This buff-colored fluffy solid, made by the action of H_2O_2 on calcium chromate at room temperature, contained three

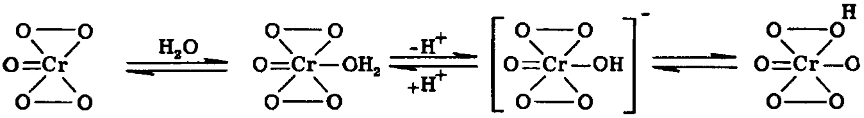
peroxy groups per chromium atom, and was probably a partly decomposed or otherwise impure sample of calcium tetraperoxychromate(V).

$M_2{}^{I}Cr_2O_8$. Purple solids of this composition were obtained by treating an ethereal solution of chromium pentoxide with potassium metal (*81*) or with the solid acetates of lithium, sodium, zinc, or other metals (*388*). The salts were analyzed by a method that may well have allowed the escape of some peroxy oxygen, and were found to contain one peroxy group to two chromium atoms. They were formulated as probably analogous in structure to perdisulfates, but it is not clear whether they are true chemical individuals. Their properties suggest that at least the potassium salt may have been the diperoxychromate, $K[Cr(O)_2(O_2)_2H]$.

Besides these compounds, it has been suggested on the basis of oxygen exchange studies that a peroxy cation of chromium may be formed as an intermediate in the action of O_2 on solutions of chromium(II) (*267*). A blue-green peroxychromium derivative seems to have been formed by the reaction between chromic acid and H_2O_2 in trifluoroacetic acid, but nothing further is known about it (*153*).

F. Discussion and Interpretation

One of the remarkable things about the peroxy compounds of chromium is their similar, but different, conditions of preparation and products of decomposition. In this context, it is interesting to bear in mind that for Cr^{+6}/Cr^{+3}, $E°$ is $+1.33$ volt and $E_B°$ is -0.13 volt; the potentials for H_2O_2 are given in Section III. With increasing pH, the reducing power of H_2O_2 rises, but the ease of reduction of chromium(VI) falls more rapidly. It is therefore a little surprising that the immediate product of the reaction between H_2O_2 and Cr(VI) at $pH < 7$ contains Cr(VI), while in alkaline solution the peroxy compound formed is a derivative of Cr(V); the Cr(V) derivative on decomposition in alkaline solution reverts to chromate, while it is only in acid solution that reduction occurs to Cr(III). The difference in products of decomposition of aqueous solutions of chromium pentoxide on the one hand, and of the violet salts $M[Cr(O)_2(O_2)_2H]$, on the other, is also strange, particularly since the hydrated pentoxide appears to be the parent acid of the violet salts; the latter compounds decompose to chromate and oxygen, while the former gives a proportion of Cr(III) that increases as the pH drops. This suggests that protonation of a peroxy group may be an important part of the reductive decomposition; if this is so, the relationship between the blue pentoxide and the violet salts may be explained in terms of a tautomerism:



This is not the only anomaly; treatment of the peroxychromates with alkali gives chromate, but treatment with ammonia gives triamminodiperoxychromium(IV). The stability of this substance, which can be regarded as containing five-coordinated chromium, is in itself a little surprising; the mechanism of its formation from the etherate of chromium pentoxide is interesting, since both the starting material and the product contain two peroxy groups per molecule:

$$Et_2O{\cdot}Cr(O)(O_2)_2 + 3NH_3 = Et_2O + Cr(O_2)_2{\cdot}3NH_3 + \tfrac{1}{2}O_2$$

It is not clear whether the oxygen is liberated as such, or whether it is involved in oxidizing ammonia (in which case the above equation would be a purely formal representation of part of the over-all reaction); what is clear is that, unless some most unusual rearrangement takes place, the oxygen atom that is eliminated is the chromyl oxygen atom, and is not derived from one of the peroxy groups.

There is much to be discovered about the peroxides of chromium; in particular, it would be interesting to have more structural information about some of the derivatives that seem well characterized, while new compounds may be obtained from reactions using very concentrated hydrogen peroxide. The oxidation-reduction relationships among the compounds already known are summarized in Fig. 5.

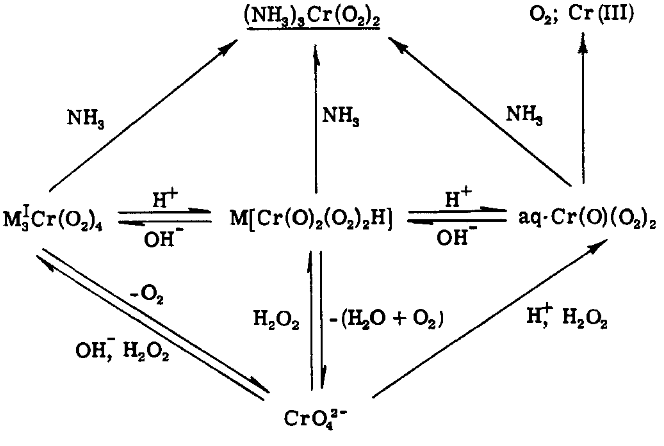


FIG. 5. Relationships among the best known peroxychromium species.

XI. Molybdenum and Tungsten

The known peroxides of molybdenum and tungsten are all apparently derived from the +6 states; nonetheless, their chemistry is complicated and in some places obscure. Alkali and alkaline earth metal salts have been prepared in which the ratio of peroxide to molybdenum or tungsten is

4:1, 3:1, 2:1, and 1:1, besides less well-defined derivatives in which the ratio is not integral; in some cases there is uncertainty as to the degree of polymerization. Peroxypolymolybdates and tungstates are also known, though it is clear that in these systems, as with vanadates (see above), the extent of polymerization is reduced by hydrogen peroxide. There is some evidence to suggest that peroxy cations exist in strongly acid media; complex peroxyoxalates, -tartrates, -phosphates, and -fluorides are formed, and in many cases have been isolated as solids. In the account that follows, a description of the various species in order of decreasing peroxide content is prefaced by a short account of the oxyanions.

A. Oxy Anions

As far as tungsten is concerned, it now seems to be generally agreed that in solution the two simplest species formed are the 1-tungstate, $WO_4^=$, and the hexatungstate, $HW_6O_{21}^{-5}$ (*436*, *473*). The hexatungstate, formed at pH < 10, polymerizes further when boiled with acid, and may exist in two forms; in recent studies no evidence has been obtained to support the suggestions (*50*, *150*, *383*) that di- or tritungstates are formed in appreciable concentration.

With molybdenum the position is less clear. An elaborate study of changes in pH using glass electrodes, in the way developed by Sillén and his school, has been interpreted in terms of the formation of the 1-molybdate ion, $MoO_4^=$, the acid 1-molybdate ion, $HMoO_4^-$, and a heptamolybdate species, $Mo_7O_{24}^{-6}$ (*474*). Other investigators believe that a tetramolybdate anion, $Mo_4O_{13}^=$, and perhaps the free acid $H_2Mo_4O_{13}$ can be obtained in solution (*88*, *115*, *436*).

B. 4:1 Peroxy Species: $M(O_2)_4^= \equiv MO_8^=$

Red salts of the cations Na^+, K^+, Ca^{+2}, Sr^{+2}, Ba^{+2}, Co^{+2}, and $Zn(NH_3)_4^{+2}$ have been obtained by the action of excess H_2O_2 on neutral or slightly alkaline solutions of 1-molybdates, or by double decomposition reactions (*62*, *63*, *173*, *284*, *293*, *357*, *463*, *502*, *504*). These substances (save for the tetrammino-zinc derivative, whose decomposition is more complicated) give almost two moles of O_2 per gram-atom of molybdenum on thermal decomposition, leaving a residue of molybdate, and so are believed to contain four peroxy groups per molybdenum atom; it is not certain, however, that all of these peroxy groups are directly bound to molybdenum. The sodium salt $Na_2MoO_8 \cdot 2H_2O$ cannot be dehydrated further without loss of peroxide oxygen, from which it was concluded that the substance contains two molecules of H_2O_2 of crystallization (*293*). On the other hand, an anhydrous potassium salt has been obtained (*173*) which must contain four directly bound peroxy groups; a spectrophotometric study indicates that $Mo(O_2)_4^{=}$ groups are present in solution, and it would be difficult to explain the difference in color between the yellow 2:1 (see Subsection D) and the red 4:1 compounds if the additional peroxide in the latter were present merely as H_2O_2 of crystallization. While the question will only be answered conclusively by crystallography, it seems likely that the $Mo(O_2)_4^{=}$ ion exists in the solid state, though it may be readily hydrolyzed in solution.

Analogous derivatives of tungsten are formed under conditions like those used in making the tetraperoxy-1-molybdates, and have been analyzed similarly (*61, 64, 65, 244, 293, 417, 463*). The salts of colorless cations are yellow; experiments involving the calcium salt indicate that some peroxide oxygen is lost on dehydration, from which it has been concluded that at least some of the peroxide oxygen is present as H_2O_2 (*65*), while one spectrophotometric study indicated that the yellow species is formed in solution from two peroxy groups per tungsten atom (*470*). A different study, however, using (among other techniques) spectrophotometry, suggested that a peroxytungstic acid containing four peroxy groups per tungsten atom is formed in solution (*437*), while a potassium salt containing one half a molecule of water of crystallization in its formula has been obtained (*463*). Thus it seems likely that, as with molybdenum, a tetraperoxy-1-tungstate anion is formed, though it may be unstable to hydrolysis. The powder photograph of $K_2[W(O_2)_4]$ has been recorded (*58*).

These compounds are all extremely unstable, exploding when struck or warmed; the most stable seems to be tetramminozinc tetraperoxy-1-molybdate, which has been kept unchanged over solid alkali in an atmosphere of ammonia for some weeks (*463*). Though the ultimate products of decomposition of the salts of simple cations are the 1-molybdates or 1-tungstates, a number of intermediate decomposition products have been described, containing 3, 2, or 1 atom of peroxy oxygen per atom of molybdenum or tungsten (*62, 63, 65, 284, 293, 417, 502*). The sodium salt $Na_2[Mo(O_2)_4]\cdot 4H_2O$, for example, gives as immediate decomposition product the yellow diperoxyspecies formulated as $Na_2[Mo(O)_2(O_2)_2]\cdot 2H_2O$ (see below), though the dihydrate decomposes directly to the 1-molybdate (*293*). The heats of decomposition of some of these tetraperoxy salts have been measured (*294, 295, 591*) and have been used to calculate a quantity described as the energy of the bond between the molybdate or tungstate group and the peroxy oxygen atom. It is not easy to see what physical significance to give to this quantity, which is presumably meant to represent $E(MoO_4\text{-}O)$. The kinetics of decomposition of sodium tetraperoxy-1-molybdate (*283, 292*) and of calcium tetraperoxy-1-tungstate (*64*) have been studied, using the rate of oxygen evolution as a measure of the rate of reaction.

Potassium tetraperoxymolybdate gives a deep red solution in water, which slowly turns yellow with evolution of oxygen (*173*) though at pH greater than 7 the ion is apparently stable in the presence of excess H_2O_2; an equilibrium with the dimeric tetraperoxy-1,2-molybdate anion has been suggested:

$$\underset{\text{(I)}}{2\text{Mo}(\text{O}_2)_4{}^{=}} + 5\text{H}_2\text{O} \rightleftharpoons \underset{\text{(II)}}{[(\text{O}_2)_2\text{Mo}(\text{O})\text{OMo}(\text{O})(\text{O}_2)_2]^{=}} + 2\text{OH}^- + 4\text{H}_2\text{O}_2$$

In strong alkali, decomposition to the 1-molybdate is rapid, though the compound $K_2[Mo(O)_3(O_2)]$ has been obtained from an alkaline solution of the tetraperoxy-1-molybdate (*34*); with dilute acid, a yellow solution results with vigorous evolution of oxygen, the yellow species being most probably the dimeric tetraperoxy-1,2-molybate (compound II) (*92*). The solution in concentrated aqueous ammonia is more stable. Tetraperoxy-1-tungstates behave similarly; in acids they give tetraperoxy-1,2-tungstates (in compound II, $Mo = W$), but in alkali they are said to give colorless solutions with only slight evolution of oxygen (*244*).

Both series of salts react almost quantitatively with acid potassium permanganate solution, though the last stages of the reaction with tetraperoxy-1-molybdates are very slow (*173*, *284*); Rosenheim found that only one fourth of the peroxide oxygen of the molybdates oxidized iodide ion (*463*), but Gleu was able to determine the peroxide content of tetramminozinc tetraperoxy-1-molybdate iodimetrically (*173*, *174*). The difference between these two results may arise from different conditions of pH.

C. 3:1 PEROXY SPECIES: $M(O)(O_2)_3{}^{=} \equiv MO_7{}^{=}$

Peroxymolybdates (*504*) and -tungstates (*65*, *417*) of calcium and strontium that contain three peroxy groups per atom of molybdenum or tungsten have been obtained from the thermal decomposition of the tetraperoxy-1-molybdates or -tungstates; strontium triperoxymolybdate is brick-red, while the tungsten derivatives are pale yellow; all are thermally unstable at room temperature, and were formulated as $M^{II}[MoO_7]\cdot aq$ or $M^{II}[WO_7]\cdot aq$. There is little to suggest that these compounds are true chemical species rather than mixtures of salts of the $M(O_2)_4{}^{=}$ and $[(O_2)_2M(O)OM(O)(O_2)_2]^{=}$ anions.

Compounds that appear to be pyridinium salts of composition $PyH_2MO_7\cdot 2H_2O$ (M is Mo or W) have been obtained by treating pyridinium tetraperoxy-1,2-molybdate or -tungstate with hydrogen peroxide (*29*). Attempts to repeat the preparation of the tungsten derivative have not been successful (*182*), the maximum amount of peroxide oxygen per atom of tungsten being 2.5 atoms. Pyridinium triperoxymolybdate decomposes at 100°C, but since it only loses oxygen and is not dehydrated, it has been argued that the peroxide cannot be present as H_2O_2 of crystallization (*29*). On the other hand, the ease with which the peroxide oxygen can be removed has been taken as showing that H_2O_2 of crystallization is present in the solid, so that the molybdenum and tungsten compounds are formulated as $(PyH)_2[(O_2)_2Mo(O)OMo(O)(O_2)_2]\cdot 2H_2O_2$ and $(PyH)_2[(O_2)_2W(O)OW(O)(O_2)_2]\cdot H_2O_2\cdot H_2O$. In support of this view (*182*), the infrared and ultraviolet spectra (the former measured for the solids, the latter for solutions) are the same as those of the tetraperoxy-1,2-molybdate or -tungstate ions.

D. 2:1 PEROXY SPECIES: $M(O)_2(O_2)_2^{=} \equiv MO_6^{=}$; $[(O_2)_2M(O)OM(O)(O_2)_2]^{=} \equiv M_2O_{11}^{=}$

From acid solutions containing alkali metal molybdates and a high concentration of H_2O_2, alkali metal salts may be obtained in which there are two peroxy groups and one alkali metal cation to each atom of molybdenum or tungsten (*36*, *92*, *182*, *244*, *463*). The anions were formulated by Rosenheim as the dimeric tetraperoxy-1,2 species $[(O_2)_2M(O)OM(O)(O_2)_2]^{=}$ (where M is Mo or W), and these dimeric anions are certainly formed under most conditions. A careful study of the changes in pH with volume for the molybdenum system (*514*) supported this view, as did an interpretation of the neutralization curves of mixtures of molybdic acid and H_2O_2 (*544*). A cryoscopic determination of the ionic weight of the tungsten species, formed *in situ* by adding sodium tungstate, nitric acid, and H_2O_2 in appropriate ratio to the sodium nitrate/water eutectic, gave the value expected for the dimer (*241*) and was considered more reliable than an earlier estimate based on dialysis, which indicated a monomeric structure (*236*, *240*). The infrared spectra of the sodium and potassium salts of both the molybdate and the tungstate as solids and in solution in D_2O, together with Raman data from solutions, have been interpreted in terms of the dimeric structure; several coincidences were observed in the infrared and Raman spectra, making a centrosymmetric structure unlikely (*182*). Finally, a crystallographic study (*126*) of the potassium salt shows that the anion is dimeric, with the structure given in Fig. 6. It is particularly interesting that the O—O distance is very close to that for the free peroxide ion. Csanyi (*109*) found two neutralization points on titrating a solution of the parent acid (prepared by passing a solution of the monosodium salt through an acid ion-exchange column) against alkali, at [Mo]:[OH] ratios of 1:1 and 1:2; he interpreted this as showing that there were two acid protons per molybdenum atom, and that the ion is monomeric. The second neutralization point, however, could arise from hydrolysis of the dimer:

$$[(O_2)_2Mo(O)OMo(O)(O_2)_2]^{=} + 3H_2O + 2OH^- \rightleftharpoons 2MoO_4^{=} + 4H_2O_2$$

(The H_2O_2 will react with some of the molybdate ion under these conditions, forming tetraperoxy-1-molybdate.) Support for the monomeric structure was also adduced from R_f values obtained by paper chromatography (*110*), though this is not particularly convincing evidence. With neutral silver nitrate solution, a neutral solution of the sodium peroxymolybdate reacted to give a precipitate, leaving a solution of pH 3.7; this was explained in terms of the reaction (*108*):

