

# THE CHEMISTRY OF BLEACHING AND OXIDIZING AGENTS

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## I. INTRODUCTION

The color of organic substances is associated with the presence of mobile electrons in chromophoric systems of conjugated double bonds. Bleaching processes involve a demobilization of such electrons, engaged in the absorption of visible light, by the formation and rupture of chemical bonds. This may be performed by addition of various active elements and compounds, either reducing agents (e.g., nascent or activated hydrogen) or, preferably, oxidants (electron acceptors) such as nascent oxygen, ozone, hydrogen peroxide (hydroxyl radicals), halogens, and halogen-oxygen compounds. Considering the chemistry of bleaching from an energetic viewpoint, color changes may essentially be interpreted as electron transitions in terms of radiation energies, and energy changes of bleaching agents may be calculated from certain fundamental atomic and molecular energies.

The power of an atom in a molecule to attract electrons is characterized by its so-called electronegativity value (45), which changes in a regular way from atom to atom in the Periodic System. This may be shown for ten common elements in Pauling's electronegativity scale:

Na	<	Ca	<	H	<	C	≈	S	<	Br	<	Cl	≈	N	<	O	<	F
(0.9)		(1.0)		(2.1)		(2.5)				(2.8)		(3.0)				(3.5)		(4.0)

For univalent atoms, such as hydrogen and the halogens, the average of the ionization energy ( $X \rightarrow X^+ + e$ ) and the electron affinity ( $X + e \rightarrow X^-$ ) should be a measure of the electronegativity, but for multivalent atoms, such as carbon, sulfur, nitrogen, and oxygen, these energies must be corrected with respect to the actual valence state.

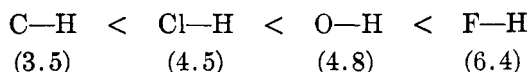
In this paper the behavior of "electronegative" elements, particularly chlorine and oxygen, is of special interest, as the chemistry of bleaching is essentially governed by the reactions of chlorine, oxygen, and their compounds with hydro-

gen and carbon atoms of conjugated bond systems, in which the mobile  $\pi$ -electrons to some extent approach the state of a metallic conductor.

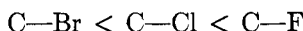
Although the conventional electronegativities of hydrogen, oxygen, and the halogens do not correspond to the oxidation-reduction potentials of these elements in aqueous solution, the sequence will be the same if the oxygen potential is referred to the active state, containing a single O—O bond. In fact, the standard state of oxygen,  $O_2(g)$  with a double bond ( $O=O$ ), is much more stable and less active than it would be if the molecule contained a single bond.

For an unsymmetrical single bond, the dissociation energy is connected with the mean of the energies of the corresponding symmetrical bonds and the electronegativity difference between the atoms.

Whilst the energies of the symmetrical single bonds H—H, C—C, Cl—Cl, O—O, and F—F do not express any definite regular variation, a very strong increase in bond energy from about 3.5 e.v. for the C—H radical ( $C-H \rightarrow C + H$ ) to ca. 6.4 e.v. for the H—F bond is observed in the following series:

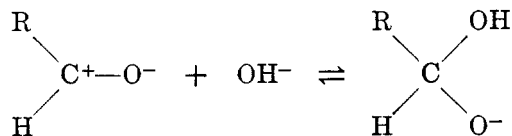


Similarly, the strength of carbon-halogen bonds increases in the sequence



accompanied by a change towards a pronounced ionic character of the bond.

An appreciable ionic character is found in the O—H bonds of water and organic hydroxy compounds, as also in the unsymmetrical C=O bonds of aldehydes and ketones. In fact, the reactions of carbonyl compounds are to a large extent determined by the tendency of the C=O group to assume the polar ionic structure  $C^+=O^-$ . The chromophoric activity of the C=O group is associated with the electronegative character of oxygen, resulting in the development of ionic structures when the C=O bond is conjugated with a C=C bond. The distinctly reducing properties of aldehydes in alkaline solutions should be due to the reversible formation of aldehydate ions by addition of hydroxyl ions to the positive carbon atom according to the presumable equilibrium (57)

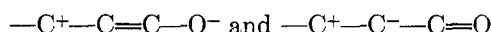


giving more or less well-defined, negative oxidation-reduction potentials.

The activated development of definite low potentials of reducing carbohydrates in the alkaline pH range may also be interpreted in this way. In strongly alkaline solutions glucose gives a yellow color with an increased absorption in the near ultraviolet. This phenomenon indicates the formation and subsequent ionization of C=O groups, accompanied by the development of definite potentials in the absence of oxygen (43).

Many colored substances of a quinoid nature have conjugated bond systems

of the type  $\text{—C=C—C=O}$ . The points of chemical attack are determined by the electron density distribution in the possible resonance forms, in particular by the participation of the ionic structures:



In such molecules with mobile  $\pi$ -electrons the positive charge can easily be transferred via conjugated  $\text{C=C}$  bonds to carbon atoms far away from the oxygen atom. It should be mentioned that the rate of oxidation of a conjugated  $\text{C=C}$  group in a side chain attached to a benzene ring may be considerably increased by the presence of a free phenolic OH group in the para position (55).

## II. ELECTRONIC ENERGIES AND LIGHT ABSORPTION

Generally, absorption of light in the visible and ultraviolet spectral regions is due to an electron transition from the ground state to an excited state of the molecule. In point of principle, these excited states can be classified in definite spectral series with a convergence limit, corresponding to the energy of ionization.

On the other hand, the infrared absorption arises from the vibrations of the atoms of specific groups, as also from the vibrations of the molecule as a whole, and the fundamental frequencies of important groups ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ ,  $\text{OH}$ , etc.) are situated in the near infrared at a wave length of about  $3\ \mu$ .

The energy equivalent,  $E_\lambda$ , of the wave length  $\lambda$  is calculated from the fundamental quantum relation

$$E_\lambda = \frac{N \cdot h \cdot c}{\lambda}$$

in which  $N$  = Avogadro's number,  $h$  = Planck's constant, and  $c$  = the velocity of light. When  $\lambda$  is given in microns ( $\mu$ ) and  $E_\lambda$  is expressed in electron volts, the following approximate relation is valid:

$$E_\lambda = \frac{1.24}{\lambda}$$

As shown in figure 1 the ultraviolet, visible, and near infrared regions include energies from more than 10 e.v. down to about 0.1 e.v. In particular, the visible spectrum comprises light quanta having  $E_\lambda$  between ca. 1.5 and 3 e.v.

The appearance of the first visible absorption band of a dye may be associated

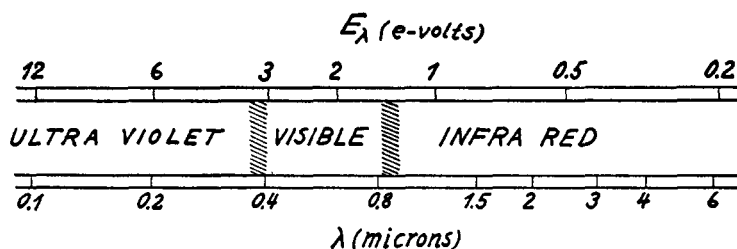
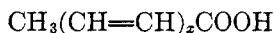


FIG. 1. Spectral regions of radiation

with the jump of a mobile  $\pi$ -electron from the highest normally occupied energy state into the next highest unoccupied state. From the fundamental concept of a "linear free-electron gas" model, the wave length of this first absorption band is related to the number of  $\pi$ -electrons and the length of the electron gas. The blue color of iodine with starch has been interpreted from this viewpoint (6).