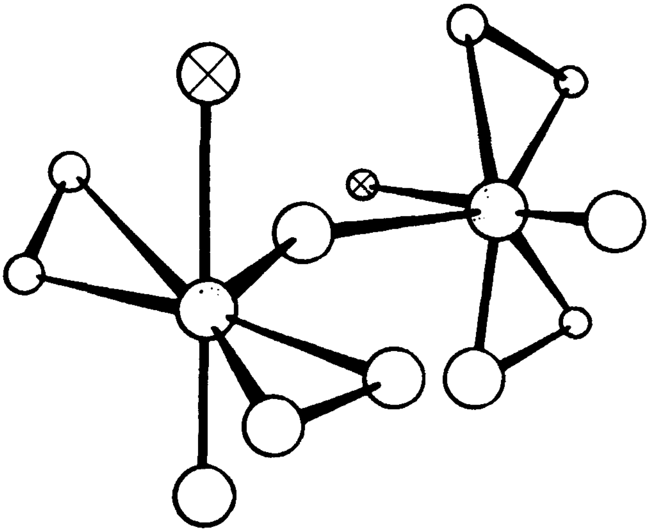


FIG. 6. Structure of the tetraperoxyditungstate ion in $K_2[(O_2)W(O)OW(O)(O_2)]\cdot 4H_2O$. One molecule of water is coordinated to each tungsten atom. Mean structural parameters are: r(W—O), peroxy, 1.91; r(W—O), apical, 1.68; r(W—O), bridge, 1.93; r(W—O), water, 2.36; r(O—O), peroxy group, 1.50 Å; ∠WOW (bridge) = 138°; ∠OWO (peroxy group) ~46°. Three-dimensional analysis, R = 0.17 (*126*). Circle, O; dotted circle, W; crossed circle, O of H_2O.

$$NaH[Mo(O)_2(O_2)_2] + 2AgNO_3 = NaNO_3 + HNO_3 + Ag_2[Mo(O)_2(O_2)_2]$$

Unfortunately, the solid does not seem to have been analyzed (*108*). Finally, the molecular weight of the sodium salt in solution in fused Glauber's salt (~32°) was determined cryoscopically, and gave the value expected for the monomer (*110*). In view of the instability of these compounds, the reliability of the last measurement is open to question; at the same time, there is nothing in any of the experiments so far described that precludes the formation of small amounts of the monomer in equilibrium with the dimer in solution:

$$2H[Mo(O)_2(O_2)_2]^- \rightleftharpoons [(O_2)_2Mo(O)OMo(O)(O_2)_2]^- + H_2O$$

Removal of the proton from the monomeric anion might lead to the formation of derivatives of the doubly charged monomeric anion by displacing the equilibrium. Compounds whose formulas are consistent with the presence of such an anion have been prepared by neutralizing solutions of the free peroxy acids or the monosubstituted salts (*34*, *35*), by thermal decomposition of the tetraperoxy-1-molybdates (*284*) or -tungstates (*58*, *65*), or by the action of H_2O_2 on molybdates (*504*) or tungstates (*417*) at temperatures below 0°. If, as indicated in at least one case by X-ray powder photography (*58*), these materials are compounds and not mixtures, they may contain the monomeric, doubly charged diperoxy anion; it has been suggested, though, that at least those substances which are obtained from strongly alkaline solutions are mixtures of the salts of the tetraperoxy-1,2 anions with alkali (*182*), while it is not impossible that even some of the salts of formulas $M_2^I[MoO_6]$·aq or their tungsten analogs contain polymeric anions. This question is unlikely to be settled without crystallographic data.

It should be added that the discussions of the neutralization curves mentioned above, and the investigation of pH changes in the system (*92*, *109*, *514*, *544*), were made on the assumption that a tetramolybdate species, $H_2Mo_4O_{13}$, is formed in solution; since it has been suggested that the simplest molybdates in aqueous solution are the 1-molybdate and the heptamolybdate ions $Mo_7O_{24}^{-6}$ (*474*), some of these results may need reinterpretation (though see *50*, *436*, *437*).

The dissociation constant of the tetraperoxy-1,2-tungstate ion to a tungstate species and H_2O_2 has been estimated spectrophotometrically (*470*) as 9.74×10^{-2}; the salt $K_2[(O_2)_2W(O)OW(O)(O_2)_2]\cdot 4H_2O$ has been dehydrated at 100° without loss of peroxide oxygen (*276*) so that the coordinated water molecules in the crystal (see Fig. 6) cannot be essential to the stability, while all of the peroxide oxygen was found to be active in the Riesenfeld titration (*245*).

These 2:1 peroxy salts are more stable thermally than the mononuclear tetraperoxy compounds, though some may explode on heating (*182*, *244*, *463*); the tungsten compounds are apparently more stable to decomposition at room temperature than their molybdenum analogs. Thermal decomposition gives molybdate or tungstate, perhaps through intermediate formation of monoperoxy species; the heats of decomposition of some of the disubstituted salts have been measured, from which the usual "bond energies to peroxide oxygen" have been calculated (*282*, *417*, *591*), and the kinetics of the decomposition of "$Na_2[Mo(O)_2(O_2)_2]$" have been investigated (*283*). The free acids are stronger acids than molybdic or tungstic acid (*78*, *92*, *437*); the dissociation constant of $H_2Mo_2O_{11}$, for example, is about 8×10^{-3} (*109*, *437*). The magnetic moments of the sodium and potassium salts of the molybdenum and tungsten anions are less than 0.5 B.M., as expected for derivatives of Mo(VI) or W(VI), while the electrical conductivities have been measured for aqueous solutions at 25° (*137*). The vibrational spectra have been analyzed in terms of a reasonable structure (*182*), which is essentially the same as that found for the hydrated potassium tungstate (*126*).

In solution, the salts react with acid permanganate to give O_2 (*244*, *295*, *463*) and in some cases the heat of this reaction has been determined (*294*, *295*, *417*); the reaction with potassium iodide, which has been mentioned, depends markedly upon pH (*245*). A study of the hydrolysis of the peroxy groups suggests that there is little hydrolysis at pH < 7, that the degree of hydrolysis at pH ~ 9 is 0.26 for the molybdenum anion and 0.5 for the tungsten species, and that the alkaline hydrolysis is unimolecular (*454*, *455*); it is not clear, however, how reliable the methods are that led to these results. It has been shown spectrophotometrically that the equilibrium shown below is set up in solutions rich in H_2O_2 (*92*):

$$[(O_2)_2Mo(O)OMo(O)(O_2)_2]^{=} + 2OH^- + 4H_2O_2 \rightleftharpoons 2Mo(O_2)_4^{=} + 5H_2O$$

Although it appears that in acid solutions, or with less than one mole of alkali per gram-atom of molybdenum, the sole peroxymolybdate species is the dimeric tetraperoxy-1,2-molybdate (*92*), Jahr detected the formation of a peroxyhexamolybdate in the presence of excess acid (*234*). In sulfuric acid more concentrated than 4.5 *M*, there is evidence that a complex peroxymolybdenum cation is formed, containing a sulfate group, two molybdenum atoms, and two peroxy groups (*92*). This is discussed further in Subsection F.

E. 1:1 PEROXY SPECIES: $M(O)_3(O_2)^{=}$ or $MO_5^{=}$

Several compounds of formulas M_2^I(or M^{II})[Mo(or W)$(O)_3(O_2)$]·aq have been obtained by neutralizing solutions of molybdic or tungstic acid containing H_2O_2 (*34*, *35*), by treating a red tetraperoxy-1-molybdate with alkali (*35*), by the action of H_2O_2 on molybdates (*504*) or tungstates (*65*), or as decomposition products of other peroxymolybdates or -tungstates richer in peroxide (*391*, *504*). The free monoperoxymolybdic acid $H_2[Mo(O)_3(O_2)]$ has also been described (*74*, *391*, *542*); it may be prepared by dissolving molybdic acid in H_2O_2 solution, evaporating excess water, and drying the product at 110°. There is, however, some doubt as to whether a monoperoxy species exists in solution (*92*, *234*, *437*, *542*). It was concluded from studies of the neutralization curves of $H_2[Mo(O)_3(O_2)]$ that the species present were tetraperoxy-1,2-molybdic acid and a condensed species that contained no peroxide oxygen (*542*), while one spectrophotometric study gave no indication of the formation of a 1:1 peroxy species in solution (*92*); it was suggested that the free acid is in fact a salt, $[Mo_2(O)_6H]^+$

$[Mo_2(O)_3(O_2)_4H]^- \cdot 3H_2O$. Richardson, however (*437*), using spectrophotometry supplemented by studies of conductivity and pH, has obtained clear evidence for the formation of soluble monoperoxy species of both molybdenum and tungsten. The conductivity of a solution of what was believed to be tetramolybdic acid, $H_2Mo_4O_{13}$, decreased slowly on addition of H_2O_2 until a peroxide:molybdenum ratio of 1:1 was reached, while over the same range the pH rose slowly. At peroxide:molybdenum ratios between 1:1 and 2:1, however, the conductivity increased quite sharply, while the pH dropped. These observations, taken with the spectrophotometric results, were interpreted as showing the presence of a 1:1 peroxymolybdic acid of the same degree of complexity as the parent molybdic acid, depolymerization occurring with the addition of the second peroxy group:

$$H_2Mo_4O_{13} + 4H_2O_2 \rightleftharpoons H_2Mo_4(O)_9(O_2)_4 + 4H_2O$$
$$H_2Mo_4(O)_9(O_2)_4 + 4H_2O_2 \rightleftharpoons 2H_2Mo_2(O)_3(O_2)_4 + 3H_2O$$

No evidence was found to support the suggested salt-like structure for $H_2Mo(O)_3(O_2)$. Attempts to replace the cation $[HMo_2(O)_6]^+$ by H^+, using a protonated ion-exchange column, were not successful, while ion migration studies supported by experiments using paper electrophoresis gave no evidence that molybdenum-containing cations were present. These results make it seem very probable that a 1:1 peroxymolybdic acid is formed in solution under the right conditions. With tungsten, the evidence obtained for the formation of a monoperoxy species was rather less decisive. A plateau of conductivity was found at a peroxide:tungsten ratio of 1:1, and from the over-all results it was concluded that peroxytungstic acids were formed in solution at all peroxide:tungsten ratios (*437*).

"Monoperoxymolybdic acid" was found to react very slowly with neutral potassium permanganate solution, though the reaction was much faster in the presence of sulfuric acid (*437*). The compound oxidized buffered potassium iodide solution (*437*). The degree (*454*) and rate (*455*) of hydrolysis of the potassium derivatives of both molybdenum and tungsten have been measured, but here again it is not clear how reliable the results are.

F. Species Containing Less Peroxide

From solutions of molybdates or tungstates that are poor in hydrogen peroxide, many solids have been isolated that contain between 0 and 1 mole of peroxide oxygen to each atom of molybdenum or tungsten; formulas such as $5BaO \cdot 12MoO_3 \cdot 3O \cdot 18H_2O$ (or $Ba_5Mo_{12}O_{38} \cdot (O_2)_3 \cdot 18H_2O$) are to be found in several of the earlier papers, and ratios of peroxide oxygen to molybdenum or tungsten such as 2:3, 1:3, 2:7, and 1:4 have been reported (*82*, *358*, *373*, *374*, *463*). Many of these compounds were obtained by the action of hydrogen peroxide upon solutions of polymolybdates. Unfortunately, however, there have been few recent studies of these compounds, and it is by no means clear how many of them are chemical individuals. Jahr concluded from his experiments using dialysis that at least some peroxypolymolybdate and -tungstate species were formed in solution (*234, 240, 244*); he described the golden yellow molybdate species as a peroxyhexamolybdate. Richardson's work (*437*) indicates that the 1:1 peroxy species are polymeric, but does not afford evidence for the formation of species containing smaller proportions of peroxide in solution.

G. Complex Peroxy Species

1. *Fluorides*

Complex peroxyfluorides of both molybdenum and tungsten (*402, 403*) were prepared by Piccini by dissolving oxyfluoromolybdates or -tungstates in warm H_2O_2, or by treating solutions of molybdates or tungstates in dilute hydrofluoric acid with H_2O_2; he obtained products with formulas $2M^IF{\cdot}MoO_3F_2{\cdot}H_2O$ (or $M_2^I[Mo(O)(O_2)F_4{\cdot}H_2O]$), $2M^IF{\cdot}WO_3F_2{\cdot}H_2O$, and $3NH_4F{\cdot}MoO_3F_2$. The potassium peroxyfluoromolybdate, which is described as being isomorphous with the oxyfluoromolybdate $K_2MoO_2F_4{\cdot}2H_2O$, decomposed on heating, giving (ultimately) O_2 and potassium molybdate; the compound could be recrystallized from dilute hydrofluoric acid, but was decomposed by dilute sulfuric acid or potassium permanganate solution.

2. *Oxalates*

Peroxyoxalates of molybdenum (*338, 344, 349, 463*) and tungsten (*338, 347, 463*) were prepared by dissolving oxalatomolybdates or -tungstates in 30% H_2O_2 at 0°. Analysis indicates that these compounds contain a dibasic anion in which there are one oxalate and two peroxy groups to each atom of molybdenum or tungsten, though compounds in which there is one peroxy group per heavy metal atom have also been described (*338*). The molybdenum derivatives are deep yellow, while the tungstates are colorless. The peroxy and oxalate groups react with acid permanganate solution; when these compounds were first prepared, their peroxide contents were determined by heating with potassium iodide solution (*344, 347, 349*), which gave results that were much too low (*463*). The degree and extent of hydrolysis has been studied (*454, 455*).

3. *Tartrates*

Evidence has recently been presented to indicate the formation of tungsten peroxy complexes with *d*-tartaric acid (*76*). Spectrophotometric measurements, combined with potentiometry, polarography, and optical rotation studies, suggest that both the tetraperoxy-1-tungstate and the dimeric tetraperoxy-1,2-tungstate anions form complexes, probably with free tartaric acid rather than with the anion.

4. Phosphorus Compounds

A series of compounds has been obtained (*143*) by allowing molybdic acid and H_2O_2 to react with trialkyl phosphates, dialkyl phosphites, dialkyl phosphonates, alkylphosphonic acids, or triphenylphosphine. Orange-red products were obtained either as crystals or oils; they contained one or two peroxy groups per molybdenum atom, and on heating gave blue products with the loss of some of their peroxide oxygen. Structures for the compounds were suggested on the basis of measurements of molecular weight, combined with infrared studies.

5. Sulfates

Spectrophotometric studies of solutions of molybdic acid and H_2O_2 in strong sulfuric acid ($>4.5\ M$) suggest that a sulfatoperoxy complex is formed (*92*, *382*, *479*). In dilute solution at least, it seems likely that the species formed contains one peroxy group per molybdenum atom, though in more concentrated solutions a higher peroxy compound may be formed. It has been suggested that the formation of the species may be described by the equation:

$$H_2[(O_2)_2Mo(O)OMo(O)(O_2)_2] + HSO_4^- + 5H^+ = 2H_2O_2 + \text{complex}$$

This means that the complex must be cationic; on the other hand, transport studies in sulfuric acid as solvent showed no signs of migration (*479*).

H. RELATIONSHIPS IN SOLUTION

In the absence of clear evidence to the contrary, it is assumed in the discussion that follows that peroxymolybdates and -tungstates are chemically similar; unless specifically stated, "M" stands for molybdenum or tungsten. The most convincing of the evidence set out in the preceding paragraphs may be summarized as follows:

(1) In peroxide-rich solutions of molybdates or tungstates, there is an equilibrium between the 2:1 and the 4:1 species:

$$[(O_2)_2M(O)OM(O)(O_2)_2]^{=} + 2OH^- + 4H_2O_2 \rightleftharpoons 2M(O_2)_4^{=} + 5H_2O \qquad (1)$$

The 4:1 species are present in appreciable concentration only in weakly alkaline solution, decomposing to the 1-molybdate (or tungstate) in strong alkali, and dissociating to the 2:1 species at low pH.

(2) In peroxide-poor solutions, there seems to be an equilibrium be-

tween the dimeric 2:1 species and a 1:1 species (which for molybdenum has been described as a tetramer) at pH < 7:

$$H_2[Mo_4(O)_9(O_2)_4] + 4H_2O_2 \rightleftharpoons 2H_2[(O_2)_2Mo(O)OMo(O)(O_2)_2] + 3H_2O \qquad (2)$$

At high pH, the 2:1 species hydrolyzes, giving the 4:1 species and 1-molybdate or tungstate:

$$[(O_2)_2M(O)OM(O)(O_2)_2]^{=} + 2OH^- + 4H_2O \rightleftharpoons M(O_2)_4^{=} + MO_4^{=} + 5H_2O \qquad (3)$$

The relationship between the 2:1 and the 1:1 compounds is not as well-defined for tungsten as for molybdenum.

(3) When H_2O_2 is added to a solution of a polymeric molybdic or tungstic acid, there is a decrease in pH when the (peroxide:molybdenum or tungsten) ratio is greater than 1:1, indicating depolymerization; this follows from Eq. (2) above. For molybdenum, there is a slight increase in pH for peroxide:molybdenum ratios between 0 and 1, implying that the 1:1 peroxymolybdic acid is of the same degree of complexity as the parent molybdic acid, which was believed to be a tetramer. For tungsten, there may be depolymerization over the whole range of peroxide concentration.

(4) The addition of H_2O_2 to a solution of an alkali metal 1-molybdate or 1-tungstate leads to an increase in pH, due to the formation of the dimeric 2:1 anion:

$$2MO_4^{=} + 4H_2O_2 \rightleftharpoons [(O_2)_2M(O)OM(O)(O_2)_2]^{=} + H_2O + 2OH^-$$

In the presence of large concentrations of H_2O_2, the pH falls again [Eq. (1) above].

XII. Manganese

When a solution of potassium permanganate in 30% potassium hydroxide is treated with H_2O_2 at temperatures below 0°, the color turns to deep red-brown; by working at $-18°$, a dark red-brown crystalline solid was obtained (*484*), which was digested with alkaline H_2O_2 at $-12°$ and washed with 3% methanolic potassium hydroxide. Manganese and potassium were present in the solid in the atomic ratio 1:2. Treatment with dilute acid decomposed the compound; for each gram-atom of manganese, 2.5 gram-atoms of oxygen were evolved as gas, while the residual solution contained about 1.5 moles H_2O_2. On this basis, the compound was formulated as a triperoxymanganate(IV), $K_2H_2[Mn(O)(O_2)_3]$; the decomposition by acid was explained in terms of an initial hydrolysis to Mn(IV) and three molecules of H_2O_2, one of which reduced the manganese to Mn(II):

$$[Mn(O)(O_2)_3]^{-4} + 4H^+ + H_2O = MnO_2 + 3H_2O_2$$
$$H_2O_2 + MnO_2 = MnO + H_2O + O_2$$

There are thus two gram-atoms of "O_2" formed in the reaction. The extra half gram-atom was put down to catalytic decomposition of some of the residual H_2O_2:

$$H_2O_2 = H_2O + \tfrac{1}{2}O_2$$

Since one mole of H_2O_2 gives one gram-atom of oxygen as gas on decomposition in this way, loss of half a mole of H_2O_2 from the hydrolysis products would be associated with the formation of half a gram-atom of "O_2," as was observed. This interpretation was further substantiated when hydrolysis at low temperatures was found to form up to two moles of H_2O_2, but no more, per gram-atom of manganese.

The solid gives a red-brown solution in water that slowly evolves O_2 and precipitates MnO_2; with acids, the compound is at once decomposed to O_2 and manganese(II). When dry, it may explode at temperatures above 0°, but it may be kept under acetone for at least 2 days at temperatures of about $-60°$ to $-70°$.

Evidence was also presented (*485*) to indicate the formation of two other potassium peroxymanganates in the preparative reaction; the compounds were formulated as $K_3H[Mn(O)(O_2)_3]$ and $K_2H_2[Mn(O_2)_4]$, but neither was isolated; it was suggested that the former reacts with methanol according to the equation:

$$MeOH + K_3H[Mn(O)(O_2)_3] = K_2H_2[Mn(O)(O_2)_3] + MeOK$$

It has been suggested that manganese(II)-phthalocyanine is an oxygen carrier (*128*), but this suggestion has been questioned (*129*). There is evidence that manganese forms a soluble, colored peroxy complex in the presence of citrate (*539*).

XIII. Rhenium

Red salts, formulated as containing the peroxy anion $[Cl_5Re(O_2)ReCl_5]^{-4}$ (with rhenium in the +4 state) are formed by oxidizing the analogous μ-oxo derivative, $[Cl_5ReOReCl_5]^{-4}$, with such oxidizing agents as cerium (IV), iodate, bromate, dichromate, iron(III), nitrite, H_2O_2, or molecular oxygen (which is only effective in the presence of a catalyst, such as nitrite or nitrate ions) (*258*, *259*, *261*). The reaction has been studied spectrophotometrically; the complexes are formed by most of the oxidizing agents in a combining ratio (chlororhenate:oxygen atom equivalents) of 1:2, but with H_2O_2 the ratio is 1:3, when the red species has a formation constant of 10^{14}. The kinetics of the reaction between H_2O_2 and the μ-oxochlororhenate ion have also been investigated (*260*). Solid cesium, rubidium, and quinolinium salts of formulas $M_2^{I}H_2[Cl_5Re(O_2)ReCl_5]$ have been obtained and analyzed. They all decompose slowly at room temperature to the μ-oxo compounds, the rubidium salt being the least stable, and dissolve in acids giving solutions that are red at pH $\leqslant 2$ but yellow in less acid systems; it has been suggested that the red species contain protonated peroxy bridges. The quinolinium salt has a paramagnetic susceptibility μ_{eff} of 3.56 B.M. (*259*).

The total oxidizing power of the anion was determined by treatment with excess iron(III) followed by titration with permanganate, and the result was consistent with the presence of two rhenium(IV) atoms and a peroxy bridge; it was claimed that titration against permanganate of a solution in 2 *M* hydrochloric acid containing H_2O_2 and the μ-oxo derivative in the molar ratio 3 H_2O_2 to 1 chlororhenate established the presence of the peroxy bridge, but this evidence seems indecisive. These compounds are most interesting, but some of the ways in which they may be prepared are unusual for peroxy compounds, and more structural information is needed.

The compound previously reported as Re_2O_8 seems to have been perrhenic acid (*583*).

XIV. Iron

Only one solid substance has been described that seems at all likely to be a peroxide of iron (*394*). This material, which is deep red, is formed by the action of 30% H_2O_2 on a suspension of ferrous hydroxide in alcohol at $-20°$ to $-60°$; when the equivalent amount of alcoholic potassium hydroxide was added to a solution of iron(II) or iron(III) chloride in alcohol mixed with 30% H_2O_2, an apparently similar precipitate was formed, though no such substance was obtained by the action of H_2O_2 on a suspension of iron(III) hydroxide. The red solid was analyzed for peroxide oxygen by treatment with potassium iodide solution that contained a little sulfuric acid, and ratios of peroxide:iron of between 0.8 and 1 were obtained.[6] The substance, which contained water, was unstable at room temperature, evolving O_2; when treated with water or acids, it gave H_2O_2. It was formulated as $Fe(O_2)$. The true nature of this substance must be considered in serious doubt until its properties have been investigated again; at the same time it is unlikely to be iron(II) ferrate, as has been suggested (*317*), in view of the oxidation potentials of the ferrate ion [Fe(VI)Fe(III), $E° > 1.9$; $E_B° > 0.9$ volt] (*302*). Rather surprisingly, ferrate has been identified spectrophotometrically in solutions of iron(III) ($\sim 10^{-3}$ *M*) in 2–7 *M* potassium hydroxide containing ethylenediaminetetraacetic acid (EDTA) and H_2O_2, though no ferrate was detected in the absence of EDTA (*285*).

Peroxy derivatives of iron are generally considered to be formed as intermediates in the catalytic decomposition of H_2O_2 by ferrous or ferric salts. Although some of the early evidence for this view is open to question (*75, 332, 333*), a spectrophotometric study (*132*) indicates the forma-

[6] This method of analysis depends on the iron being in the ferrous state.

tion of a peroxyferric species at pH ~ 1.5, containing iron and peroxide in the ratio 1:1 and formulated as $Fe(O_2H)^{+2}$. Similar 1:1 complexes are formed in the presence of EDTA (*28*, *451*) or 1,1-diaminocyclohexanetetraacetic acid (*28*) at pH > 9, with formation constants of $\sim 4 \times 10^3$ for the EDTA complex and $\sim 7 \times 10^2$ for the diaminocyclohexane derivative. Peroxide-iron(III) complexes may well be of major importance in mechanisms of catalysis (*202*, *310*) or of the operation of iron(III)-containing enzymes such as peroxidase or catalase (*159*); they are also clearly related to the oxygenated compounds of the ferrous species called oxygen carriers. The ferrous oxygen carriers include ferrous dimethylglyoxime (*117*) and derivatives of heme (iron(II) protoporphyrin) such as hemoglobin, and hemerythrin (which despite its name does not contain heme); these compounds all take up O_2 reversibly. Hemoglobin itself contains four heme groups, and can combine with up to four molecules of O_2, though the four dissociation constants are not the same (*161*); it appears that the oxygen molecules displace water ligands (*275*), and can in turn be displaced by carbon monoxide; oxyhemoglobin and carboxyhemoglobin are low-spin complexes, in contrast to the high-spin hydrated hemoglobin. The stereochemical arrangement of the oxygenated complex is not yet known. The non-heme derivative hemerythrin may take up one molecule of O_2 to each pair of iron atoms (*334*); here again oxygenation reduces the paramagnetic susceptibility.

Heme itself is not an oxygen carrier; it is fairly readily oxidized by O_2 to hemin (ferri-heme). Imidazole-protohemochrome (*106*) (heme with one imidazole ligand) and diimidazole-protohemochrome (*107*) are oxygen carriers, the latter combining with O_2 in the absence of solvent, though heme itself when dissolved in pyridine does not take up O_2 unless imidazole is added (*106*). In neutral or alkaline solution, many derivatives of iron(II) take up O_2, but are oxidized rapidly to iron(III). The oxygen carriers are remarkable, not because of the ease with which they take up oxygen, but because the process of dissociation with electron transfer from the metal to the O_2 group has somehow been inhibited.

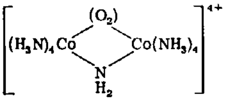
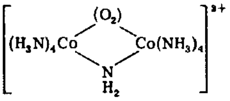
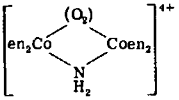
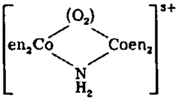
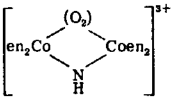
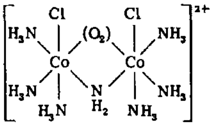
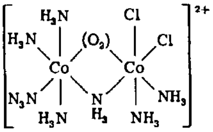
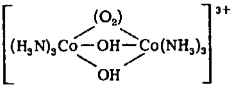
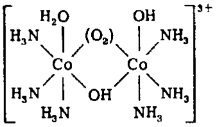
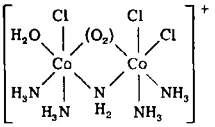
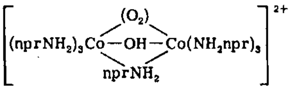
XV. Cobalt

The best known peroxy compounds of cobalt are binuclear, and usually cationic. Two series of these derivatives have been described, in each of which the cobalt atoms are linked through a peroxy bridge (though other bridging groups, such as $-NH_2$, may also be present). Salts of the one series are usually red or brown; they are diamagnetic, and have formulas that can be expressed in terms of two cobalt(III) atoms connected by a peroxide ion:

$$[Co^{+3}—O_2—Co^{+3}]$$

TABLE III

Conventional Labeling Adopted for Some of the Peroxydicobalt Species

$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{5+}$	P_a^1	$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+}$	D_a^1
	P_a^2		D_a^2
	P_{en}^2		D_{en}^2
	$[P_{en}^2]'$	-	-
	$[P^2_{a,2\,Cl}]_s$	-	-
	$[P^2_{a,2\,Cl}]_a$	-	-
	P_a^3	-	-
	$[P^{2,ol}_{a.aq,ol}]$	-	-
	$[P^2_{a,\,3\,Cl,aq}]$	-	-
$[(NC)_5Co(O_2)Co(CN)_5]^{5-}$	P_{CN}^1	$[(NC)_5Co(O_2)Co(CN)_5]^{6-}$	D_{CN}^1
	-		$D^{3,ol}_{npr}$

The remaining 5 coordination positions on each cobalt atom are filled by amino, chloro, cyano, or other ligands. Members of the second series are usually green; they are paramagnetic, and can in many cases be obtained as one-electron oxidation products of the diamagnetic derivative. Werner formulated them as containing two nonequivalent cobalt atoms:

$$[Co^{+3}—O_2^{=}—Co^{+4}]$$

More recent work, however, has shown that their electronic structures cannot be described in simple terms; the cobalt atoms are equivalent, and of oxidation state between 3 and 4. We have labeled the paramagnetic derivatives "P" salts, in contrast to the diamagnetic (D) derivatives (see Table III).

Besides these compounds, several complexes of cobalt have been prepared which act as oxygen carriers; these are briefly considered in this section. Finally, an ill-defined "simple" peroxide has from time to time been mentioned in published work.

A. Preparations

In the synthetic reactions that are described below, the peroxy bridge is introduced using air, ozone, or H_2O_2, but changes in the remaining ligands are achieved by a variety of methods.

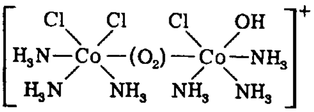
1. *Monobridged Species*

The brown salts obtained by air oxidation of ammoniacal solutions of cobalt(II) salts (*151*, *265*, *335*, *559*, *573*), and called oxocobaltiates by Frémy (*151*), were shown by Werner to contain the (diamagnetic) cation $[(H_3N)_5Co\cdot(O_2)\cdot Co(NH_3)_5]^{+4}$, D_a^1; salts of the green paramagnetic ion $[(H_3N)_5Co\cdot(O_2)\cdot Co(NH_3)_5]^{+5}$, P_a^1, which is formally a one-electron oxidation product of D_a^1, may be prepared similarly (*151*, *265*, *335*, *559*, *573*). It appears that the complex $[(H_3N)_2Co(OH_2)_4]^{+2}$, which is formed initially, is further substituted until the pentammine $[(H_3N)_5Co(OH_2)]^{+2}$ is produced, and that this then reacts with molecular oxygen (*266*). Preparation by this method, however, is slow and inefficient, and ozone (*177*) or H_2O_2 and ammonium persulfate (*175*) have been used in making salts of the green cation. Among the anions in these salts may be noted thiocyanate (*339*), perchlorate (*124*), permanganate (*124*), dichromate (*124*), and bromide (*124*) obtained by double decomposition.

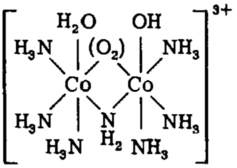
The action of air on a solution containing cobalt(II) and cyanide ion at 0° gives a brown crystalline solid containing the diamagnetic anion $[(NC)_5Co\cdot(O_2)\cdot Co(CN_5)]^{-6}$, D_{CN}^1 (*203*); oxidation of this species with bromine in alkaline solution gives the paramagnetic $[(NC)_5Co\cdot(O_2)\cdot Co(CN)_5]^{-5}$,

$P_{CN}{}^1$, which is red, an unusual color for a P-type derivative. The potassium salt of this anion was originally described as $K_3[Co(CN)_6(OH)]\cdot H_2O$ (*513*).

A dark green salt which Werner (*570*) believed to contain the unsymmetrical cation



was obtained by the action of cold dilute acetic acid on the dibridged species

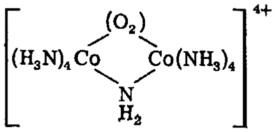


$(P^2_{a,ol,aq})$

followed by concentrated hydrochloric acid. The structure implies that the salt should be paramagnetic.

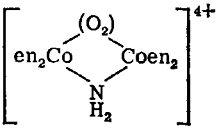
2. *Dibridged Species*

Oxidation by air of an ammoniacal solution of cobalt(II) sulfate gives a red solid, which Vortmann (*559*) called "fusco-salt" and which is a mixture of complex cobalt species (*572*); from it the green paramagnetic dibridged cation



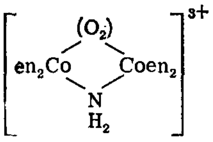
(P^2_a)

can be extracted (*568*, *570*). The yield is very poor, but may be improved by using ozonized air (*177*, *525*). This cation may be reduced to its diamagnetic analog in a one-electron step (*570*). When treated with ethylenediamine (*570*), the ammonia ligands are replaced, giving



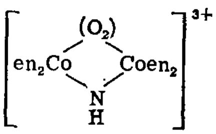
(P^2_{en})

In the presence of excess of base, reduction occurs to the diamagnetic analog



(D_{en}^2)

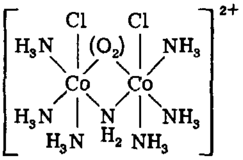
which is usually obtained from nitrate solution as an acid salt of formula $D_{en}^2 \cdot (NO_3)_3 \cdot HNO_3 \cdot 2H_2O$ (*537*). The cation



$(P_{en}^2)'$

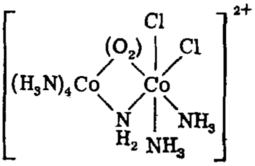
which was described by Werner (*570*) as formed by the action of aqueous ammonia on P_{en}^2, is perhaps identical with D_{en}^2 (*537*).

The insoluble chloride of the dark green paramagnetic cation formulated by Werner as the symmetrical dichloro species



$([P_a^2, 2Cl]_s)$

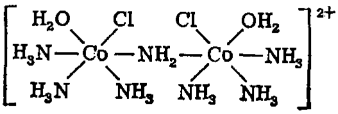
is precipitated by the action of ammonium chloride and hydrochloric acid on P_{en}^2 (*570*). If, however, ammonium carbonate is used instead of ammonium chloride, another dark green salt is obtained, which was formulated as containing the isomeric unsymmetrical cation



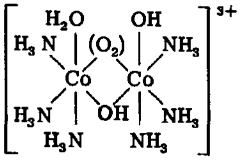
$([P_a^2, 2\ Cl]_a)$

on the basis of degradative experiments (*570*) (see below).

One other green salt, which is probably paramagnetic, is obtained from the so-called "melanochloride" shown by Werner to have the structure



by treatment with silver nitrate and dilute nitric acid (*570*); the cation of the product was described as

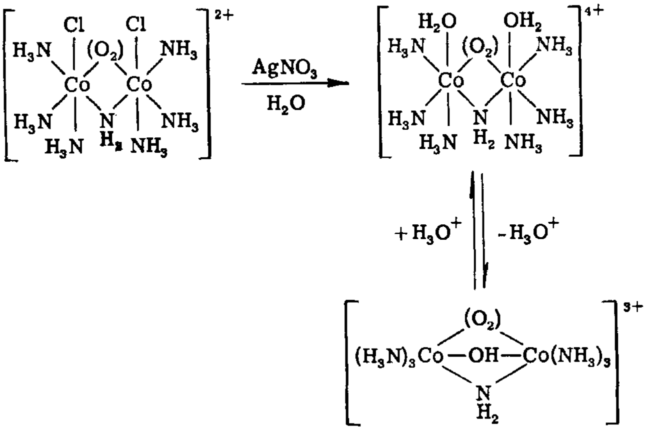


$(P^{2,ol}_{a,aq,ol})$

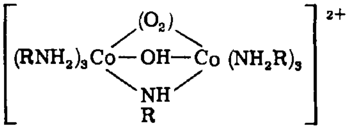
but it is not clear where the oxygen for the peroxy bridge came from.