When the  $\pi$ -electrons do not really constitute any free-electron gas, e.g., in such organic compounds as the linear polyenes, the length of the carbon chain is a determining factor for the light absorption. Generally the absorption moves from the ultraviolet towards the visible spectrum by the accumulation of conjugated double bonds. For instance, in the series of aliphatic unsaturated acids of the following type

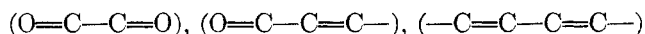


the first members ( $x = 1-3$ ) absorb only in the ultraviolet, whilst for  $x = 4$  the color is sharply yellow.

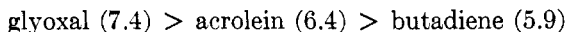
The  $\text{C}=\text{O}$  group itself (in aldehydes, ketones, and carboxylic acids) will cause characteristic absorption in the middle to far ultraviolet ( $\lambda \sim 0.2 \mu$ ) corresponding to electron transition energies from ca. 5 to 6 e.v.

The conjugated complex  $\text{O}=\text{C}-\text{C}=\text{O}$ , e.g., in glyoxal and biacetyl, will give an additional absorption at the violet end of the visible spectrum ( $\lambda \geq 0.4 \mu$ ). In the conjugated double bonds of quinones the shortest ultraviolet absorption ( $\lambda \leq 0.3 \mu$ ) is ascribed to the  $-\text{C}=\text{C}-\text{C}=\text{O}$  system, and the visible band ( $\lambda \geq 0.4 \mu$ ) to absorption in the  $\text{C}=\text{O}$  groups, which is appreciably changed with the electrochemical potentials of the quinone-quinol systems. In aromatic compounds auxochrome groups, such as  $\text{OH}$ ,  $\text{OCH}_3$ ,  $\text{NH}_2$ , and  $\text{N}(\text{CH}_3)_2$ , have a tendency to form double bonds with the benzene ring, and the conjugated bond system serves as the path over which the color-promoting resonance is transmitted between the chromophoric electron acceptor and the auxochromic electron donor.

The ionization potentials of the individual  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  groups are ca. 10 and 12 v., respectively, corresponding to the removal of a  $\pi$ -electron from the double bonds. The conjugating power of the mobile  $\pi$ -electrons in these double bonds is dependent upon the ionization potentials, giving an increasing conjugation between terminal  $\text{C}=\text{O}$  groups and  $\text{C}=\text{C}$  groups in the sequence:



This is reflected in the decreasing values of the first transition potentials (volts) in the following series of simple compounds (56):

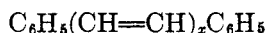


Each additional conjugated ethylenic double bond, e.g., when passing from acrolein or crotonaldehyde (with the bond system  $-\text{C}=\text{C}-\text{C}=\text{O}$ ) to sorbaldehyde (with the system  $-\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\text{O}$ ), will shift the absorption spectrum towards the visible region, corresponding to a decreasing electron transi-

tion energy. On the other hand, the decrease of the ionization energy corresponds to a lower energy of the excited states.

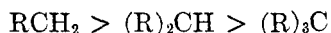
The larger the system of conjugated double bonds, the less fixed are the bonds, because of delocalization of the charges, and the more like a metallic conductor does the system behave.

In the beautiful series of synthetic diphenylpolyenes of the comprehensive formula

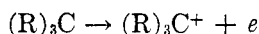


the first members ( $x = 1-3$ ) are white, yellowish, and greenish yellow, whilst the last members ( $x = 6-8$ ) are orange-brown, bronze-colored, or even bluish copper-red.

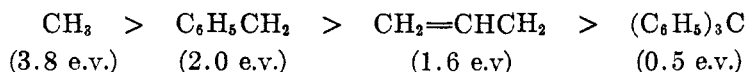
For all substituted methyl radicals the ionization potential should decrease with increasing number of substituents, as in the sequence



where R may be any arbitrary radical, such as  $\text{CH}_2=\text{CH}$  and/or  $\text{C}_6\text{H}_5$ . This phenomenon, corresponding to an increased tendency to the formation of a carbonium ion, e.g.,



is accompanied by a strongly decreasing dissociation energy of the central C—C bond in a series of symmetrical hydrocarbons (e.g.,  $\text{RCH}_2\text{CH}_2\text{R}$ ), as strikingly shown by the following data calculated from Evans (11):



According to Scheibe and Fauss (50) the potential differences between the ionized state and the first and second excited states of various organic molecules, such as hydrocarbons, polyenes, and dyes, are approximately equal to the corresponding differences of the hydrogen atom:

$$(\text{Ionization potential}) - (\text{First transition potential}) = \text{ca. } 3.4 \text{ v.}$$

and

$$(\text{Ionization potential}) - (\text{Second transition potential}) = \text{ca. } 1.5 \text{ v.}$$

In linear native polyenes with from ten to twelve conjugated  $\text{C}=\text{C}$  groups the ionization potential appears to be about 6 v. and the first transition potential ca. 2.6 v.

The approximate ionization and excitation potentials of some typical unsaturated hydrocarbons, particularly  $\beta$ -carotene, are represented in figure 2.

Under certain conditions color changes by photochemical processes are of great importance. The leuco form of a dye in solution may be reversibly colored by ultraviolet light, and the transformation of a carbinol base of a triarylmethane dye,  $\text{Ar}_3\text{COH}$ , to a true base by ultraviolet radiation involves an electron dis-

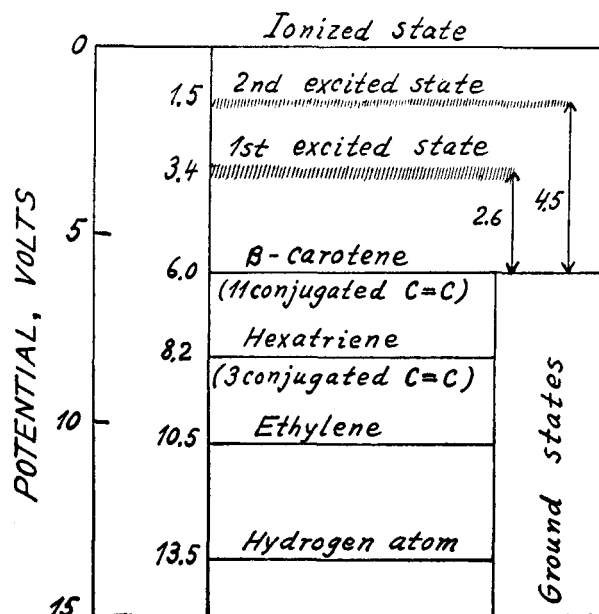
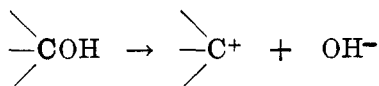


FIG. 2. Ionization and transition potentials of unsaturated hydrocarbons

placement from the carbon atom to the attached hydroxyl group, giving a positively charged carbon complex and a negatively charged hydroxyl group.

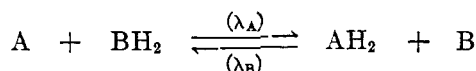


Generally, bleaching processes by visible and near ultraviolet light are associated with a primary excitation of colored compounds, whilst the bleaching action of energy-rich x-rays in aqueous systems involves a transient formation of free hydrogen atoms and hydroxyl radicals by decomposition of water. Also the far ultraviolet solar radiation may dissociate water vapor into hydrogen atoms and hydroxyl radicals with a possible subsequent production of  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  in reactions with the allotropic forms of oxygen.