3. Tribridged Species

Treatment of the symmetrical dichlorodibridged cation $[P^2_{a,2Cl}]_s$ with acidified silver nitrate solution gives the symmetrical diaquo complex $[P^2_{a,2aq}]_s$, which appears to be in equilibrium with the tribridged species P_a^3 (*570*):



It may also be prepared from melanochloride (*570*). Red salts, formed by the action of air on solutions of cobalt(II) chloride in ethanol containing *n*-propylamine or allylamine (*79, 395, 405, 406*), are believed (*101*) to contain tribridged diamagnetic cations where R is allyl or *n*-propyl:



4. The Simple Peroxide

A cobalt peroxide was obtained by adding H_2O_2 to a solution of cobalt(II) chloride in alcohol at −20°, followed by the slow addition of dilute sodium hydroxide solution. The material apparently has the formula $Co(O_2)$ (*503*). Other higher oxides of cobalt have been reported, but there is no evidence to suggest that they are peroxides.

B. STRUCTURES

1. *General Features*

The presence of peroxide oxygen in these salts was first inferred from their reaction with acids to give oxygen (*151, 265, 335, 559, 573*), though their behavior in the Riesenfeld titration is erratic (*101*). Reduction of the monobridged species $[(H_3N)_5Co{\cdot}(O_2){\cdot}Co(NH_3)_5]^{+5}$, P_a^1, with arsenic(III) oxide in the presence of traces of osmium tetroxide catalyst established the presence of five oxidizing equivalents per mole, four of which were liberated as oxygen gas (*175*):

$$2[(H_3N)_5Co{\cdot}(O_2){\cdot}Co(NH_3)_5]^{+5} + 20\ H^+ + As^{+3} = 2O_2 + 4Co^{+2} + As^{+5} + 20\ NH_4^+$$

This showed there was an odd number of electrons associated with the cation; this, the red cyanide, and others of the green salts have paramagnetic moments close to 1.73 B.M. (*30, 175, 203, 331, 342*), indicating the presence of one unpaired electron to each pair of cobalt atoms; the Curie-Weiss law is obeyed between 77° and 273° (*331*). Several of the brown D-type cations have been shown to be diamagnetic (*139*).

These observations, coupled with the results of chemical analysis, establish the stoichiometry of the compounds concerned; the questions that are not solved in this way are: How are the nuclei arranged? Where is the unpaired electron located?

The best crystallographic data available indicates that (*549*), as suggested by Vlceck (*556*), the O_2 group lies with its axis perpendicular to the Co—Co axis (see Fig. 7) with distances and angles as shown[7]; the bonding may then be regarded as analogous to that found in platinum-ethylene complexes. At the same time, such a description no more than establishes the equivalence of the cobalt nuclei. Electron resonance studies (*48, 124, 177, 482, 483*) confirm this conclusion, and show that there is appreciable unpaired electron density at the cobalt nuclei in the monobridged and dibridged species studied, while work on dilute single crystals of P_{en}^2 in a matrix of μ-aminotetrakisethylenediaminecobalt(III,III) nitrate (*177*) has shown that the unpaired electron behaves as a spin arising from a *d*-like hole in an otherwise filled molecular orbital. At the same time, the magni-

---

[7] It is most interesting that an analysis of the structure of D_a^1, though still incomplete, indicates a "skewed" arrangement for the peroxy group; the cobalt and the peroxide oxygen atoms are coplanar, with Co—O—O angles of ~122° and ~31° (*548*).

tudes of the cobalt hyperfine interaction tensors were best explained in terms of a structure in which the O—O axis was skewed relative to the Co—Co axis (*177*). These results indicate that in the green salts the unpaired electron is in an antibonding molecular orbital with appreciable density on both cobalt nuclei (*177*). While this conclusion may depend to

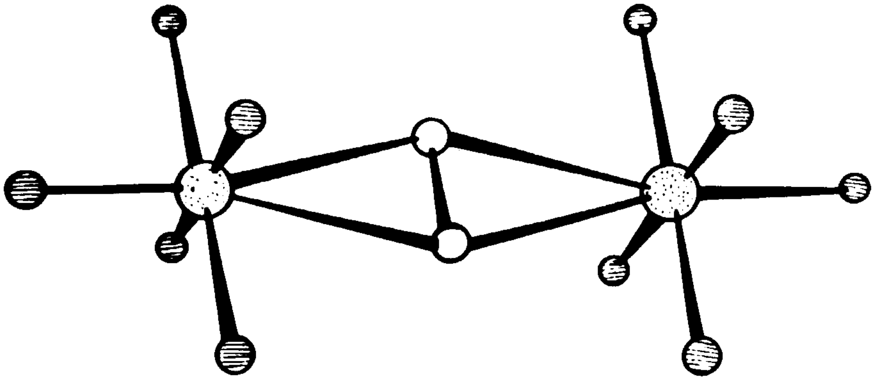
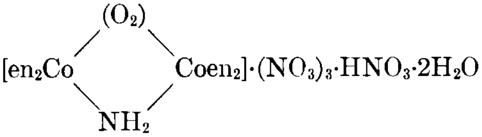


FIG. 7. The heavy atoms in the cation $[(H_3N)_5Co\cdot(O_2)\cdot Co(NH_3)_5]^{+5}$ from a study of the anhydrous pentanitrate (*549*). The structural parameters are: r(Co—N), 1.96–2.01 (three different values, all ±0.04); r(Co—O), 2.38 ± 0.04; r(O—O), 1.45 ± 0.06 Å; ∠NCoN, 84–96°, all ±4°; ∠CoOCo, 144°, ∠CoOO, 72°, both ±4°. Three-dimensional analysis, $R = 0.2$. Circle, O; dotted circle, Co; lined circle, N.

some extent on the other ligands, it appears to hold for mono-, di-, and tribridged amino species P_a^1, P_a^2, P_a^3, for P_{en}^2, and for P_{CN}^1 (*48, 124, 125, 177, 562*). Polarographic studies support this view (*557*), while the absence of semiconducting properties (*141, 142*) is also in accordance with the equivalence of the cobalt atoms.

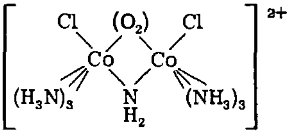
2. Particular Cases

(*a*) 

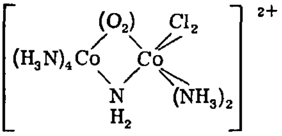
$$[en_2Co\overset{(O_2)}{\underset{NH_2}{\diamond}}Coen_2]\cdot(NO_3)_3\cdot HNO_3\cdot 2H_2O$$

This was described by Werner (*570*) in terms suggesting that he regarded it as analogous to the paramagnetic P_{en}^2. The compound, however, is diamagnetic and the ultraviolet spectrum strongly suggests that the cation present is the diamagnetic D_{en}^2. The additional proton may be coordinated to the peroxy bridge (*537*).

(*b*) Isomerism of

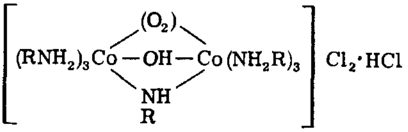


and

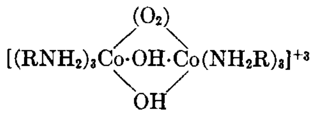


The structure of the symmetrical species seems to have been decided on the basis of its hydrolysis to the tribridged species (*570*). The unsymmetrical compound, on the other hand, decomposed when heated with hydrochloric acid to give cobalt(II) and chloropentamminecobalt(III) species, from which it was concluded that the cation had the unsymmetrical structure (*570*). Analogous symmetrical and unsymmetrical dibromides have also been prepared, and the evidence as to their structures is much the same as for the chlorides; the symmetrical dibromide was made by the action of hydrogen bromide on the tribridged $P_a{}^3$, which is further evidence for the symmetrical structure. The symmetrical and unsymmetrical isomers differ in solubility; nonetheless, the evidence as to their structures is not decisive, and there is room for further investigation before Werner's suggestion can be accepted with confidence (*570*).

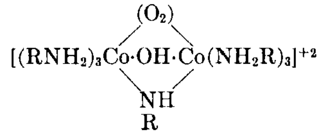
(*c*)



(where R is *n*-propyl or allyl.) The cation in these salts was formulated (*79, 395*) as



but salts of such a cation should be paramagnetic; the *n*-propylamino derivative, however, is diamagnetic (*101*), hence this structure cannot be right. The analytical data are most satisfactorily reconciled with the magnetic measurements if the compound is regarded as an acid salt of the diamagnetic cation



$$[(RNH_2)_3\underset{\underset{R}{NH}}{\overset{(O_2)}{Co\cdot OH\cdot Co}}(NH_2R)_3]^{+2}$$

rather like the acid salt of the ethylenediamine derivative D_{en}^2 mentioned above (*537*).

C. Other Physical Properties

The absorption spectra of several of the complexes of both P and D series have been recorded, sometimes without agreement as to the details of the spectra, in a number of media, as shown in the tabulation.

Cation	Range (mμ)	References
P_a^1	200–700	(*89, 313, 500, 590*)
D_a^1	200–750	(*89, 500, 590*)
P_a^2	200–750	(*500, 525*)
P_{en}^2	400–750	(*341, 537*)
D_{en}^2	300–750	(*537*)
$[P_{en}^2]'$	450–700	(*341*)

The spectra have not been analyzed in detail in terms of electronic structure, though in some cases (*313*, *341*) comparison is made with the spectra of related derivatives, and some very general assignments are made. The circular dichroism of P_a^1, D_a^1 (*590*) P_{en}^2, and $[P_{en}^2]'$ (*341*) have been investigated; the refractive indices of D_a^1 (*587*) and P_a^2 (*587*) have been measured. Werner (*571*) succeeded in obtaining *d* and *l* forms of the cations P_{en}^2, D_{en}^2, and $[P_{en}^2]'$ as the bromcamphorsulfonates, and their rotatory dispersions have been measured (*341*). The X-ray powder photographs of P_{en}^2 and D_{en}^2 nitrates were recorded, as was that of the acid nitrate $D_{en}^2(NO_3)_3\cdot HNO_3\cdot 2H_2O$ (*537*), while parts of the infrared spectrum of P_a^1 (*549*) and P_a^2 have been briefly described (*90*, *157*). There is a band at ~820–840 cm^{-1}, a region often associated with coordinated peroxide, in the spectrum of P_a^1, but other absorptions might also be expected in this region. The molar conductances of a number of P_a^1 salts have been measured (*435*).

D. Chemical Properties

1. *Stability*

These salts are most stable when dry, but they all decompose slowly at room temperature or more quickly on heating. Derivatives of the diamagnetic cation $[(H_3N)_5Co\cdot(O_2)\cdot Co(NH_3)_5]^{+4}$, $D_a{}^1$, are particularly unstable, being difficult to obtain quite free from paramagnetic impurities, for they are decomposed by water or acids (*203, 500, 570, 573*). The decomposition in dilute sulfuric acid is extremely complicated, one gram-ion of $D_a{}^1$ reacting with 2.9 moles of acid to give at least 8 cobalt-containing species, including $P_a{}^1$; a mechanism has been proposed for the process that invokes formation of the intermediate $[H_3N)_5Co(O_2H)]^{+3}$ (*89*). Acidification of aqueous solutions of $D_{CN}{}^1$, $[(NC)_5Co\cdot(O_2)\cdot Co(CN)_5]^{-6}$, leads to the formation of $[(NC)_5Co(OH_2)]^{-2}$ (*203*).

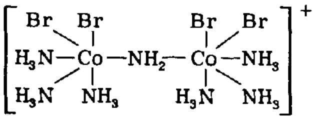
Salts of $P_a{}^1$ dissolve in concentrated sulfuric or phosphoric acid to give solutions stable for some weeks at room temperature (*48, 124*), but decomposition begins after a few minutes in water (being fast once begun) and is rapid in alkali (*125, 570, 573*). The dibridged species $P_a{}^2$ and $P_{en}{}^2$ give more stable solutions in water, though $P_a{}^2$ decomposes irreversibly in alkali; $P_{en}{}^2$ is reduced to the diamagnetic $D_{en}{}^2$ by base (*537*), but the peroxy framework is preserved. This implies that ionization of a proton from a coordinated amino group may be an important step in the irreversible decomposition, though it has also been suggested that $P_a{}^1$ is stabilized in acids by hydrogen bonding to the peroxy bridge (*313*). The perchlorates of $P_a{}^1$ and $P_a{}^2$ are soluble in acetone, and many $P_a{}^1$ and $P_a{}^2$ salts give solutions in liquid ammonia that are stable for a few minutes at least at −35° (*124*); liquid ammonia reacts with the halogenated species to replace the coordinated halogen atoms by ammonia (*570*).

2. Oxidation-Reduction Reactions

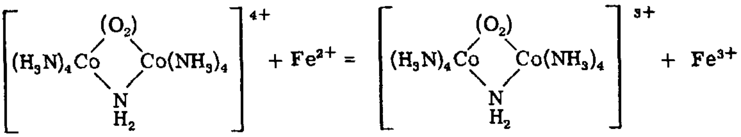
The reduction of P salts and of their D analogs has been studied polarographically (*30, 435, 557*); from the chemical point of view, the most thoroughly studied P–D change is in the system (*537*):

$$e^- + P_{en}{}^2 \rightleftharpoons D_{en}{}^2$$

The reductive step is achieved rapidly by hydrazine, nitrite, ferrocyanide, arsenite, thiosulfate, or hydroxyl ions (*537*); tin(II), iron(II), iodide, or sulfite ions destroy the peroxy bridge. The reverse reaction is brought about rapidly by permanganate, nitrate, or bromate ions, hypochlorous acid, or bromine, but there is no immediate reaction with H_2O_2, iron(III), silver(I), mercury(II), or dichromate ions. This rather oddly assorted collection of effective and ineffective oxidizing and reducing agents makes it clear that the process is very much influenced by activation effects; it was suggested that an even more unexpected reaction, the apparent one-electron oxidation of $D_{en}{}^2$ by bromide ion, was really a catalytic disproportionation (*537*), though little direct evidence was presented to support this view. The action of bromine and sulfur dioxide on the tribridged P_a^3 breaks the peroxy bridge, giving the cation (*570*):



Attempts to prepare the diamagnetic D_a^1 by reducing P_a^1 in solution have led to the formation of decomposition products, probably because of the instability of D_a^1 in solution, but the intermediate formation of D_a^1 in the reduction is suggested by the polarographic results; intermediate formation of D_a^1 has also been postulated in the cathodic reduction of P_a^1 at a platinum electrode (*23*), in the reduction of P_a^1 by iron(II), vanadium(IV), tin(II), thiosulfate, or iodide ion (*501*) (though with iodide ion the mechanism is more complicated) (*528*) and in the reduction by arsenic(III), both uncatalyzed and in the presence of silver powder (*23*). It is proposed that attack by the peroxy group at the reducing center is the step that precedes electron transfer, and which prevents the protonation of the bridge that is the preliminary step in the complex decomposition in acid solution; the stoichiometry of the reactions shows that there is a one-electron transfer, with evolution of O_2. The reaction with iron (II) is catalyzed by anions, an effect that has been discussed in terms of ion pair formation (*527*). A study of the kinetics of the reduction of P_a^2 by ferrous ion (*525*) indicates that here too the initial step is the one-electron reduction to the diamagnetic cation D_a^2:



The effect of acid on the reaction rate is consistent with extensive protonation of the peroxy bridge in solutions of D_a^2; it is suggested that the dissociation constant of the protonated species is less than 10^{-3}. The reaction between P_a^1 and sulfite or nitrite ions appears to follow a different mechanism (*526*).

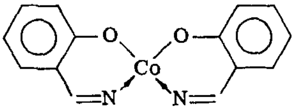
3. Other Chemical Properties

It has been claimed that in aqueous solutions of sulfate or oxalate ions, P_a^1 and D_a^1 give complex anionic species formulated on the basis of studies of ion migration and of dialysis (*73*) as $[D_a^1{\cdot}4L{\cdot}18H_2O]^{-4}$ or $[P_a^1{\cdot}4L{\cdot}18H_2O]^{-3}$, where L is sulfate or oxalate. Though some of the evidence is impressive, the conclusions are hard to reconcile with the observation (*48*) that the ultraviolet spectra of $P_a{}^1$ in concentrated sulfuric acid and in a potassium bromide disc are virtually the same. This matter requires further investigation.

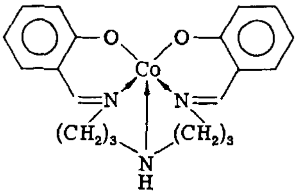
Various ligand-exchange reactions are mentioned in the section dealing with preparations. In particular, ammine and halogen ligands in dibridged species can be exchanged under appropriate conditions (*570*); halide ligands can be hydrolyzed and ammonolyzed (*570*) without disrupting the peroxy bridge, while the hydrolysis can be reversed by hydrogen halide. Ligand-exchange reactions have been less extensively studied for the monobridged species, probably because of their greater tendency to decompose in solution.

E. COMPLEXES OF BIOLOGICAL INTEREST

Certain complexes of cobalt with chelating ligands can behave as oxygen carriers. Among derivatives of a substituted salicylaldehyde and an amine, two types of complex emerge as being able to carry oxygen both in the solid state and in solution (*17, 22, 84, 85, 208, 229, 580*); they may be represented as



(I)



(II)

Complexes of type I have paramagnetic susceptibilities corresponding to the presence of one unpaired electron to each cobalt atom, and can absorb up to half a mole O_2 per mole; absorption of O_2 leads to a linear decrease in paramagnetism. Complexes of type II, on the other hand, have magnetic moments close to 3.8 B.M., indicating the presence of three unpaired electrons per mole; in absorbing one mole O_2 per cobalt atom, the magnetic moment decreases to a value corresponding to one unpaired electron. The oxygenated products are brownish red in color, and are unstable in solution at low pH (for review see *336*).

Studies involving peptides and a number of amino acids (*80, 167*) have shown that yellow-brown complexes of cobalt(II) with glycylglycine (GG) and with histidine (H) are reversibly oxygenated, and undergo spontaneous conversion to pink, irreversibly oxidized forms. Two moles of GG and half a mole of O_2 combine with one mole of Co(II) to form a red-brown crystalline complex, which is not formed under anaerobic conditions and which is formed irreversibly at pH less than 2. Once the complex is formed, part of the constituent chelating peptide cannot be enzymatically hydrolyzed, whereas in the free state GG is very rapidly hydrolyzed under similar conditions. The oxygenated complex is reminiscent in many of its properties of the D-type peroxy complexes discussed in Subsection B, and was consequently formulated as having the structure

$$X_2Co\cdot(O_2)\cdot CoX_2$$

where X represents the chelating peptide or amino acid (*83*).