More than twenty-five years ago Sheppard (51) reported some interesting observations and experiments on the yellowing and bleaching actions of different ultraviolet rays in transparent sheets of cellulose nitrate containing phenolic compounds. The yellow coloration produced by the ultraviolet radiation of shorter wave length ( $\lambda < 0.3 \mu$ ) was essentially ascribed to a liberation of nitrogen dioxide from the cellulose nitrate and subsequent nitration of the phenols. The reverse bleaching effect, obtained when the shorter ultraviolet rays were screened off, was attributed to a partial renitration of the cellulose residue by a photochemical reaction with the nitrophenols, absorbing in the near ultraviolet and the blue-violet spectrum ( $\lambda = 0.30\text{--}0.45 \mu$ ).

A pronounced antagonism of visible rays in the action on a light-sensitive

system in aqueous solution was discovered and investigated by the present author (22) for an equilibrium of the following type



with a blue dye A (methylene blue) and a yellow compound B (benzene azo-sulfonate) as photoactive components, absorbing light of different wave length ( $\lambda_A = 0.5\text{--}0.7 \mu$ , and  $\lambda_B = 0.4\text{--}0.5 \mu$ ) in the visible spectrum.

### III. ENERGY CHANGES OF PROCESSES IN AQUEOUS SYSTEMS

A characteristic feature of chemical processes, and particularly electron transitions, occurring in aqueous solutions is the hydration of ionic components, and pronounced color changes may occur by the influence of hydration due to shift of electronic levels. In a vacuum, the valence electron of such negative ions as  $I^-$  and  $Br^-$  is very loosely bound with a ionization energy ( $X^- \rightarrow X + e$ ) of only ca. 3.2 and 3.5 e.v., respectively, corresponding to radiation energies near the violet end of the visible spectrum. In solution, this energy quantum is insufficient to eject the electron from the hydrated ions, and the absorption spectra of alkali halide solutions are situated in the middle and far ultraviolet, corresponding to energy equivalents of about 5 e.v. or more.

It is possible to calculate approximately the total energy change ( $E_{tot}$ ) of various oxidation-reduction processes in aqueous solutions from known energies of dissociation ( $D$ ), ionization ( $J$ ), and hydration ( $W$ ). For example, for molecular hydrogen ( $H_2$ ) to give hydrated hydrogen ions,

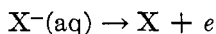
$$E_{tot} = \frac{1}{2}D_{H_2} + J_H - W_{H^+}$$

and for aqueous halide ions ( $X^-(aq)$ ), to give molecular halogens ( $X_2$ ):

$$E_{tot} = W_{X^-} + J_{X^-} - \frac{1}{2}D_{X_2}$$

These expressions have been evaluated and collected in table 1 from numerical values given by Gurney (16).

From available energy data in the literature (14, 16, 20, 58) the spectrum of electronic energies has been projected in figure 3, comprising particularly a number of simple electron transitions



$X = Cl, OH, Br, ClO, ClO_2.$

TABLE 1  
*Energy changes between molecular and hydrated ionic states*

ELECTRON TRANSFER	ENERGY IN ELECTRON VOLTS			
	$\frac{1}{2}D$	$J$	$W$	$E_{tot}$
$H_2 \rightarrow H^+(aq)$ .....	2.25	13.54	12.0	3.8
$I^-(aq) \rightarrow I_2$ .....	0.77	3.22	2.1	4.5
$Br^-(aq) \rightarrow Br_2$ .....	0.98	3.53	2.5	5.1
$Cl^-(aq) \rightarrow Cl_2$ .....	1.23	3.75	2.8	5.3
$F^-(aq) \rightarrow F_2$ .....	1.37	4.13	4.2	7.0

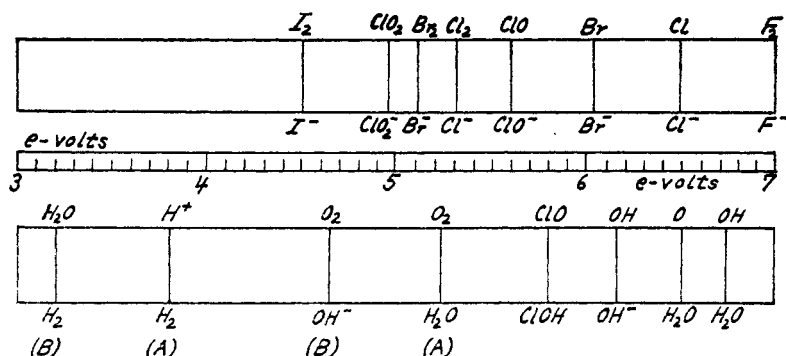


FIG. 3. Spectrum of electronic energies in aqueous solutions

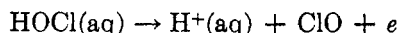
The energy difference between correlative half-reactions A and B, involved in the decomposition of water in acid and alkaline solutions, as illustrated in figure 3 is equal to 0.59 e.v., corresponding to the heat of neutralization of a strong acid by a strong base in dilute aqueous solution.

As pointed out by Gurney (16), the latent heat of solution of single charged ions in water is usually not more than a few (as an average only about 2) per cent of the hydration energy ( $W$ ), and equal to a thermal energy  $3RT$ , retained by the hydrated ions. This small energy quantum (about 0.075 e.v. at ordinary temperature) is equivalent to an infrared wave length  $\lambda = 16.5 \mu$ , and involved in the heat of dissociation of weak electrolytes in aqueous solution.

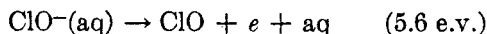
The complete energy change of the practically important half-reaction



may be calculated to be  $2 \times (5.5)$  e.v., and the energy change of the half-reaction



is found to be ca. 5.8 e.v. Correcting for the small energy of electrolytic dissociation of  $\text{HOCl}(\text{aq})$  (ca. 0.2 e.v.), the energy of formation of  $\text{ClO}$  from  $\text{ClO}^-(\text{aq})$  may be obtained.

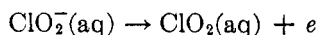


This value (5.6 e.v.) is in excellent agreement with the value (128 kcal.) given by Weiss (58).

According to the same author the energy change of the following half-reaction



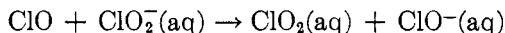
should be 121 kcal. (= 5.25 e.v.). Combining this with the small heat of solution of gaseous chlorine dioxide (ca. 0.3 e.v.), the complete energy change of the simple electron transfer



would be ca. 4.95 e.v.

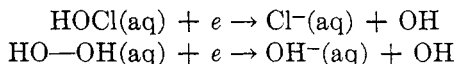


The distinctly exothermic reaction

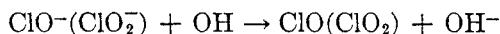


may possibly be involved in the activation of aqueous chlorite solutions by hypochlorite-hypochlorous acid.

The transient generation of unstable OH radicals from hypochlorous acid and hydrogen peroxide may be possible by an efficient electron transfer from suitable electron donors according to the imaginable half-reactions:



In such cases activation of hypochlorite and chlorite solutions may readily take place by the formation of ClO and ClO<sub>2</sub>.



By the use of available entropy data in the literature (29) and adjusting the complete energy changes in figure 3 with respect to the conventional standard states, it may be possible to evaluate the corresponding free-energy changes and oxidation-reduction potentials from the thermodynamic relation

$$\Delta F = \Delta H - T\Delta S = 23,070 E \text{ (kcal.)}$$

where  $\Delta F$  = free-energy change,

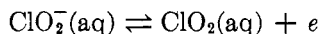
$\Delta H$  = complete energy change,

$\Delta S$  = entropy change, and

$E$  = oxidation-reduction potential (volts).