This reversible binding of oxygen has been studied (*215*, *511*, *512*) by a variety of physical methods. The red-brown oxygenated form is probably diamagnetic (*83*, *511*, *512*); it has a strong charge-transfer band ($\lambda_{max} = 29{,}000\ cm^{-1}$, $\ln \epsilon = 3.47$) in its ultraviolet spectrum, and it is polarographically reduced to H_2O_2. A kinetic study of the absorption of O_2 by cobalt(II)-glycylglycine in the pH range 7–12.5 indicates that an intermediate is formed containing hydroxyl ions, which is of the form

$$[(HO)(GG)_2Co\cdot(O_2)\cdot Co(GG)_2(OH)]$$

and is obtained by the addition of O_2 to $[Co(GG)_2(OH)_2]^-$ (*532*). It has been shown polarographically that the product of the irreversible reaction does not contain peroxide oxygen, but corresponds to the general formula $[CoX_2(OH)_2]^-$ or $[CoX_2(OH)]$; the red complex $[Co^{III}(GG)_2(OH)]_2\cdot H_2SO_4$ has been isolated and characterized (*83*).

Bishistidinatocobalt(II) also takes up O_2 in the molar ratio O_2:Co of 1:2; the oxygenated species is diamagnetic, in contrast to the parent complex, and slowly changes to a red cobalt(III) derivative (*215*, *336*). The solid oxygenated species has recently been isolated, and from the infrared spectrum it has been deduced that each cobalt atom is six-coordinated, with a peroxy bridge like that in the perdisulfate ion (*472*).

Vitamin B_{12a}, containing cobalt(III), also takes up oxygen, apparently dimerizing in the process (*251*); it is not clear whether the oxygenation is reversible.

The decomposition of H_2O_2 by catalytic amounts of cobalt(II)-glycinate complexes (*589*) results in the formation of stable red-violet cobalt(III) complexes which have been shown to be mixtures of *cis*- and *trans*-hydroxoaquobis(glycinate)cobalt(III), but unstable amber-colored solutions are produced in the formation of these compounds. A careful investigation of the amber-colored solution has shown it to contain μ-peroxotetrakisglycinedicobalt(III):

$$[(G)_2Co\cdot(O_2)\cdot Co(G)_2]$$

H_2O_2 is also decomposed by solutions of aquo(ethylenediaminetetraaceto)-cobalt(II), $[YCo(OH_2)]^{=}$; a kinetic study of this reaction (*588*) suggests that a μ-peroxo complex is formed as an intermediate. It is suggested that the first step is

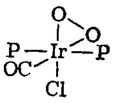
$$[YCo(OH_2)]^{=} + O_2H^- \rightarrow [YCo(O_2)]^{-4} + H_3O^+$$

followed by fast reactions which include the formation of the oxidized dimer containing a μ-peroxo group, $[YCo\cdot(O_2)\cdot CoY]^{-4}$.

XVI. Iridium

The iridium complex $(Ph_3P)_2Ir(CO)Cl$ (*552*) does not react with O_2 as a solid, but in solution in benzene it takes up one mole of O_2 per iridium atom; the oxygenation is associated with a color change from yellow to red (*550*, *551*). The oxygenated species, $(Ph_3P)_2Ir(O_2)(CO)Cl$, may be obtained as a crystalline solid by evaporating the solvent.

The oxygenated solid is quite stable at room temperature in an atmosphere of O_2 in the dark, though an irreversible photochemical oxidation occurs in the light. The O_2 may be removed in solution by lowering the pressure; the oxygenated solid loses O_2 only slowly in vacuum unless the temperature is raised. Treatment with acid gives H_2O_2; the molecular weight in benzene or chloroform shows that in these solvents the compound is monomeric. The infrared spectrum contains no absorption associated with OH groups, but there is a band at 860 cm^{-1}, a frequency associated with a coordinated peroxy group (*181*); it is interesting that the CO stretching frequency drops on oxygenation. The oxygenated solid is diamagnetic; from these data and from the dipole moment (5.9 D), the oxygenated species has been described as a *trans*-bis(triphenylphosphine) derivative of iridium(IV):

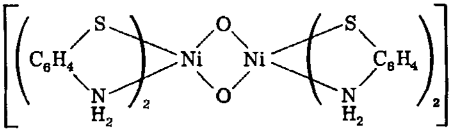


This most interesting compound is the simplest oxygen carrier yet described.

XVII. Nickel

There is no well-characterized peroxide of nickel. A gray-green crystalline solid was obtained by treating a solution of nickel(II) chloride with 30% H_2O_2 and the equivalent amount of alcoholic potassium hydroxide, at −50°; this product, which gave H_2O_2 when treated with water or acids at room temperature, was found iodimetrically to contain up to two oxidizing equivalents per nickel atom and was formulated as $Ni(O_2)\cdot aq$. The solid decomposed in a desiccator and more rapidly in air, losing most of its oxidizing power in air in 11 days at room temperature. The substance is regarded as distinct from black NiO_2 (*393*). Evidence has also been obtained to indicate that nickel peroxides are formed in the catalysis by nickel(II) hydroxide of the decomposition of H_2O_2 (*66*), while there is some suggestion (*318*) that soluble peroxynickel species may be formed.

By the action of oxidizing agents, including O_2, on an alkaline suspension of bis(*o*-aminothiophenol)nickel(II), a blue solid has been obtained, which is formulated as a dimeric derivative of nickel(IV) (*221*):



It seems possible that there may be a bond between the two oxygen atoms, and that the substance should be regarded as a binuclear peroxide, analogous to the cobalt peroxides, but a decision on this point must await structural studies.

XVIII. Copper

A dark-colored solid containing peroxide oxygen has been obtained by the action of H_2O_2 on solid copper(II) hydroxide (*299*, *371*) or by adding H_2O_2 and alcoholic potassium hydroxide in equivalent amounts to a solution of a copper(II) salt in alcohol at low temperatures (*372*, *536*, *579*); the reaction between copper(II) ion and H_2O_2 at room temperature and low pH causes a color change, but no precipitate is formed (*7*, *371*, *457*), while at high pH the decomposition of the added H_2O_2 is rapid and violent. No product containing peroxide oxygen was obtained by treating copper(II) acetylide with ethereal H_2O_2 (*372*) or from sodium peroxide and copper(II) sulfate, from potassium perdisulfate and copper(II) sulfate, or from copper(II) sulfate and ozone (*371*).

There is little agreement as to the formulas and properties of the product or products. The dark brown solid obtained by Moser from copper(II) hydroxide and H_2O_2 at 0° (*371*), like the product of the reaction between alcoholic copper(II) chloride, alcoholic potassium hydroxide, and H_2O_2 at −40° (*372*), contained copper, peroxide oxygen, and water in the approximate molar/atomic ratios 1:1:1; the peroxide oxygen was determined by using acid hydrolysis, measuring the amount of O_2 evolved, and using permanganate to estimate the H_2O_2 formed in solution. This product should therefore be described as $Cu(O_2)\cdot H_2O$, or $Cu(OH)(O_2H)$, a formula corresponding with that suggested by Krüss (*299*, *368*); the water was not removed by vacuum drying. It has, on the other hand, been suggested (*536*) that the product obtained from ethanolic copper(II) nitrate and H_2O_2 at $-10°$ is always a mixture of $Cu(O_2)$ with varying proportions of CuO formed by thermal decomposition, while phase studies indicate (*324*) that at temperatures between -36 and $+20°$ the solid phase $Cu(O_2)\cdot H_2O_2\cdot H_2O$ exists, as well as the 1:1 phase $Cu(O_2)\cdot H_2O$. By working at $-79°$ and using 30% H_2O_2 an olive-green solid has been obtained, which (after being washed until the washings were peroxide-free) was found to contain 1.5 atoms of peroxide oxygen per copper atom, and hence was given the structure $Cu_2(O_2)(O_2H)\cdot aq$.

This uncertainty as to composition of the product (or products) obtained in the preparative reactions is reflected in the descriptions of its properties. The solid is variously described as yellow-brown (*536*), olive-green (*457*), and black (*579*). There is general agreement that peroxide oxygen is lost slowly at room temperature and more rapidly on heating (*372*) and that the loss is least rapid when the solid is dry, but differing impressions are given as to the speed of thermal decomposition (*299*, *536*). The compound is decomposed to H_2O_2 by dilute acid, only a little O_2 being evolved (*372*); it is also decomposed by dilute ammonia or sodium hydroxide (*286*); with hydrochloric acid, H_2O_2 and a little O_2 are formed (*566*).

When H_2O_2 is added to a solution of copper(II) sulfate containing citrate, an unstable brown color is produced, but no precipitate comes down (*169*); the brown color is probably due to a complex peroxycitrate, tentatively formulated as $[\text{cit-Cu}(O_2)]^-$.

Copper is also the metal in the naturally occurring oxygen carrier hemocyanine. In this system, the copper seems to be in the +1 state (*160*) and neither oxygenated nor deoxygenated species give electron resonance spectra at room temperature (*375*), though on acid hydrolysis some copper(II) is formed (*160*). One molecule of O_2 is taken up to each two copper atoms (*214*, *430*, *432*).

XIX. Silver

It has been clearly established that the solid of formula AgO is not a peroxide of silver (*377*, *477*, *478*); other higher oxides of silver have been reported (*271*, *499*), but there is no evidence that any of them contains a peroxy group. The solubility of silver(I) in concentrated H_2O_2 has been measured (*322*) and used to calculate a solubility product for silver(I) hydroperoxide, which may be an intermediate in the catalytic decomposition of H_2O_2 by silver ions, but the solid material has not been isolated.

XX. Gold

It has been suggested that unstable peroxides of gold are formed in the electrolysis of acid or alkaline solutions using gold electrodes (*262*, *263*), but no solid has been isolated that has been shown to contain a peroxy group.

XXI. The Actinides

A. Thorium

Thorium forms several peroxides, but only one is well defined; all are of course derived from the +4 state. Neutral or weakly acid solutions of thorium salts and H_2O_2 yield gelatinous precipitates on standing or on heating (*86, 96, 119, 205, 291, 408, 489, 585, 586*); similar compounds have been obtained by the action of ozone or perdisulfate ion on solutions of thorium salts (*408*). The solids have been described by various formulas, such as $Th(O)_2 \cdot 3H_2O_2 \cdot 3H_2O$ (*119*), $Th(O)(O_2) \cdot 4H_2O$ (*492*), or $Th(OH)_3(O_2H)$ (*155*), but the most detailed studies of these compounds that have so far appeared (*205, 291*) indicate them to be of variable composition, the maximum peroxide content being 1.75 moles per gram-atom of thorium (*205*); they also contain water and anions (nitrate, sulfate, or chloride, depending on the anions present in solution). Solids with the highest peroxide content were obtained from solutions allowed to stand overnight or heated for long periods to about 40°, but samples prepared under conditions that seemed almost identical were found to differ widely in composition. From nitrate solutions, the product after washing contained about half a gram-ion of nitrate per gram-atom of thorium (*205*), though it seems possible that the freshly precipitated material may contain one nitrate per thorium atom (*86*); the chloride content of the chloride derivatives was found to be between 0.5 and 1. Dialysis of a colloidal sample of the chloride for 56 days, however, reduced the chloride content to 0.03 gram-ion per gram-atom of thorium, while the ratio of peroxide to thorium remained as high as 1.45:1 (*86*). The water content of the nitrates varied between 1 and 4 moles per gram-atom of thorium (*205*).

The addition of ammonia to a solution containing H_2O_2 and thorium also gives a gelatinous precipitate, but in this material the ratio of peroxide to thorium is close to 1:1 (*205*).

All of these compounds, particularly those rich in peroxide oxygen, lose peroxide slowly at room temperature, and decomposition is apparently rapid at 130° (*155*); the chlorides are particularly unstable. The X-ray patterns of material precipitated from acid nitrate solutions contained only a few broad lines, which could be interpreted in terms of a two-dimensional hexagonal structure (*592*); it has been suggested that the hexagonal layers are made up of peroxide groups and thorium atoms in ratio 3:1, with anions, hydroxyl ions, or water molecules between the layers (*205, 592*). Little is known of the chemical properties of these materials; the solid precipitated from hot neutral nitrate solutions is said to be soluble in cold dilute hydrochloric acid (*155*), while no iodine is liberated in the Riesenfeld test (*492*).

Although solids like the ill-defined peroxide nitrate and chloride are precipitated from thorium solutions containing sulfate ion at low acidity, solutions that are at least 0.3 M in sulfuric acid give a much more granular precipitate on heating (*205*, *206*, *291*). This substance has the formula $Th(O_2) \cdot SO_4 \cdot 3H_2O$; the water molecules are tenaciously held, and the compound itself is remarkably stable thermally. Its powder photograph consists of a large number of sharp lines, in contrast to that of the other derivatives, indicating that the solid has a well-defined structure.

B. PROTACTINIUM

The action of H_2O_2 on weakly acidic solutions of protactinium compounds precipitates a solid that appears to be a peroxide (*188*, *189*, *521*). The speed of precipitation, which is slow, is increased by increasing the concentration of H_2O_2 or by decreasing the acidity; the peroxide seems to be rather less soluble than the analogous compounds of thorium, uranium, neptunium, or plutonium.

C. URANIUM

As with molybdenum and tungsten, the peroxide chemistry of uranium is confined to the +6 oxidation state; in view of the small potential for the +6/+5 change (0.063 volt), this is not surprising. The best characterized peroxy derivative is the tetroxide, $UO_4 \cdot nH_2O$ (where n is 2 or 4); many peroxyuranates are known, in which the ratio of peroxide to uranium is 3:1, 5:2, 2:1, 3:2, 1:1, and 1:2 and, in addition to these, series of mixed peroxyoxalates and -carbonates have been described. In general, the peroxide content increases with pH; acids decompose the compounds to uranium(VI) salts and oxygen, while the triperoxyuranate ion is stable at pH 12–16.

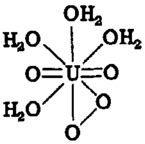
1. *Uranium Tetroxide*

Uranium tetroxide, characterized by Fairley (*135*), is formed by the action of H_2O_2 on a uranyl salt at pH ~ 2 (*8*, *111*, *121*, *135*, *178*, *207*, *250*, *367*, *461*, *471*, *582*). The compound, which has been shown by reaction with potassium permanganate to contain one peroxy group per uranium atom, is precipitated as a hydrate; Fairley (*135*) claimed to have obtained a small amount of the anhydrous tetroxide by the action of H_2O_2 on uranyl acetate in the presence of a large excess of sulfuric acid, but attempts to repeat his experiment have failed. Two definite hydrates are known. The air-dried material usually contains four molecules of water of crystallization, but a dihydrate is obtained if the compound is dried at 90° (*69, 121, 135, 308, 459, 461, 475*). Several series of experiments have shown that the dihydrate is formed without loss of peroxide oxygen (*104, 121, 281, 459, 461, 475, 510*) despite suggestions to the contrary (*231*). There is an apparent conflict of evidence as to the effect of further heating (*69, 179, 308, 459, 476*); some of the contradictions may arise from differences in experimental conditions, and some from the slowness with which thermal equilibrium is reached, though it seems that one set of results (*231*) is inconsistent with the rest. On heating in an atmosphere of O_2 to temperatures between 100° and 130°, an intermediate peroxide of formula U_2O_7 or $[U_2(O)_5(O_2)]$ has been obtained (*69, 75*), though this may be hydrated (*459*); no such intermediate was detected in the course of thermal decomposition under vacuum (*179*). It is clear that dehydration of the dihydrate is accompanied by loss of peroxide oxygen, since the ultimate product of decomposition at temperatures greater than 130° is uranium trioxide. The rate of decomposition, as measured by oxygen evolution, follows first order kinetics (*69*); the heat of the reaction

$$UO_4\cdot 2H_2O = UO_3\cdot 2H_2O + \tfrac{1}{2}O_2$$

has been measured indirectly (*407*).

Because two molecules of water of crystallization are constitutional and cannot be removed without loss of peroxide oxygen, it has been suggested that the peroxide is present as H_2O_2 of crystallization (*120, 231*). Studies of the thermal decomposition of samples containing O^{18}, however (*75, 179*), show that the dihydrate contains three types of oxygen atom, present in atomic ratio 1:1:1, a state of affairs most simply explained if the compound has the structure $[U(O)_2(O_2)\cdot 2H_2O]$. The broad line NMR spectrum is consistent with this formulation (*413*), though it seems that the sample studied contained a different molecular species as well, perhaps $[U(O)_2(OH)(O_2H)\cdot H_2O]$ or $[U(O)(OH)_2(O_2)\cdot H_2O]$; there may be proton migration through the crystal. The presence of the hydroxylated form would also account for the observation that three of the oxygen atoms exchange 0^{18} with enriched water at room temperature, though it is not entirely obvious why the fourth of the nonperoxy oxygen atoms did not exchange as well (*315*). To use an analogy developed by Russian workers (*93, 190*), the tetrahydrate may well have a structure like that of the triacetatouranyl anion (*593*) with a planar arrangement of peroxy and water oxygen atoms around the uranium atom and in the plane perpendicular to the axis of the uranyl group:



Two other structures have been proposed. A dimeric formulation is given by Russian workers (*190, 287*), while the compound has several times been described as uranyl triperoxyuranate, $[U(O)_2]_2[U(O)_2(O_2)_3]$ (*135, 543, 544*). This last suggestion is based partly on a description of the reaction with alkali that is not consistent with later work (*196*) and partly on analysis of the infrared spectrum. The spectroscopic evidence by no means establishes the presence of uranyl ions in the solid, and in view of the hydrolysis of the $[U(O)_2(O_2)_3]^{-4}$ ion at low pH it seems unlikely that this ion is present in the tetroxide.