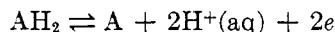
As the hydration energies ( $W$ ) of most ions are rather uncertain (with probable errors of about 0.1–0.2 e.v.) such calculations have been omitted, but the approximately linear relation between electrochemical oxidation-reduction potentials and complete energy changes is clearly demonstrated in figure 4.

For instance, the energy change of the equilibrium



corresponds to an approximate potential of 1.0 v., referred to the standard hydrogen-hydrogen ion potential as zero, on the straight line in figure 4, in fairly good agreement with the experimental value (0.95 v.) previously given by the author (24, 25).

It is interesting to state that a relationship similar to that shown in figure 4 is valid for numerous electrochemical half-reactions of the general type



in aqueous solution (23). In this formula A may represent various organic molecules, such as unsaturated carbonyl compounds, quinones, azo compounds, and several dyes, containing C=C, C=O, N=N, and C=N double bonds in conjugated systems. In general, these compounds are reversibly hydrogenated

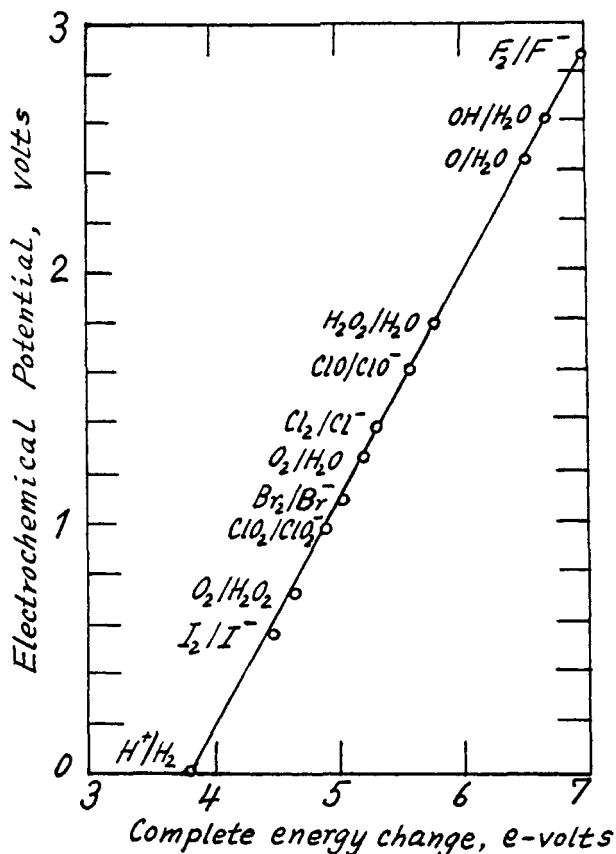


FIG. 4. Electrochemical potentials in relation to complete energy changes

with an approximately constant entropy change, nearly equal to the molar entropy of hydrogen, in spite of the widespread electronic levels and energy changes observed.

The development of ionic structures by displacement of mobile electrons in chromophoric systems is reflected in the characteristic color changes of pH indicators in aqueous solution. A color shift from red to yellow, with a change in light absorption from green ( $\lambda_1 \approx 0.55 \mu$ ) to blue ( $\lambda_2 \approx 0.45 \mu$ ), corresponds to an energy difference of absorbed radiation roughly equal to

$$E_{\lambda_2} - E_{\lambda_1} = 1.24 \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \approx 0.5 \text{ e.v.}$$

A similar calculation for a shift from yellow to colorless, presuming an average displacement of the spectral absorption from blue ( $\lambda_1 \approx 0.45 \mu$ ) to the near ultraviolet ( $\lambda_2 \approx 0.35 \mu$ ), gives an energy difference of about 0.8 e.v., which is of the same magnitude as the free-energy change in the electrolytic dissociation of water ( $= -RT \ln K_w$ ).

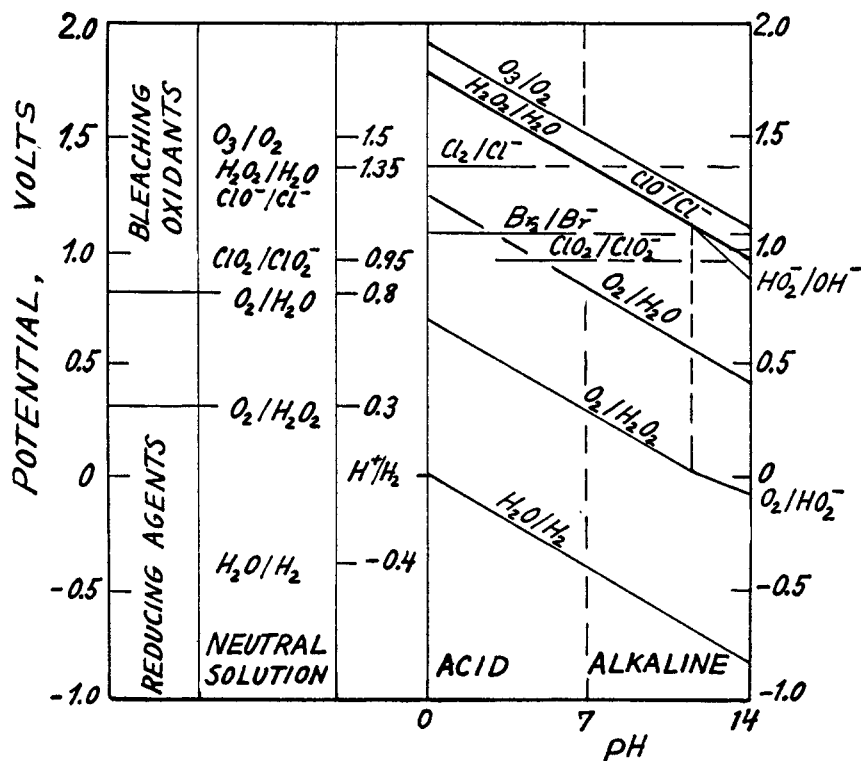


FIG. 5. Oxidation-reduction potentials in neutral, acid, and alkaline solutions, referred to the standard hydrogen potential.

When the energy difference between electronic levels is 0.5 e.v. or more, reactions easily may go to completion, but when the levels have nearly the same energy, the electrons will distribute themselves among the available energy levels, giving an equilibrium. The relative number of reverse electron transfers is governed by the mean thermal energy ( $RT$ ) and the molar concentration ( $c$ ), corresponding to the familiar term  $RT \ln c$  in the expression of electrochemical potentials. At ordinary temperature the small energy of  $RT = 0.025$  e.v. is equivalent to a quantum in the far infrared ( $\lambda = \text{ca. } 50 \mu$ ) within a characteristic absorption band of liquid water (37).

As shown in figure 5, the potentials of the usual bleaching oxidants are situated above the  $O_2$ - $H_2O$  level in neutral solution, i.e., more than 0.8 v. above the standard hydrogen-hydrogen ion potential. Chlorine dioxide has the lowest value (0.95 e.v.); hypochlorite-hypochlorous acid and hydrogen peroxide have a much higher potential (ca. 1.35 e.v.), a little below the high ozone-oxygen level (1.5 e.v.).

On the other hand, the potentials of various reducing agents, including such organic compounds as phenols, aldehydes, and sugars, are essentially situated below the oxygen-hydrogen peroxide level down to (or even below) the water-hydrogen level.

From figure 5 it will further be recognized that the chlorine-chloride potential in alkaline solutions is situated above the peroxide and hypochlorite levels, and even above the ozone-oxygen level at  $\text{pH} > 10$ . At high alkalinity chlorine dioxide is just as powerful an oxidant as hypochlorite and peroxide. In slightly acid to neutral solutions the two last-mentioned agents have about the same oxidation potentials as free chlorine, whilst at  $\text{pH} < 5$  the oxygen-water potential rises above the chlorine dioxide-chlorite level.