Both hydrates are yellow compounds which are stable for long periods at room temperature, though the dihydrate is apparently thermodynamically unstable with respect to the trioxide at room temperature (*308*). The infrared spectra (*69, 120, 543, 544*) and X-ray powder photographs (*459*) have been described; both hydrates have body-centered lattices. The corrected paramagnetic susceptibility, χ_M, of 111×10^{-6} cgs units, is temperature-independent (*540*) as would be expected for a derivative of uranium(VI) (*93*). The chemical properties have been relatively little studied. The compound is a powerful oxidizing agent, and with strong acids it gives H_2O_2. With sodium hydroxide it has been said to form a mixture of uranate and triperoxyuranate (*543, 544*); more recent work, however, (*196*) suggests that the reaction is more complicated, and depends on the concentration of the alkali used. Between pH 8 and 14, sparingly soluble salts of the anions $[U_2(O)_5(O_2)_2H]^-$ or $[U_2(O)_5(O_2)_2]^=$ are formed; with 10 *M* potassium hydroxide, the monoperoxyuranate $K_2[U(O)_3(O_2)\cdot 4H_2O$ is precipitated (*114*), while with strong sodium hydroxide a soluble colored species is formed, whose ultraviolet spectrum is not the same as that of the triperoxyuranate anion (*196*).

2. U_2O_7

This compound, which contains one peroxy group to two uranium atoms, has been obtained as an intermediate product of the thermal decomposition of the tetroxide in an atmosphere of oxygen (*69, 296*), though it appears that the proportion of the compound formed at 195° is greatest at a partial pressure of oxygen gas of less than 15 mm (*75*), an observation hard to reconcile with other descriptions of the thermal decomposition (*179*). The solid obtained by Boggs and El-Chehabi is orange and hygroscopic (*69*), while another report describes the compound as hydrated (*459*); it reacts with water or dilute acids to give O_2, treatment with dilute sulfuric acid, for example, giving 94% of the O_2 calculated from the equation

$$2U_2O_7 + 8H^+ = 4U(O)_2^{+2} + 4H_2O + O_2$$

The remaining 6% could be accounted for in terms of its solubility in the solution (*69*). The compound decomposed slowly at temperatures greater than 150° to give uranium trioxide (*69*), though another report claims that decomposition occurs at temperatures greater than 195° (*75*). It may have been this compound that was obtained by heating uranium(VI) derivatives in oxygen (*77*, *272*); one of these products (*77*), which oxidized halide ion, also reacted with water to give O_2. The product obtained by heating the tetroxide did not decompose potassium permanganate solution (*69*).

3. 3:1 Peroxy Species

Salts of formulas $M_4{}^IUO_8 \cdot nH_2O$ are obtained by the action of hydrogen peroxide on uranates at pH > 12 (*93*, *190*, *354*, *462*); the cations include Na^+, K^+, Li^+, $NH_4{}^+$, Ba^{+2}, and the guanidinium ion. The compounds are orange-red, and have been shown spectrophotometrically (*93*, *190*) and by reaction with permanganate solution (*354*, *462*) to contain three peroxy groups per uranium atom. Since the sodium salt can be dehydrated at 100° without loss of peroxide oxygen (*31*) while the guanidinium salt is obtained without water of crystallization from aqueous solution (*462*), the anion should probably be represented as $[U(O)_2(O_2)_3]^{-4}$; the six peroxy oxygen atoms may well lie in the plane containing the uranium atom and perpendicular to the axis of the UO_2 group. The potassium salt of formula $K_4H_4UO_{16}$, obtained from solutions of pH 11 that are rich in H_2O_2 (*190*), is probably best represented as $K_4[U(O)_2(O_2)_4] \cdot 4H_2O_2$; it reacts with concentrated potassium hydroxide solution to give the 3:1 derivative.

These salts are relatively stable thermally, as is apparent from the conditions used to dehydrate the sodium salt (*31*) [whose X-ray power photograph has been recorded (*190*)]. The solubilities of the 3:1 potassium salt (*197*) and of the much less soluble 7:1 potassium salt (*197*) (see above) and 3:1 sodium salt (*426*) have been measured at 0°; the pH of the solution of the sodium salt was 11.6, and the solubility dropped with increasing pH. Though it has been claimed on the basis of potentiometric studies that two molecules of H_2O_2 are formed by hydrolysis when the sodium salt dissolves in water (*31*), spectrophotometric studies (*199*, *200*) have shown that when the pH > 12 the ion $[U(O)_2(O_2)_3]^{-4}$ is present even in solutions as dilute as $10^{-4}\,M$; a cryoscopic determination using the potassium chlorate/water eutectic (in which it was established spectrophotometrically that the anion did not decompose) indicated that the sodium salt gave five particles on dissolving, which is consistent with the presence of the triperoxyuranate ion in solution. On the addition of acid, hydrolysis occurs; apparently the first step is the addition of a proton to the anion, which then loses H_2O_2 and gives a dimeric species (*191*, *199*, *200*, *426*):

$$[U(O)_2(O_2)_3]^{-4} + H^+ \rightleftharpoons [HU(O)_2(O_2)_3]^{-3}$$
$$2[HU(O)_2(O_2)_3]^{-3} + 2H^+ \rightleftharpoons [U_2(O)_4(O_2)_4]^{-4} + 2H_2O_2$$

In alkaline solutions, the decomposition products are very complicated and depend on the conditions (*190, 193, 194, 195, 412, 427, 429*). In solutions that are very dilute in uranium ($\sim 10^{-4}$ *M*), the initial product of decomposition is a mononuclear monoperoxy anion, $[U(O)_2(O_2)(OH)_2]^{-2}$, which in turn decomposes to give an anion containing no peroxy oxygen (*190, 193*). The decomposition of solutions 0.5–1.0 *M* in uranium gives a range of products which contain varying ratios of peroxide to uranium and differ in the extent to which they are polymerized (*190, 193, 194, 195, 412, 429*). The kinetics of the decomposition have also been studied (*201, 428*). The addition of uranyl ion to solutions of triperoxyuranates leads to a drop in pH, with the formation of peroxyuranyl anions containing less than 3 moles of peroxide per uranium atom (*544*).

The chemical properties of the triperoxyuranate ion have been little studied. The salts react quantitatively with acid permanganate (*354, 462*); the electrolytic reduction at a platinum cathode in dilute solutions apparently involves formation of a 1:1 (peroxide:uranium) peroxyuranate, and the electrolytic deposit contains uranium(IV) as well as uranium(VI) (*192, 201*). The 7:1 potassium salt $K_4[U(O)_2(O_2)_3]\cdot 4H_2O_2$ gave 14 electron equivalents of iodine per mole with acid potassium iodide solution, but with buffered potassium iodide in the modified Riesenfeld test only two equivalents were produced (*492*).

4. 5:2 Peroxy Species

It is by no means clear that any compounds of this group have been isolated. Zahn (*594*) prepared salts to which he gave formulas $M_3{}^IUO_7\cdot nH_2O$, and in which the peroxide:uranium ratio was 5:2; Rosenheim and Daehr (*462*), however, on repeating his work obtained compounds in which the peroxide:uranium ratio was 2:1, and which they formulated as $M_2{}^IU_2O_{13}\cdot nH_2O$. One Russian review (*93*) seems to accept Zahn's work, while another (*190*) appears to agree with Rosenheim and Daehr. The evidence for the formation of the dimeric 2:1 species is strong, and is discussed in the next section; nonetheless, it is not possible to dismiss Zahn's results without more thorough reinvestigation. It has been suggested that the anion $[U_2(O)_4(O_2)_5]^{-6}$ is an intermediate in the alkaline hydrolysis of the triperoxyuranate ion (*190*).

5. 2:1 Peroxy Species

Orange-red compounds of formulas $M_2{}^IUO_6\cdot nH_2O$, $M_6{}^IU_2O_{13}\cdot nH_2O$, and $M_8{}^IU_4O_{24}\cdot nH_2O$, in all of which the peroxide:uranium ratio has been shown to be 2:1, have been obtained from solutions containing alkali, H_2O_2, and uranium(VI) in moderately high concentrations (*190, 194, 195, 412, 462*);

these species are also formed in the hydrolysis of triperoxyuranates, but it is not clear how the different 2:1 anions are related to one another. Cryoscopic measurements, in which the ion formulated as $UO_6^{=}$ was synthesized *in situ* by the action of the calculated amount of nitric acid on the triperoxyuranate ion, indicate that this species is largely dimerized in aqueous solution (*191*); there does not seem to be direct evidence for writing the ion $U_4O_{24}^{-8}$ as a tetramer rather than a dimer, and it seems possible that all these compounds contain dimeric anions, though it has been claimed (*190*) that monomers are also formed, at least in solution.

Although the disodium salt "$Na_2UO_6 \cdot nH_2O$" has been precipitated by the action of alcohol on an aqueous solution at 90° (*544*), these compounds are not particularly stable thermally (*190, 195, 462*); the salts $M_6^IU_2O_{13} \cdot nH_2O$ are rather more stable, but "Na_2UO_6" loses oxygen "rapidly and completely" when dry at 100°, and "$K_2UO_6 \cdot nH_2O$" decomposes in a day or so in air (*195*). The potassium salt "$K_2UO_6 \cdot nH_2O$" is not very soluble in water, and hydrolyzes in aqueous solution to a monoperoxy species (*190*). The X-ray powder photographs of some of these salts have been described (*190, 195, 298*). Chemically, they are strong oxidizing agents and give chlorine with hydrochloric acid, though reaction with potassium iodide may not be quantitative (*462*).

6. 3:2 Peroxy Species

Here again two series of salts have been described. Rosenheim and Daehr (*462*) made sodium, potassium, and ammonium salts of one series by treating the appropriate hydroxide with uranyl nitrate and H_2O_2, the alkali being less concentrated than that used in making the peroxide-richer species. Reaction with potassium permanganate established the peroxide: uranium ratio, and on the basis of analysis the salts were described as $M_2^IU_2O_{10} \cdot nH_2O$. The sodium salt (in this case described as a monomer, $NaUO_5$) was made by adding alcohol to a solution of sodium diuranate in H_2O_2 (*544*) and has also been obtained, with other products, by heating a solution of sodium triperoxyuranate in 2 *M* sodium hydroxide (*412*). Little is known of these compounds, save that they have moderate thermal stability, they react quantitatively with permanganate solution, and all their peroxide oxygen is active to potassium iodide (*462*).

A different series of compounds, sometimes described as $M_8^I[U_4O_{22}]$ (*194, 412*), has been considered by Gurevich (*190*) to contain the ion $[U_2(O)_5(O_2)_3]^{-4}$. The sodium and potassium salts have been obtained as decomposition products of triperoxyuranates (*412*) and their X-ray powder photographs have been described (*190, 194, 298*). The sodium salt, whose color varies from one sample to another from brown to red, is thermally very stable; it may be dried at 100°, is not decomposed by hot water in which its solubility is very low, and has been kept without decomposition for a year at room temperature (*190*).

7. *1:1 Peroxy Species*

The 1:1 peroxyuranates that have been described are of four types. Compounds of formula $M^IHU_2O_9 \cdot nH_2O$, $M_2^IU_2O_9 \cdot nH_2O$, and $M_2UO_5 \cdot nH_2O$ have been obtained by the action of uranyl nitrate on alkaline H_2O_2 (*114*, *196*) and as decomposition products of alkaline solutions of triperoxyuranates (*194*, *195*); the potassium salt $KHUO_5 \cdot 2H_2O$ has also been obtained, by treating uranium tetroxide hydrate with carbonate-free potassium hydroxide solution[8] (*114*). All these compounds have been shown by reaction with potassium permanganate to contain one peroxy group per uranium atom, but it is not entirely clear how they are related to one another.

Spectrophotometric evidence, coupled with studies of pH, makes it plain that species containing one peroxy group to each uranium atom are formed in solution (*198*, *200*, *544*); the effect of adding H_2O_2 to uranyl nitrate solution upon the pH and ultraviolet absorption of the system has been interpreted in terms of the formation of diperoxydiuranic acid:

$$2U(O)_2^{+2} + H_2O + 2H_2O_2 \rightleftharpoons H_2U_2O_9 + 4H^+ \quad (K_{\text{formation}} = 2.1 \times 10^{-3})$$

This species is stable in solution at pH 3–6. If this is correct, then the salts of formulas $M^IUO_5 \cdot nH_2O$ should probably be described as $M_2^IU_2O_9 \cdot (2n + 1)H_2O$, while those of formulas $M_2^IUO_5$ are presumably derived from this system by further removal of protons. There is not enough evidence to decide whether monomeric as well as dimeric species have been prepared. Since in any case all the salts are hydrated, it is likely that coordination at uranium is higher than is implied by the above formulas (*190*).

These salts are relatively stable, though the potassium derivatives $KHUO_5 \cdot nH_2O$ and $K_2UO_5 \cdot nH_2O$ decompose on heating, giving O_2 and uranate or diuranate (*114*). The X-ray powder photographs of $KHUO_5 \cdot 2H_2O$, $K_2UO_5 \cdot 3H_2O$ (*114*), $K_2U_2O_9 \cdot 5H_2O$, $KHU_2O_9 \cdot 6H_2O$, $NaHU_2O_9 \cdot 7H_2O$, and $Na_2U_2O_9 \cdot 7H_2O$ have been recorded [data for the last four compounds are given in reference (*190*)]. The sodium salt $Na_2U_2O_9 \cdot 7H_2O$ is apparently insoluble in water, and dissolves only to a very small extent in *N* alkali at 100° (*190*).

Besides these salts, there are other reports of 1:1 peroxides. The salts Na_2UO_5, K_2UO_5, and $BaUO_5$ were obtained by fusing uranyl chloride, UO_2Cl_2, with the appropriate hydroxide in air (*381*); the products were orange-red solids which evolved O_2 when heated, leaving uranates, and

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[8] The (1:1) anion $U_4O_{19}^{-6}$, detected spectrophotometrically (*200*), should perhaps be regarded as $H_2[U_4O_{20}]$, i.e., $H_2[U_4(O)_{12}(O_2)_4]^{-6}$ or $H[U_2(O)_6(O_2)_2]^{-3}$.

whose other properties were said to correspond with those of the peroxyuranates made by Fairley (*135*). The published analytical information, however, is extremely meager; the preparative reaction is so unexpected, in view of the thermal instability of other peroxyuranates, that a reinvestigation of these results would be valuable. There is also evidence that a 1:1 peroxy species is formed in the electrolytic reduction of peroxyuranates (*201*).

8. *Complex Peroxyuranates*

a. Carbonates. The effect of carbonate and bicarbonate ions on the ultraviolet absorption of peroxyuranates has been noted (*9, 495, 496*), but it has not always been appreciated that peroxycarbonatouranates are formed. Spectrophotometric and cryoscopic studies indicate that in the presence of bicarbonate the reaction between uranyl ion and H_2O_2 leads first to the formation of diperoxydiuranic acid, which then combines with bicarbonate to form a monomeric monoperoxymonocarbonatouranate anion:

$$2U(O)_2^{+2} + 2H_2O_2 + 4HCO_3^- \rightleftharpoons H_2U_2O_9 + 4CO_2 + 3H_2O$$
$$H_2U_2O_9 + 6HCO_3^- \rightleftharpoons 2[U(O)_2(CO_3)_2(O_2H)]^{-3} + 2CO_2 + 3H_2O$$
$$[U(O)_2(CO_3)_2(O_2H)]^{-3} + HCO_3^- \rightleftharpoons [U(O)_2(CO_3)_3]^{-4} + H_2O_2$$

It should be noted that there is no evidence for locating the proton on the peroxy group. Addition of alcohol to a solution of uranyl nitrate, potassium bicarbonate, and H_2O_2 in molar proportions 1:7:1 precipitates a solid that was identified by analysis as the potassium salt $K_3[U(O)_2(CO_3)_2(O_2H)]$, possibly contaminated with potassium bicarbonate (*288*). When carbonate is taken instead of bicarbonate, spectrophotometric evidence indicates that at higher pH the proton is removed from the peroxyanion (*190, 290*)

$$[U(O)_2(CO_3)_2(O_2H)] \rightleftharpoons [U(O)_2(CO_3)_2(O_2)] + H^+ \qquad (K = 2.5 \times 10^{-11})$$

(see also *337*). Cryoscopic measurements, using the potassium nitrate/water eutectic, were consistent with the formation of a monoperoxydicarbonato anion (*290*). The monocarbonate derivative $(NH_4)_2[U(O)_2(CO_3)(O_2)]\cdot 2H_2O$ was prepared by the addition of alcohol to a solution containing carbonate, uranate, and ammonium ions (*346*), but (as with the rest of these complexes) little is known about its chemical properties.

b. Oxalates. It has been shown spectrophotometrically that a peroxyoxalatouranate anion is formed when H_2O_2 is added to a solution of uranyl oxalate (*289*):

$$2[U(O)_2(C_2O_4)] + H_2O_2 \rightleftharpoons [U_2(O)_4(O_2)(C_2O_4)_2]^{=} + 2H^+$$
$$(K = 2.4 \times 10^{-2} \text{ at ionic strength } 0.05)$$

The change in pH in the titration of a solution of uranyl perchlorate, H_2O_2, and sodium oxalate against sodium hydroxide affords further evidence for the formation of this ion in solution (*93*). A solid of composition $(NH_4)_2[U_2(O)_4(O_2)(C_2O_4)_2]$ was precipitated by the addition of H_2O_2 to a saturated solution of ammonium uranyl oxalate (or a concentrated solution of ammonium and uranyl oxalates in appropriate proportions) (*289*, *346*); the analysis, though not exact, supports the proposed formula quite closely.