The varying overvoltage of oxygen—from 0.4–0.5 v. on bright gold and platinum, about 0.2 v. on spongy platinum, down to only 0.05 v. on spongy nickel in normal alkaline solution—indicates that the anodic evolution of oxygen is a retarded process, and that the varying formation and decomposition of more or less stable metal oxides are responsible for the difficulties in reproducing consistent electrode potentials. Under normal conditions, chlorine does not give any appreciable evolution of oxygen, as the readily generated hypochlorite in alkaline solution is substantially stable. However, in the presence of certain catalysts, e.g., nickel, cobalt, and copper compounds, hypochlorites are easily decomposed to chloride and oxygen, and a similar decomposition into water and oxygen is even more pronounced for hydrogen peroxide.

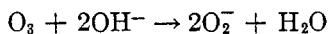
Organic compounds which are readily oxidized or reduced with a sharp color change may be used as visual indicators for definite potentials, and sometimes also as efficient accelerators to get stable equilibrium potentials in sluggish systems (21). A number of such oxidation-reduction indicators comprises a potential range between ca. 0.2 and 1.3 v. in acid solution (31), the highest potentials being associated with the presence of nitro groups. For instance, introduction of a nitro group into diphenylamine raises the potential of this compound in acid solution from ca. 0.3 v. to above 1 v. Certain polynitro compounds, on which even very strong oxidants are without action, may be used as chlorine-resistant pH indicators.

As a whole, the oxidation-reduction levels of most available reversible processes are situated in a potential range of about 1.2 v. (between the levels of  $\text{O}_2\text{-H}_2\text{O}$  and  $\text{H}_2\text{O-H}_2$ ), and in general the systems of organic compounds will be found below the oxygen-hydrogen peroxide ( $\text{O}_2\text{-H}_2\text{O}_2$ ) level.

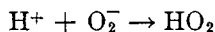
#### IV. OXIDATION POTENTIALS AND REACTIONS OF SPECIAL BLEACHING OXIDANTS

##### *A. Ozone and hydrogen peroxide*

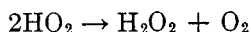
The high ozone-oxygen potential decreases from about 1.9 v. in acid solution to 1.1 v. in alkaline solution, and the rate of decomposition increases with increasing alkalinity. In acid solutions the reduction of ozone usually involves the formation of water from one oxygen atom, whilst the two other atoms are liberated as molecular oxygen. In alkaline solutions the perhydroxyl ion  $\text{O}_2^-$  is generated in the following reaction:



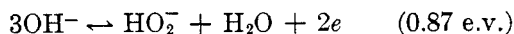
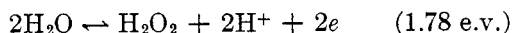
At low alkalinity  $\text{O}_2^-$  is converted to perhydroxyl radicals



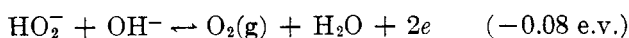
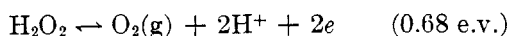
which may be decomposed into hydrogen peroxide and free oxygen.



The oxidizing intensity of hydrogen peroxide in the conversion to water is defined by the potentials of the half-reactions in acid and alkaline solutions:



On the other hand, the reducing intensity of hydrogen peroxide in the formation of free oxygen will be determined by the following potential levels:



The development of both oxidizing and reducing properties of hydrogen peroxide is a fact of great general importance in the use of this chemical. With respect to the high oxidizing power of concentrated hydrogen peroxide it should be noted that chlorine is evolved when dry hydrogen chloride is passed into

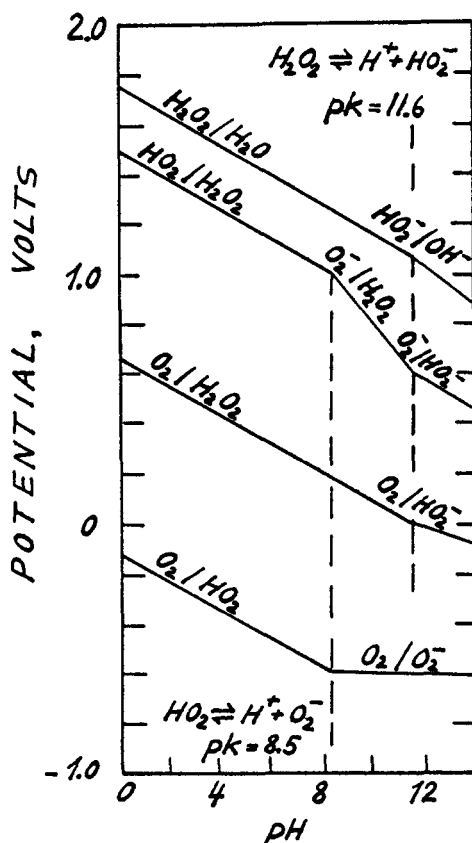


FIG. 6. Potentials governing the formation and decomposition of hydrogen peroxide in aqueous solutions.

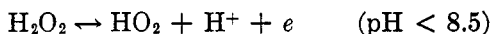
anhydrous hydrogen peroxide (38). On the other hand, powerful oxidants, such as chlorine, hypochlorite, and chlorine dioxide in alkaline solutions, liberate oxygen from hydrogen peroxide.

The inherent tendency of a spontaneous evolution of oxygen appears in the presence of certain multivalent, active metal compounds as catalysts, e.g., freshly precipitated hydroxides of copper, cobalt, and nickel. In direct contrast, hydroxides of such metals as tin and magnesium have a favorable influence on the stability by removing even traces of the harmful catalyst (7).

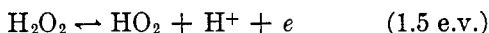
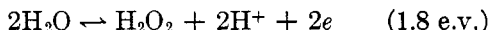
In order to get an insight into the characteristic behavior of aqueous hydrogen peroxide solutions, and particularly the important influence of alkalinity on the rate of decomposition, the transient generation and existence of the two unstable forms  $\text{HO}_2$  and  $\text{O}_2^-$  should be considered.

From potentials referring to the stepwise reduction of oxygen in acid and alkaline solutions (36), the fundamental potential-pH graph in figure 6 has been projected.

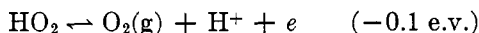
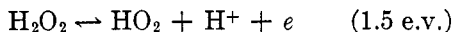
The presumable tendency of producing  $\text{HO}_2$  and  $\text{O}_2^-$  from hydrogen peroxide in solutions of varying pH should be determined by the potentials of the following half-reactions:



In acid solution the slow generation of  $\text{HO}_2$  radicals may be defined by the difference between the potentials of the half-reactions



whilst the great potential difference of the half-reactions



should govern the subsequent evolution of oxygen.

As previously mentioned, it is a well-known fact that minute traces of impurities, particularly those of certain heavy metals, act as powerful catalysts in this decomposition, which is greatly increased by the presence of alkali. By addition of various substances—such as sodium silicate and sodium stannate, which by hydrolysis give extremely fine, colloidal dispersions of silicic or stannic acid—dilute or concentrated aqueous solutions of hydrogen peroxide may be stabilized. Obviously the strongly adsorptive properties of silicic and stannic acids are responsible for the effective suppression of such catalysts.

According to certain patents (8, 10) a particularly good stabilizing effect is obtained by the addition of small amounts of soluble tin compounds, e.g., sodium stannate, in acid hydrogen peroxide solutions. Utilizing experimental

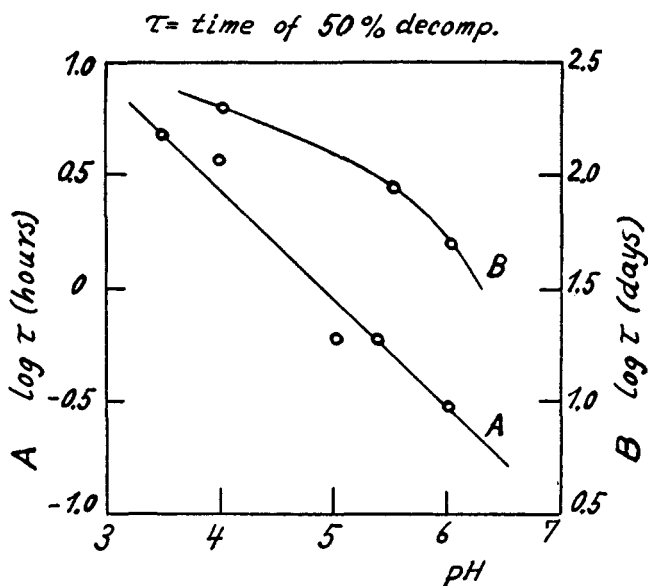
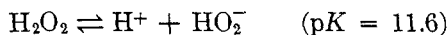
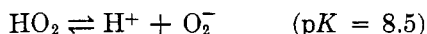


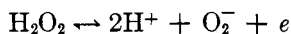
FIG. 7. Decomposition of hydrogen peroxide in dilute, slightly acid solutions (a) without stabilizer and (b) with sodium stannate (20 mg. of tin per liter) as stabilizer.

data given elsewhere (8) the logarithm of time ( $\tau$ ) of 50 per cent decomposition has been represented in figure 7. It is observed that the value of  $\log \tau$  without a stabilizer in the actual case decreases about proportionally with increasing pH, corresponding to  $\tau = 4.5$  hr. at pH 3.5 and 0.25 hr. at pH 6. About thousandfold longer times (200 days at pH 4 and 50 days at pH 6) were obtained in the stabilized solutions.

In the range of low alkalinity (pH 8.5–11.6), corresponding to the presumable  $pK$  values of the dissociation equilibria



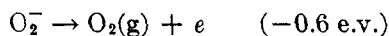
the potential of the rate-determining half-reaction



sinks from about 1.0 to 0.6 v. according to the graph of figure 6, and the driving force in the formation of  $\text{O}_2^-$  will increase to a maximum value at pH about 11.6. This fact should be reflected in an increasing rate of decomposition, according to the possible reaction:



The potential of the half-reaction



is constant on a very low level and corresponds to a simple discharge process, which may be readily performed by the presence of any efficient electron acceptor, e.g., by unstable OH radicals, acting on a very high potential level.

In fact, measurements of the rate of decomposition of hydrogen peroxide in slightly alkaline solutions of varying pH, expressed as the time in minutes ( $\tau$ ) for a fall in oxygen content from 1 vol. to 0.5 vol. concentration, seems to support these considerations.

The following data (40) may illustrate the influence of alkalinity on this time of fall in oxygen content, using the logarithm of "half-time" ( $\tau$ ) as a relative measure of decomposition (table 2 and figure 8).

As shown in the graph of figure 8 there is a linear decrease in the logarithm of decomposition time ( $\tau$ ) with increasing pH and also a pronounced discontinuity in the slope of the  $\log \tau$ -pH curve at pH 8.5.

From recent investigations (30) it has been concluded that the unstable ion  $O_2^-$  (generated by reduction from  $O_2$ ) may readily react with  $H_2O_2$  to produce free OH radicals according to the equation

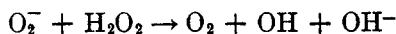


TABLE 2  
Decomposition of hydrogen peroxide solutions of 1 volume strength  
 $\tau$  = half-time

pH	$\tau$	LOG $\tau$	pH	$\tau$	LOG $\tau$
	minutes			minutes	
6.8	190	2.28	8.9	70	1.85
7.1	170	2.23	9.9	25	1.40
7.9	130	2.11			

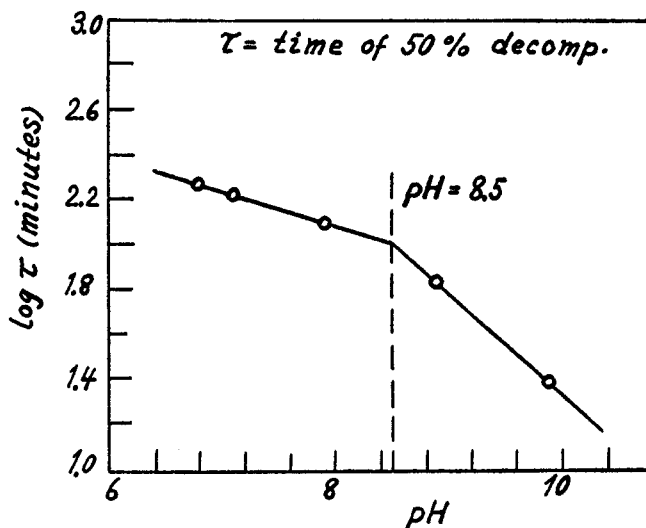


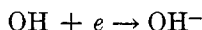
FIG. 8. Decomposition of hydrogen peroxide in slightly alkaline solutions according to table 2.



faster than with hydrogen ions in the formation of  $\text{HO}_2$  radicals. The  $\text{OH}$  radicals will either react with  $\text{H}_2\text{O}_2$ ,

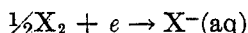


or be reduced to hydroxyl ions in the presence of oxidizable compounds, acting as electron donors.

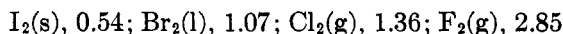


*B. Halogen-oxygen compounds: chlorine, hypochlorite, chlorite, and chlorine dioxide*

The reactions of halogens ( $\text{X}_2$ ) in aqueous solutions are primarily dependent on the electron transitions

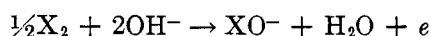


which are characterized by their well-defined electrochemical standard potentials (in volts):



Owing to its extremely high potential, fluorine, unlike the other halogens, easily liberates hydroxyl radicals or atomic oxygen, reacting in a nascent state to give ozone or fluorine monoxide.

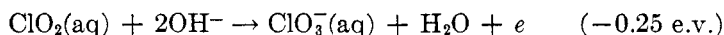
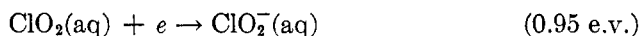
The halogen-hypohalite potentials according to the half-reactions



$\text{X} = \text{Cl, Br, I.}$

are all roughly about 0.5 v. in normal alkaline solution, and therefore the hydrolytic conversion of halogens is essentially governed by the halogen-halide potentials.

By comparison, the hydrolysis of chlorine dioxide (25) is determined by the half-reactions



It is a remarkable fact that the conversion  $\text{ClO}_2 \rightarrow \text{ClO}_3^-$  and still more pronounced the conversion  $\text{NO}_2 \rightarrow \text{NO}_3^-$  are associated with very low potential levels; for  $\text{NO}_2 \rightarrow \text{NO}_3^-$  the level is even below the hydrogen potential in normal alkaline solution (47), indicating the possibility of induced oxidation processes.