In the presence of excess oxalate ion, the formation of a peroxy dioxalato species was detected spectrophotometrically:

$$2[U(O)_2(C_2O_4)_2] + H_2O_2 \rightleftharpoons [U_2(O)_4(O_2)(C_2O_4)_4]^{-6} + 2H^+$$
$$(K = 2.2 \times 10^{-4} \text{ at ionic strength } 0.312)$$

By adding H_2O_2 to a solution saturated in both uranyl and ammonium oxalates, a yellow solid of composition $(NH_4)_6[U_2(O)_4(O_2)(C_2O_4)_4]\cdot 7H_2O$ was obtained (*346*); when H_2O_2 was added to a solution containing less ammonium oxalate, no precipitate was formed but alcohol precipitated a different hydrate of the same anion, $(NH_4)_6[U_2(O)_4(O_2)(C_2O_4)_4]\cdot 3H_2O$ (*346*).

A third ammonium peroxyoxalate, formulated as $(NH_4)[U(O)_2(O_2)(C_2O_4)]\cdot nH_2O$, has been obtained by adding 30% H_2O_2 to a 14% solution of ammonium uranyl oxalate (*289*) while a fourth, described as $(NH_4)_2[U_2(O)_4(O_2)_2(C_2O_4)]\cdot nH_2O$, has been mentioned in a Russian review (*93*); it is not clear whether the last two compounds are really different (*289*).

c. Carboxylic Acids. The addition of dilute H_2O_2 to a solution of uranyl nitrate and ammonium acetate leads to the precipitation of yellow crystals which are soluble in ammonium acetate solution but which decompose slowly to give uranium tetroxide hydrate, and analyzed to the composition $(NH_4)_2UO_4\cdot UO_2(C_2H_3O_2)_4$ or $(NH_4)_2[U_2(O)_4(C_2H_3O_2)_4(O_2)]$ (*346*). (The formula given by Mazzucchelli and Bimbi at first sight seems to show only one ammonium ion, but this does not agree with the calculated percentage of ammonia in the table they give.) A similar sodium peroxyvaleratouranate was obtained, contaminated with sodium valerate. The action of H_2O_2 on a solution of barium and uranyl acetates precipitated the yellow salt $Ba[U(O)_2(C_2H_3O_2)(O_2)]\cdot 6H_2O$. A crude sample of a sodium peroxyphthalatouranate was precipitated by the addition of alcohol to a solution of uranyl nitrate, sodium phthalate, and H_2O_2; it contained uranium and peroxide in the ratio 1:1 (*346*).

A spectrophotometric study (*105*) of the effect of H_2O_2 on a solution of uranyl nitrate containing salicylic acid showed that the only complex formed at pH's 9 and 10.3 contained peroxide and uranium in the ratio 1:1. It is not clear whether the species was a simple peroxyuranate or a peroxysalicylatouranate; the latter is the more likely, since no sign was detected of the triperoxyuranate anion that might have been formed at the higher pH, and salicylate ion interferes with the spectrophotometric determination of uranium with H_2O_2 (*458*). Finally, it is possible to use sodium tartrate instead of sodium carbonate in the spectrophotometric determination of uranium with H_2O_2 at high pH, implying that there may be tartrato complexes analogous to the carbonato complexes (*458*).

d. Pyrophosphate. An orange solid was obtained by the action of H_2O_2 on a solution containing uranyl, sodium, and pyrophosphate ions (*346*); it analyzed according to the formula $Na_4[U_2(O)_4(O_2)_2(P_2O_7)]\cdot 18H_2O$. Phosphate ion interferes in the spectrophotometric determination of uranium using carbonate and peroxide, which also indicates complex formation (*458*).

e. Fluoride. The action of H_2O_2 on sodium uranyl fluoride, $Na[U(O)_2F_3]\cdot nH_2O$, gave a yellow solution which on heating to 60–70° deposited yellow crystals of formula $Na[U(O)_2(O_2)F(OH_2)]\cdot 4H_2O$; four molecules of water of crystallization were lost at 100°. Treatment of a solution of the potassium salt $K_3U(O)_2F_5$ with H_2O_2 gave similarly a yellow solid which had the composition $K_4U_4(O_2)_4(O)_7F_6\cdot 4H_2O$, a formula very difficult to rationalize (*316*). Uranium tetroxide, however, is only sparingly soluble in many fluoride solutions (*113*).

f. Sulfate. The interference of sulfate ion in the spectrophotometric determination of uranium with carbonate and H_2O_2 may indicate the formation of a peroxysulphato complex (*458*).

9. Relationships between Compounds

At first sight the formulas of the peroxyuranates and their complex derivatives present a bewildering and unrelated complexity. Recently, however, it has been suggested (*93*, *190*) that their structures may be rationalized if it is assumed that the peroxy group acts as a bidentate ligand, and that in general the uranyl ion is six-coordinated, the remaining coordination positions being occupied by water molecules. This fits in with what is known about the coordination of complex uranyl compounds, and explains the formation of mixed peroxycarbonato, -oxalato, and -acetato anions. The formulas, based on these schemes, look a little cumbersome; they are set out in Table IV, with the formulas by which the various compounds have been best known in the past, and the rough pH range over which the species are stable. There is no evidence at present to show whether the binuclear species are linked by oxo or peroxo bridges.

It is clear that high pH favors the formation of monomers that are rich in peroxide, but that these may be persuaded to condense in the course of thermal decomposition in solution. Figures 8 and 9 give some idea of the ways in which these peroxy compounds may be converted into one another; they are based on data in reference (*190*).

TABLE IV

STRUCTURAL FORMULAS SUGGESTED FOR SOME PEROXYURANIUM COMPOUNDS

pH stable	O_2/U	Usual formula	Rationalized formula[a]
12.5	3:1	$M_4^IUO_8 \cdot nH_2O$	$M_4[U(O)_2(O_2)_3] \cdot nH_2O$
10.7–12	3:1	$[HUO_8]^{-3}$	$[U(O)_2(O_2)_3H]^{-3}$
—	5:2	$M_3^IUO_7 \cdot nH_2O$	$M_6[U_2(O)_4(O_2)_5(OH_2)_2](2n - 2)H_2O$
14.0	2:1	$M_6^IU_2O_{13} \cdot nH_2O$	$M_6[U_2(O)_4(O_2)_4(OH)_2(OH_2)_2](n - 3)H_2O$
10.7–12	2:1	$M_2^IUO_6 \cdot nH_2O$	$M_4[U_2(O)_4(O_2)_4(OH_2)_4](2n - 4)H_2O$
14.0	2:1	$M_8^IU_4O_{24} \cdot nH_2O$	$M_4[U_2(O)_4(O_2)_3(O_2H)(OH)(OH_2)_4]\left(\frac{n}{2} - 5\right)H_2O$
14.0	3:2	$M_8^IU_4O_{22} \cdot nH_2O$	$M_4[U_2(O)_4(O_2)_3(OH)_2(OH_2)_4]\left(\frac{n}{2} - 5\right)H_2O$
~10.5	3:2	$M_2^IU_2O_{10} \cdot nH_2O$	$M_2[U_2(O)_4(O_2)_3(OH_2)_6](n - 6)H_2O$
14.0	1:1	$M_6^IU_4O_{19} \cdot nH_2O$	$M_3[U_2(O)_4(O_2)_2(OH)_3(OH_2)_5]\left(\frac{n - 13}{2}\right)H_2O$
13.0–14.0	1:1	$M_2^IUO_5 \cdot nH_2O$	$M_4[U_2(O)_4(O_2)_2(OH)_4(OH_2)_4](2n - 6)H_2O$
13–14	1:1	$M_2U_2O_9 \cdot nH_2O$	$M_2[U_2(O)_4(O_2)_2(OH)_2(OH_2)_6](n - 7)H_2O$
~8	1:1	$MHU_2O_9 \cdot nH_2O$	$M[U_2(O)_4(O_2)_2(OH)(OH_2)_7](n - 7)H_2O$
6	1:1	$H_2U_2O_9 \cdot nH_2O$	$[U_2(O)_4(O_2)_2(OH_2)_8](n - 7)H_2O$
—	1:1	$UO_4 \cdot 4H_2O$	$[U(O)_2(O_2)(OH_2)_4]$
—	1:1	$K_3HU(CO_3)_2O_4$	$K_3[U(O)_2(CO_3)_2(O_2)H]$
—	1:1	$BaU(C_2H_3O_2)_2O_4$	$Ba[U(O)_2(C_2H_3O_2)_2(O_2)]$
—	1:1	$NaUO_4F \cdot 5H_2O$	$Na[U(O)_2(O_2)(OH_2)_3F] \cdot 2H_2O$
—	1:2	$(NH_4)_6U_2(C_2O_4)_4O_6 \cdot 7H_2O$	$(NH_4)_6[U_2(O)_4(C_2O_4)(O_2)(OH_2)_2] \cdot 5H_2O$

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[a] The rationalized formulas assume that the uranyl ion is six-coordinated, and in some cases the degree of polymerization has not been determined experimentally.

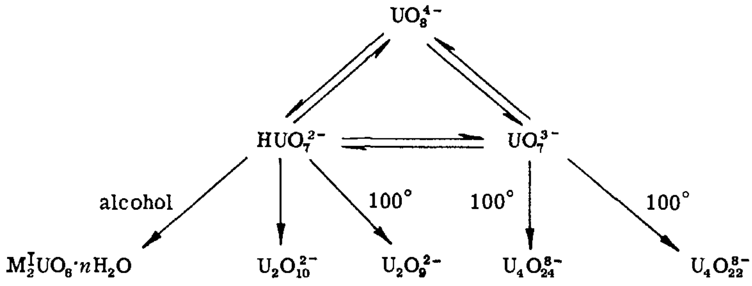


FIG. 8. Relationships between peroxyuranium species in aqueous solution, at [U] $\leq 10^{-4}$ *M* (*190*). The simple formulas used may be converted to "rationalized" formulas by using Table IV.

When the peroxy group is considered with other bidentate ligands to uranium(VI), the displacement reactions in which, for instance, peroxycarbonatouranates are formed from H_2O_2 and uranium carbonates show that the bonding between the peroxy group and the uranium atom must be relatively strong.

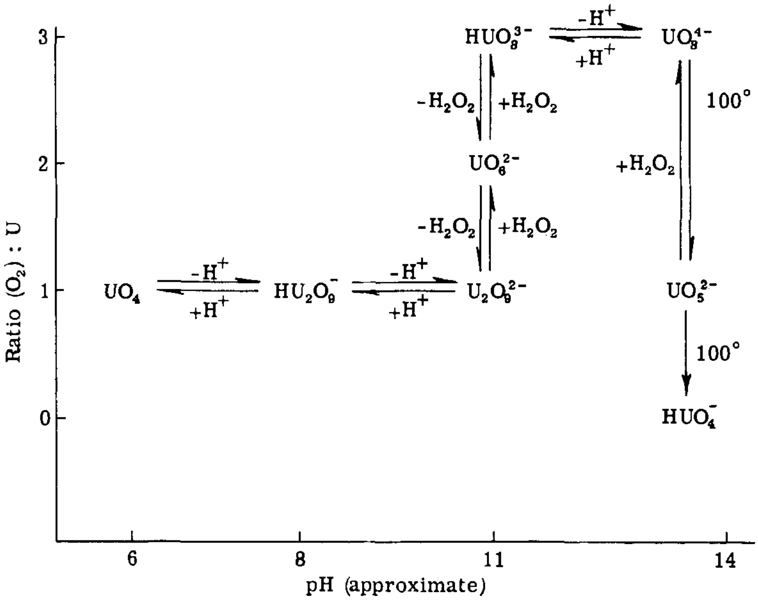


FIG. 9. Relationships between peroxyuranium species in aqueous solution, at 0.1 $\leq$ [U] $\leq$ 1.0 *M* (*190*). The simple formulas used may be converted to "rationalized" formulas by using Table IV.

D. NEPTUNIUM

The oxidation potentials for neptunium ions in solution (*274*) are summarized below. They indicate that the +6 state is less stable with respect to the lower states than for plutonium or uranium, but that complex oxidation-reduction reactions might be expected with H_2O_2.

$$E^\circ \quad NpO_2^{+2} \overset{1.14}{\text{———}} NpO_2^{+} \overset{0.74}{\text{———}} Np^{+4} \overset{0.16}{\text{———}} Np^{+3} \text{———} Np$$

In 0.5 M nitric acid it seems that neptunium (VI) is rapidly reduced by H_2O_2 to the +5 state, but that there is little further reduction over a period of 24 hours at room temperature (*300*). Neptunium(IV) is slowly oxidized to the +5 state by O_2 in 1 M sulfuric acid (*323*), but in general the details of the interaction between neptunium and H_2O_2 have not been extensively studied.

The addition of H_2O_2 to a solution of neptunium(IV) hydroxide in nitric acid leads to the slow precipitation of a grayish purple solid that has been formulated as $NpO_4 \cdot 2H_2O$ (*300, 323*), presumably by what may be an unfortunate analogy with uranium. As with plutonium, there are two forms: the compound precipitated from 1.0 M nitric acid has a face-centered cubic lattice with $a = 17$ Å, and contains 2.9 moles of peroxide oxygen to each two neptunium atoms; the substance precipitated from 3.0 M nitric acid has a hexagonal lattice, and contains 3.0 moles of peroxide oxygen to each two neptunium atoms. There was no sign of the formation of soluble complexes like the brown plutonium compounds (*118*).

E. PLUTONIUM

The complicated oxidation-reduction relationships in the solution chemistry of plutonium have their effect on reactions between H_2O_2 and solutions of plutonium compounds. The oxidation potentials (*273*) are summarized below:

$$E^\circ \quad Pu(O)_2^{+2} \overset{0.91}{\text{———}} Pu(O)_2^{+} \overset{1.19}{\text{———}} Pu^{+4} \overset{0.97}{\text{———}} Pu^{+3} \overset{-2.03}{\text{———}} Pu$$

$$E_B^\circ \quad Pu(O)_2(OH)_3^{-} \overset{0.26}{\text{———}} Pu(O)_2(OH) \overset{0.76}{\text{———}} Pu(OH)_4 \overset{-0.95}{\text{———}} Pu(OH)$$

In acid solution, plutonium(VI) is reduced to plutonium(V) by H_2O_2, but further reduction to plutonium(IV) is slow. Plutonium(IV) is reduced to plutonium(III) in certain acids, but plutonium(III) is slowly oxidized by air or by H_2O_2 in dilute solution to plutonium(IV) (*99, 100*). There is, however, a marked change in ultraviolet absorption when H_2O_2 is added to a solution containing Pu(III) (*98*).

Dilute solutions of plutonium(IV) form soluble brown peroxy complexes on the addition of H_2O_2; green solids are precipitated if the solution is more concentrated. The solid derivatives, which are rather ill-defined, are in many ways like the peroxides of thorium. No peroxides of plutonium derived from any oxidation state other than the +4 state have been isolated.

1. *Soluble Peroxides*

When dilute solutions of plutonium(IV) are treated with H_2O_2, they first turn brown and then red; no O_2 is evolved, and it was concluded that the plutonium remained in the same oxidation state (*97*, *98*, *100*). Spectrophotometric studies indicate that both brown and red species are binuclear, the brown containing one peroxy group, and the red two, to each two plutonium atoms. These results were corroborated by EMF measurements; the effect on the system of altering the pH suggested that the brown species contained an OH group. The equilibrium constants for the two equations below were determined spectrophotometrically:

$$2Pu^{+4} + H_2O_2 + H_2O \rightleftharpoons [Pu(O_2)PuOH]^{+5} + 3H^+ \qquad (K = 8.8 \times 10^6)$$
$$2Pu^{+4} + 2H_2O_2 \rightleftharpoons [Pu(O_2)_2Pu]^{+4} + 4H^+ \qquad (K = 6.3 \times 10^8)$$

2. *Insoluble Peroxides*

Careful analysis of the solids precipitated from acid solutions of plutonium(IV) compounds by the addition of H_2O_2 confirmed the presence of plutonium(IV) (*291*), but also showed that the composition of the precipitate depends to some extent on the conditions of precipitation (*204*, *291*, *304*, *305*). The peroxide oxygen content, determined either gas-volumetrically, or by reaction with iodide, is usually very close to 3 O_2 groups to each two atoms of plutonium (*204*, *227*, *228*, *291*, *304*, *305*); in wet precipitates the ratio has been found to be closer to 3.3:2, but in most of the dried materials it was a little less than 3 (*204*, *304*). The highest ratio, 4.56:1, was obtained from a precipitate formed in a solution containing sulfate and nitrate ions, and which had been digested for some hours at 50–70°. Besides peroxide oxygen, however, the solids always contain water, nonperoxidic oxygen, and anions. Precipitates from sulfate solutions, for example, contain between 0.24 and 0.38 gram-ion of sulfate to each gram-atom of plutonium (*304*, *305*); even precipitates formed in nitrate solutions contained small amounts of sulfate, which was traced to contamination in the H_2O_2 used (*204*). The nitrate content of precipitates formed from nitrate solutions is proportionally less (*204*); chlorides have also been obtained (*204*, *304*).