The constants of hydrolysis ( $K_h$ ,  $\text{p}K_h = -\log K_h$ ) of the halogens have been

TABLE 3  
*Constants of halogen hydrolysis ( $K_h$ ) and dissociation of hypohalogenous acids ( $K$ )*

$\text{X}_2$	$K_h$	$\text{p}K_h$	$\text{HXO}$	$K$	$\text{p}K$	REMARKS
$\text{Cl}_2$	$2.1 \times 10^{-4}$	3.7	$\text{HClO}$	$5.6 \times 10^{-8}$	7.3	$\text{p}K > \text{p}K_h$
$\text{Br}_2$	$4.2 \times 10^{-9}$	8.4	$\text{HBrO}$	$2 \times 10^{-9}$	8.7	$\text{p}K \approx \text{p}K_h$
$\text{I}_2$	$4.6 \times 10^{-13}$	12.3	$\text{HIO}$	$1 \times 10^{-11}$	11.0	$\text{p}K < \text{p}K_h$

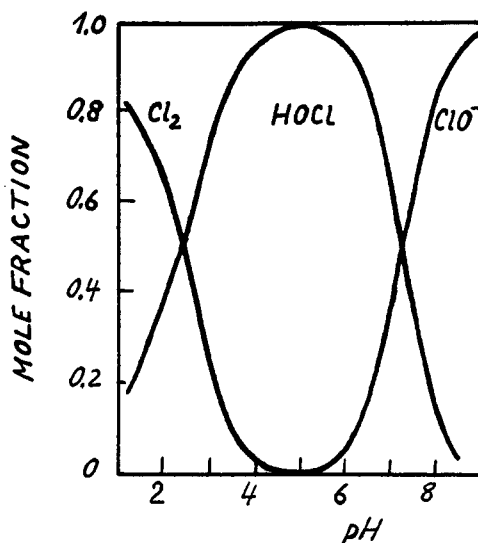


FIG. 9. Equilibrium distribution of  $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{ClO}^-$  in aqueous solutions. Chlorine concentration, 0.09 mole per liter at  $20^\circ\text{C}$ .

determined at  $25^\circ\text{C}$ . by pH measurements with the glass electrode (18, 19, 26), and the values are given in table 3 together with the constants of dissociation ( $K$ ,  $\text{p}K = -\log K$ ) of the hypohalous acids (33).

The hydrolysis of chlorine in a diluted buffer solution of fixed acidity is determined by the chlorine strength ( $C$ ) and the constant of hydrolysis ( $K_h$ ). Putting  $(\text{HClO}) = CX$ , and  $(\text{Cl}_2) = C(1 - X)$ , the following relation should be approximately valid:

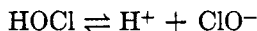
$$\log \left( \frac{X^2}{1 - X} \right) = \text{pH} + \text{p}C - \text{p}K_h \quad (\text{p}C = -\log C)$$

At  $20^\circ\text{C}$ . and 1 atm. the solubility of chlorine in water  $C_s = 0.09$  mole per liter (35), and the value of  $K_h/C_s$  is about  $2 \times 10^{-8}$ . Consequently, as shown in the graph of figure 9, the hydrolytic equilibrium



is in favor of  $\text{HOCl}$  above pH 3.

The amount of chlorine becomes considerable only at pH values below 3.5, whilst the dissociated hypochlorite ion  $\text{ClO}^-$  predominates at pH values above 7.5 according to the equilibrium:

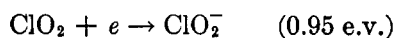


As seen from table 3, the stability of hypobromous and hypoiodous acids with respect to the reconversion of the corresponding free halogens, bromine and iodine, decreases very rapidly with decreasing alkalinity.

The hypohalous compounds are further easily converted into halate and halide via the possible formation of unstable compounds (e.g.,  $\text{XO}$ ,  $\text{XO}_2^-$ ,  $\text{XO}_2$ ), the

optimum speed being dependent on the amounts of HOX and XO<sup>-</sup> in the actual pH range.

The equilibrium potential of the system



in a diluted (equimolar) aqueous solution has a constant value about 0.40 v. below the standard potential of the system Cl<sub>2</sub>(g)-Cl<sup>-</sup>. Therefore, the action of chlorine (and hypochlorous acid) on a solution containing ClO<sub>2</sub><sup>-</sup> may produce chlorine dioxide.

The oxidation-reduction potentials of chlorine dioxide, chlorite, and hypochlorite in aqueous solution are represented in the graph of figure 10.

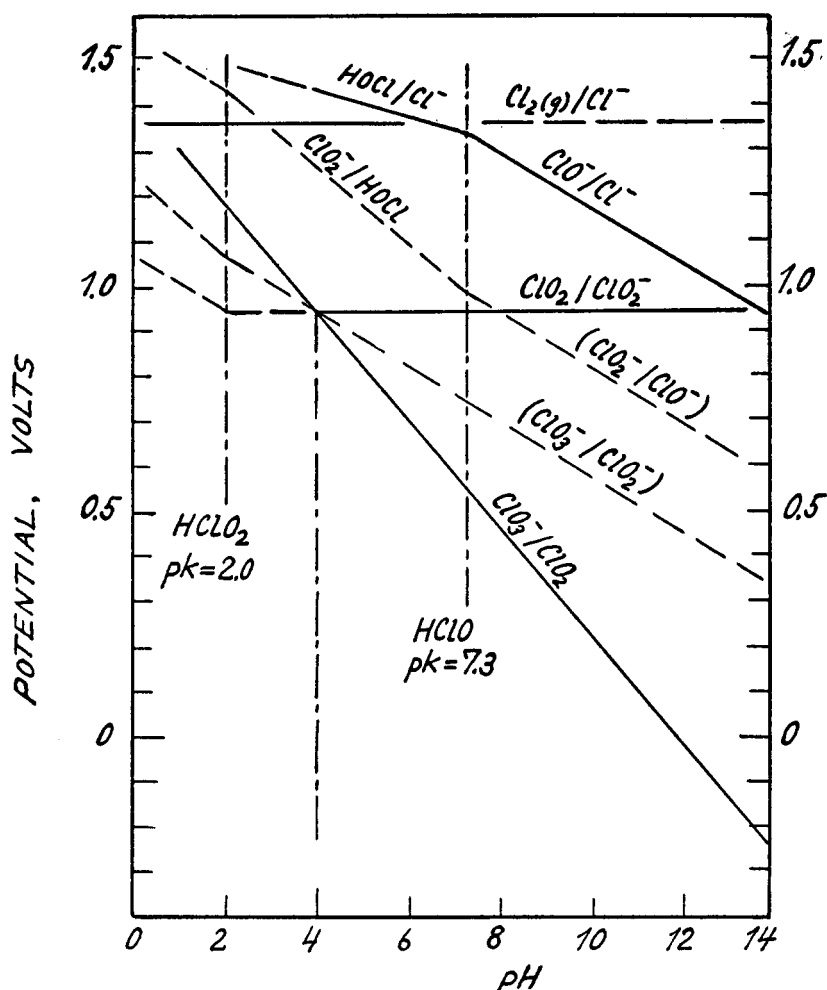
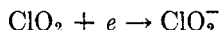


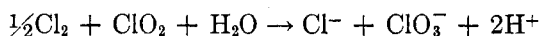
FIG. 10. Oxidation-reduction potentials of hypochlorite, chlorite, and chlorine dioxide in aqueous solutions.

The potentials of the coherent half-reactions

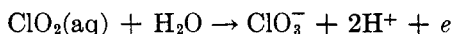
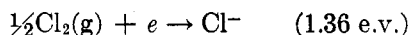


have the same value (0.95 v.) at pH = 4; above this pH value there is an increasing tendency toward formation of chlorate by the influence of such strong oxidants as free chlorine and hypochlorite.