All of these materials were hydrated, and could be kept for a matter of days at room temperature without extensive decomposition, though the chloride-containing materials were the least stable. Drying for short periods gave products with less than 5 molecules of water of crystallization, without substantially affecting the peroxide content, but prolonged drying reduced the ratio of peroxide:plutonium to less than 1:1, while there was some evidence that in the 3:2 materials two of the peroxy groups might be more tightly bound that the third (*204*). X-ray studies show that the materials form two distinct types of lattice—a hexagonal layer lattice, analogous to one form of thorium peroxide, and a face-centered cubic phase with lattice constant $a = 16.46$ Å (*304*). Which phase is precipitated depends on the acid and on its concentration (*304, 305*); the hexagonal phase is precipitated from sulfuric acid more concentrated than $2\,M$, from hydrochloric acid more concentrated than $3.6\,M$, and from some concentrations of perchloric acid, while $0.4\,M$ sulfuric acid, for example, gives the face-centered cubic phase (*305*). The hexagonal phase contains a higher proportion of sulfate than the cubic if both are precipitated from sulfuric acid solutions (*304, 305*), while it appears that the cubic phase can tolerate a peroxide:plutonium ratio as low as 1.1:1 without a change of lattice. It has been suggested (*204, 369*) that the hexagonal form consists of layers of peroxide groups and plutonium atoms, while the other groups—anions, water molecules—are held between the layers; this would explain the variable composition, and would account for the high peroxide content of digested precipitates, which would be supposed to contain interlayer peroxide as well as the peroxide of the layers themselves. The infrared spectrum of the hexagonal form contains bands at 2953 and 861 cm^{-1}; in material prepared from D_2O solutions, these shifted to 2120 and 879 cm^{-1}, from which the presence of hydroperoxide $-O_2H$ groups in the substance was deduced, the higher frequency being assigned to the OH or OD stretching mode and the lower to the OO stretching vibration. In the spectrum of the cubic form, the higher-frequency band was not observed; a band at 834 cm^{-1}, which was assigned to the OO stretching mode, was not shifted in material prepared from D_2O. On this basis it was suggested that the cubic form should be represented as $Pu_2(O)(O_2)_3$ (*304*).

Chemically, little is known of these materials. They are partly reduced in aqueous hydrochloric acid by prolonged boiling; they decompose when heated, and react with hydrogen halides at temperatures greater than 100° to give halides of plutonium (*216, 227*).

XXII. Catalytic Decomposition of H_2O_2

The mechanisms by which derivatives of transition metals act as homogeneous catalysts in the decomposition of H_2O_2 are generally supposed to involve the formation of unstable peroxy derivatives. Kinetic studies have often been used to deduce the formulas of active intermediates, and in some cases further study has led to the isolation of solid derivatives that have formulas corresponding with those of the suggested intermediates (*59, 68*). Unfortunately, however, those species that are active in catalysis are likely to be unstable enough to be difficult to handle as solids. Recent studies of the catalytic decomposition of H_2O_2 by chromium(VI), for example, suggest that the active intermediate is a 1:1 peroxychromate(VI), and that a more stable diperoxychromate(VI) species is formed at the same time (*144, 202*); when the instability of the diperoxychromium(VI) compounds is recalled, it seems unlikely that the proposed monoperoxy derivatives would be particularly stable at room temperature. Conversely, the relative inactivity of molybdate (*376*) or tungstate (*282*) ions as catalysts is presumably associated with the relatively greater stability of their peroxy derivatives.

In some cases, notably for chromium(VI), the kinetic curves are very complex (*144, 202, 282, 518, 520*), and their interpretation is correspondingly difficult. Several types of intermediate have been suggested for this system, but it is not easy to assess the certainty with which the species can be identified, or to decide how far it is possible on the basis of any one scheme to exclude the formation of other species. The situation is further complicated by the marked effects of promoting ions (*54, 376, 416, 502*), which are in some cases very difficult to explain in chemical terms. In general, it seems that the most active transition metals are those that have more than one oxidation state of rather similar stability—notably iron, chromium, or vanadium; the topic was extensively reviewed by Baxendale (*27*) in 1952, and reference may be made to papers dealing with the effects of compounds of vanadium (*237*), niobium (*237*), chromium (*59, 202, 517, 518, 520*), molybdenum (*519*), tungsten (*282*), manganese (*148, 149*), iron (*202, 310*), ruthenium (*122*), osmium (*152*), cobalt (*56*), nickel (*264*), copper (*380*), and plutonium (*127*).

XXIII. Analytical Applications

H_2O_2 has been used in analysis as a precipitant for uranium (*458*) (a reaction which is also of technical importance), but by far the most important application of the properties of transition metal peroxides to analytical chemistry lies in their color reactions. The usefulness of these in qualitative analysis needs no stressing here; some of the elements that may be determined spectrophotometrically using the absorption bands of their peroxy derivatives are given in Table V.

H_2O_2 has also been used in the separation of transition metal ions by paper chromatography (*307*) or electrophoresis (*307*).

It should perhaps be pointed out that peroxy species do not necessarily show the color reactions of the normal (i.e., oxy) ions, and that therefore

TABLE V

EXAMPLES OF THE USE OF H_2O_2 IN THE SPECTROPHOTOMETRIC DETERMINATION OF TRANSITION ELEMENTS

Element	Wavelength (mμ)	Acidity, etc.	Reference
Ce	370–380	pH 8.7, in presence citrate	(*539*)
Ti	405–410	1.5–3 *N* H_2SO_4, HCl, or $HClO_4$	(*156*)
V	450	0.6–6 *N* acid	(*564, 584*)
	290	10–20% acid	(*534*)
Nb	365[a]	96% H_2SO_4	(*382*)
Ta	287	96% H_2SO_4	(*382*)
Cr	565	Extracted from acid solution with ethyl acetate[b]	(*170*)
Mo	330	20% $HClO_4$	(*533;* see also *154*)
Re	390	96% H_2SO_4	(*382*)
Fe	520	pH 9–12; with EDTA	(*451*)
Co	(460)[c]	HCO_3^-	(*535*)
	260	HCO_3^-	(*535*)
U	370–400	pH 2; in presence of OH^-, $CO_3^=$, $SO_4^=$ (pH 4–5)[d]	(*458*)

[a] This band shifts to shorter wavelengths in more dilute acid; λ_{max} = 320 mμ in 30% H_2SO_4.

[b] Method impaired by the instability of the complex.

[c]

[d] The lower pH range has been used with an acetate buffer, but is less satisfactory.

the precipitation reactions of such species as molybdate or tungstate are markedly affected by H_2O_2 (*136*).

XXIV. Oxygen Carriers

The properties of naturally occurring (*334*) and synthetic (*558*) O_2 carriers have recently been reviewed, while much interesting information about these substances and the related enzyme catalysts for biological oxidations involving O_2 is to be found in a collection of articles published in 1963 (*213*). A transition metal seems to be present in almost all naturally occurring O_2 carriers; the metals found in biological systems are iron or copper, but simple cobalt (*326*) and iridium (*551*) O_2 carriers have been synthesized, there is a suggestion that the rhenium complex anion $[Cl_5ReOReCl_5]^{-4}$ may combine reversibly with O_2 (*259*), and there is a less well-established claim for nickel dimethylglyoxime (*498*). It now appears that manganese(II) phthalocyanine does not show O_2-carrying properties (*129*). In most of these systems, up to one mole of O_2 is taken up to each atom of transition metal present, but some derivatives of iron, cobalt, and copper are known in which the fully oxygenated form contains one molecule of O_2 to each two atoms of the transition metal. No structure of an oxygenated species has yet been determined, though one has been proposed for the oxygenated form of the cobalt(II)-histidine complex (*472*); it has been variously suggested that the O_2 molecule in oxyhemoglobin lies with its axis perpendicular (*390*), at 60° (*389*), or parallel (*180*) to the plane of the protoporphyrin ring. The last arrangement is most in keeping with the structures of transition metal peroxides that have been determined, though the structure proposed for the cobalt(II)-histidine complex is more like the 60° model.

The list of O_2-carrying transition metals is an interesting one, for of the metals in it only cobalt forms a well-defined and well-known series of peroxides; the peroxides of the earlier transition metals—titanium, vanadium, and chromium—are much better known, but so far no O_2-carrying compounds of these elements have been described. Another interesting feature is that all the O_2-carrying complexes contain the metal in a relatively low oxidation state; since in hemocyanine the copper atoms are apparently in the $+1(d^{10})$ state (*160, 375*), there seems to be no great significance in the number of *d* electrons in the metal. What is probably much more important is the ease with which electron transfer occurs from the metal to the O_2 ligand. In the reversible combination between O_2 and a complex of an oxidizable metal, there is the possibility of a redox reaction:

$$O_2 + M^{+n} \overset{(1)}{\rightleftharpoons} M(O_2)^{+n} \overset{(2)}{\rightarrow} M^{+(n+1)}(O_2)^-$$

If a molecule is to be an efficient O_2 carrier, step 2 must be prevented. This is clearly the function of the globin in hemoglobin, though the way in which this is achieved is not clear; it has been suggested that the environment of low dielectric constant hinders the charge separation that is involved in the redox reaction (*560*). In the iridium derivative $[Ir(Ph_3P)_2Cl(O_2)CO]$, the electron-acceptor properties of the carbonyl and phosphine systems presumably stabilize the lower state of iridium, and so make possible the reversible dissociation to O_2 and iridium(I), though the oxygenated complex has been described as containing iridium(III) (*551*). The redox step 2 is of great importance in the operation of the oxygenase enzymes; many of these contain transition metals, and may operate through the intermediate formation of unstable peroxy or oxygenated complexes (*159, 340*).

XXV. Summary and Conclusions

Several different types of peroxide have been described in this review. The solid hydrated peroxides of elements such as copper(II), praseodymium(III), or cerium(IV) may well contain $O_2^=$ ions (though there is no crystallographic evidence to support this view); the only roughly stoichiometric peroxides of thorium and plutonium represent a slightly different class of compound, but may still be essentially ionic. The peroxides of transition metals either in complexes or in high oxidation states (or in both), however, contain peroxide linked to the metal by directed bonds, and are closely related to the oxygenated O_2-carrying complexes. The characteristic and interesting properties of transition metal complexes are largely associated with compounds of the last two classes (see Table VI).

TABLE VI
DIFFERENT TYPES OF PEROXIDE FORMED BY THE TRANSITION ELEMENTS[a]

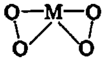
Type	*Elements forming peroxides of this type*[b]
Solid, "ionic"	Sc, rare earths, Ti, Zr, Hf, ?Fe, ?Co, ?Ni, Cu
Solid, "non-stoichiometric"	Th, ?Pa, Np, Pu
Complex	Ce, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, ??Ni, ?Cu, ?Th, U, Pu
Oxygen-carrying systems	??Re, Fe, Co, Ir, ?Ni, Cu

[a] See Section XXIV.
[b] Question mark means doubtful.

Most of the known transition metal peroxides have been obtained by the action of H_2O_2 on some derivative of the metal; in aqueous solution, the proportion of peroxide in the product increases with increasing pH, though this may not be true in solvents other than water. Peroxides of rhenium and cobalt, and of course the oxygenated O_2-carrying species containing iron, iridium, or copper, have been made from O_2 instead of H_2O_2; there is evidence that peroxy derivatives of uranium have been obtained by heating compounds of uranium(VI) in air, while peroxides are often postulated as unstable intermediates in the oxidation by air of such species as chromium(II). Most peroxy compounds in which the metal is in a high oxidation state are unstable thermodynamically with respect to decomposition into O_2 and a metal oxide or derivative at room temperature; the formation of a peroxide from O_2 involves formal reduction of the oxygen, and it seems likely that reaction with O_2 to form a peroxide occurs either when lattice energies are favorable (as, presumably, with uranium), or when a low-oxidation state species is involved. In the latter case, though redox reactions frequently occur with formation of an oxidized metal derivative, electron transfer may be inhibited if the lower state of the metal is stabilized by other ligands; reversible dissociation may then lead to oxygen-carrying properties.

In all the peroxy complexes of transition metals whose structures have so far been described (save for the diamagnetic cobalt cation

$[(H_3N)_5Co{\cdot}(O_2){\cdot}Co(NH_3)_5]^{+4}$, D_a^1, details of whose structure are not yet available), the peroxy group is "laterally" coordinated to the metal, that is, with M—O—O angles of the order of 90° or less. The arrangement shown below, with one O—M—O angle close to 180°, is found in all the peroxides of chromium and tungsten whose structures are known:



Despite this, the peroxy group seems to behave as a monodentate ligand; it replaces single-atom groups such as $O^{=}$, or would give the metal an improbable coordination number (7 for cobalt in P_a^1, 8 for chromium in $[Cr(O_2)_4]^{-3}$) if regarded as a bidentate ligand. Similarly, in oxyhemoglobin the O_2 group replaces the monodentate water. The bonding in these "monodentate" systems has in some cases been described in terms of molecular orbital theory. In uranium complexes, there is a suggestion (not so far supported by X-ray evidence) that the peroxy group occupies two coordination positions, while the structure proposed for the oxygenated iridium complex $[(Ph_3P)_2Ir(O_2)(CO)Cl]$ also involves bidentate O_2. It seems quite likely that the steric requirements for coordination around the uranyl ion are different from those in other transition metal complexes.

The values reported for the O—O bond lengths in complex peroxides are collected in Table VII. Most of them do not differ significantly from the 1.49 ± 0.04 of $O_2^{=}$, though it is possible that in peroxychromium compounds O—O distance may be a little less than this. This is consistent with the observation of infrared bands in the spectra of complex peroxides

TABLE VII

VALUES FOR THE O—O DISTANCES IN PEROXY COMPLEXES

Compound	r(O—O) (Å)	Reference
$K_3[Cr(O_2)_4]$	1.405 ± 0.039	(*524*)
	1.472 ± 0.025	(*522a*)
$PyCr(O)(O_2)_2$	1.405 ± 0.02	(*522*)
$(H_3N)_3Cr(O_2)_2$		
Orthorhombic	1.42 ± 0.03	(*522b*)
Monoclinic	1.31	(*320*)
	1.2–1.4[a]	(*522b*)
$K_3[(CN)_3Cr(O_2)_2]$	1.445 ± 0.016	(*522c*)
$K_2[(O_2)_2W(O)OW(O)(O_2)_2]{\cdot}4H_2O$	1.50	(*126*)
$[(H_3N)_5Co{\cdot}(O_2){\cdot}Co(NH_3)_5](NO_3)_5$	1.45 ± 0.06	(*549*)

[a] This range of values comes from a least-squares refinement of the experimental data from reference (*320*).

at frequencies close to that assigned to the O—O stretching mode of H_2O_2, though no significance should be attached to the small differences observed. Most peroxides in which no internal oxidation-reduction process is possible are thermodynamically unstable with respect to the reaction

$$2M(O_2) \rightarrow 2M{=}O + O_2$$

mainly because of the high bond energy in O_2 itself. The Russian thermochemical work that undertakes to measure the hypothetical energy E(MO—O), and which finds it to be rather less than in H_2O_2, should probably be reinterpreted in terms of a comparison between $E(M{=}O)$ and $E[M{=}(O_2)]$, but there are many uncertainties involved. The evidence suggests that $E[M{=}(O_2)]$ is a little less than $E(M{=}O)$.

As far as bonding in peroxy complexes is concerned, it is not clear what is the best way to describe the metal-peroxide interaction. Perhaps the simplest way is through a comparison of $O_2^{=}$ and C_2H_4 as ligands.[9] In the ethylene complexes, the olefin is usually considered as donating electrons from the π-bonding orbital to the metal, while the metal donates electrons from an appropriate, filled d orbital to the empty, antibonding π^* orbital of the olefin. In the peroxide ion, the π^* orbital is already filled, so that no back-bonding is possible. At the same time, there may be donation to the metal both from the π- and the π^* orbitals of the peroxy group, at least when the metal is in a high oxidation state. The effect of coordination on the O—O bond would then depend on the relative strengths of the two interactions—in other words, on whether donation was principally from π- or from π^* orbitals of the peroxy group (see Fig. 10).

For metals with many d electrons, this description is less satisfactory. At the same time, it is worth noting that the cation $[(H_3N)_5Co{\cdot}(O_2){\cdot}Co(NH_3)_5]^{+5}$ has a "π-complex" structure; the reduced species $[(H_3N)_5Co{\cdot}(O_2){\cdot}Co(NH_3)_5]^{+4}$, on the other hand, in which the t_{2g} orbitals of the cobalt atoms are filled, has a structure for which the "π-complex" description is clearly inappropriate.

As yet there are few generalizations that can usefully be made about the chemical properties of these compounds. The complicated relationships between the peroxides of individual elements are only beginning to be understood; it is to be hoped that as more information becomes available, something more like an over-all pattern will emerge.

Warning. Many peroxy complexes are thermodynamically unstable with respect to spontaneous decomposition at room temperature and may explode when touched or gently warmed, as we have found. The derivatives of Cr, Mo, and W are particularly treacherous, but great care should

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[9] An even closer comparison can be made of peroxide and acetylene as ligands.

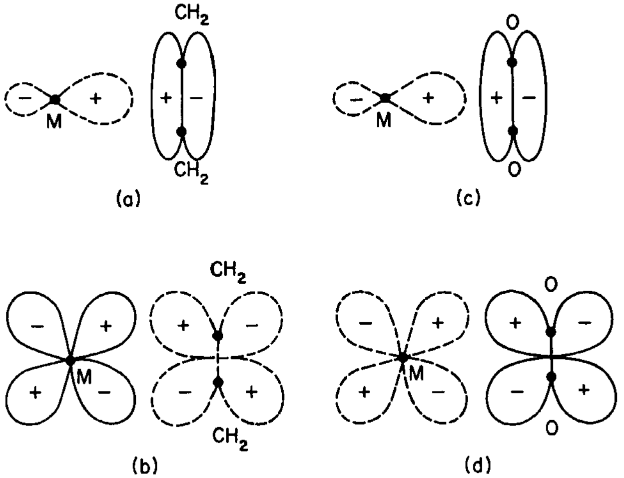

FIG. 10. Possible scheme for representing the interaction between a transition metal atom and ethylene or peroxide as ligands. (a) Donation to the metal from a π-bonding orbital of ethylene; (b) donation from the metal to a π-antibonding orbital of ethylene; (c) donation to the metal from a π-bonding orbital of peroxide; (d) donation to the metal from a π-antibonding orbital of peroxide. An orbital indicated by full lines contains an electron-pair; those indicated by broken lines are empty. For simplicity, the metal orbital interacting with the *π-bonding* ligand orbitals have been drawn as *sp* hybrids, although they will probably have d-character.

be taken when handling even very small amounts of any solid peroxy complex.

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