Appreciable losses of available chlorine from gaseous mixtures of chlorine and chlorine dioxide may be possible in neutral and slightly alkaline solutions by the (reversible) conversion



corresponding to the extremely situated potential levels of the half-reactions

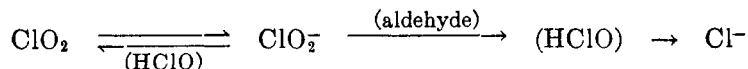


the difference being nearly 0.8 v. in neutral solution and 1.6 v. in normal alkaline solution.

The formation of  $\text{ClO}_3^-$  by interaction between chlorine dioxide and hypochlorous acid has been demonstrated from kinetic radioactivity measurements (9). It has been stated that a solution of chlorite can be activated by the presence of hypochlorite (including small amounts of free hypochlorous acid) in slightly alkaline solutions (pH ca. 9), giving good bleaching effects even at ordinary temperatures (3). This may be due to the possible formation of active chlorine dioxide. In practical textile bleaching a pH of at least 7 and temperatures between ca. 40° and 100°C. have been recommended (5).

By reactions with certain reducing agents, e.g., aldehydes, in neutral or slightly acid solutions the chlorite ion may be at first partially oxidized (activated) to give chlorine dioxide (pH 4-7), and a mixture of chlorite and aldehyde in the ratio 1:1 has been suggested for bleaching purposes in neutral solution (42).

Generally, the successive reduction steps

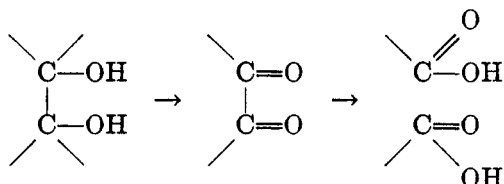


should be favored by a low acidity, as the difference between the potentials of the final and second steps increases with decreasing acidity. However, in order to maintain a rapid formation of active chlorine dioxide from chlorite, a certain moderate acidity may be established, and this will make a pH of about 5 most suitable. Under these slightly acid conditions even very sensitive proteinaceous fiber materials can be bleached safely (52).

#### V. SOME ASPECTS OF OXIDATION PROCESSES IN PRACTICAL BLEACHING OPERATIONS

Destruction of organic substances by the action of powerful oxidants involves a stepwise conversion to the oxidized states of simpler compounds by the crack-

ing of carbon chains, e.g.:

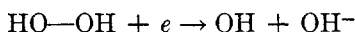


The appearance of hydroxyl and oxygen substituents at adjacent carbon atoms enables the further oxidizing attack on the remaining single C—C bonds, and this fact may be responsible for the sensitivity of the carbohydrates, particularly cellulose, to powerful oxidants. It will also be of importance in the possible breakdown of aromatic rings via the transient formation of quinones.

Alcohols and carbohydrates are rapidly oxidized to aldehydes and carboxylic acids by activated hydrogen peroxide in acid solution.



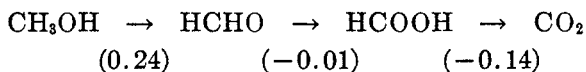
Such oxidation processes, initiated by the presence of an active electron donor, e.g., ferrous ions, according to the following electron transition



have been interpreted as chain reactions with unstable OH radicals as chain carriers (41).

The slow oxidation of aldohexoses by chlorine water yields aldonic acids, but in alkaline solutions a more profound oxidation takes place by the splitting of carbon chains.

It should be of interest to mention that the oxidation-reduction potential decreases from the alcohol to the carboxylic acid state in the following oxidation steps in aqueous acid solution (34):



These potentials (volts at 25°C.) refer to the standard hydrogen-hydrogen ion couple as zero in the European system.

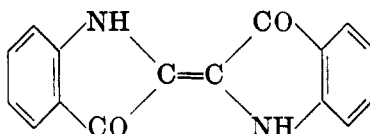
The oxygen content of lignin substances is distributed on several functional groups, viz., free phenolic and alcoholic hydroxyl (OH), ketonic carbonyl (C=O), methoxyl (OCH<sub>3</sub>), phenolic, and aliphatic ether bonds (13, 17). The color produced by oxidizing agents may chiefly be due to the presence of free phenolic OH groups in the ortho position.

Generally the so-called "critical oxidation potential" of a series of phenols will reflect the relative ease of removal of the phenolic hydrogen in the primary step

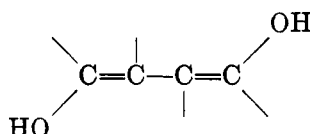


when the concentration of the RO· radical is very small (12).

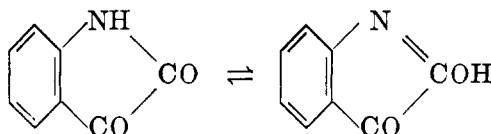
## The classical blue indigo dye



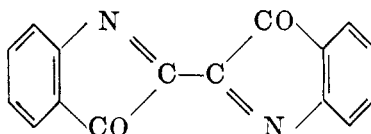
may be reversibly reduced to the alkali-soluble leuco form, the colorless dihydro-indigo, having an enolic structure with slightly acidic hydroxyl groups in the conjugated bond system:



This leuco form is very sensitive to oxidants, and is easily reconverted to the blue dye by atmospheric oxygen. On the other hand, indigo is remarkably stable to oxidation. The chromophoric group of this molecule occurs as a member of two ring systems, and permanent bleaching requires the breakdown of this chromophore by the action of intense oxidants in the irreversible conversion to isatin.



Under special conditions the indigo dye can be reversibly dehydrogenated to dehydroindigo of the presumed structure:



An oxidizing attack on the central C—C bond of this molecule, e.g., by activated hydrogen peroxide or free OH, should result in the formation of isatin.

Chlorine will also convert indigo to dehydroindigo, but since the latter compound is more readily chlorinated than indigo itself, the process (in anhydrous acetic acid) can be continued to give highly chlorinated products.

The formation of conjugated C=C bonds from simple reactive compounds, e.g., aldehydes and sugars, by repeated combined condensation and dehydration processes is considered a general phenomenon of fundamental importance in the native synthesis of plant pigments (e.g., carotene) and wood components, such as the numerous derivatives of pyrones (flavones, etc.). The simultaneous presence of polyhydroxy compounds with both alcoholic and phenolic hydroxyl groups makes the whole complex very reactive, with a strong tendency to be

converted into higher condensation products of a resinous nature. The polyphenol derivatives, which are extensively found as glucosides in many tannins and resins, are generally unstable in the air, especially in aqueous alkaline solutions, and are readily oxidized to quinones or other compounds of more or less unknown composition.

The chemical bleaching processes of multistage operations in the pulp and textile industries today are directed towards a selective destruction of colored substances with a minimum degradation of the fiber material by the properly combined use of two or more agents, such as chlorine water, hypochlorite, chlorine dioxide, or activated sodium chlorite, and peroxide.

By chlorination in an acid medium lignified substances become soluble in alkali, and the chlorinated products can be removed by alkaline extraction, thanks to the good resistance of cellulose in the absence of oxidants (15). Generally, the halogenation of aromatic compounds is acid-catalyzed. In a review of earlier investigations Bradfield and Jones (2) have stated that hypochlorous acid is without appreciable action on a phenolic ether. Addition of a small amount of hydrochloric acid to a solution of hypochlorous acid accelerates the reaction with phenols and phenol ethers by the formation of free chlorine as an efficient chlorinator.

It has also been stated that breakdown of cellulose can be prevented in the chlorine bleach (involving the presence of both chlorine and hypochlorous acid), but not the oxidation of OH and CHO groups (48). On the other hand, a prolonged or repeated treatment with hypochlorite under usual bleaching conditions (in which the real oxidant may be  $\text{ClO}^-$  and the activator hypochlorous acid in a very low concentration) will cause degradation of the cellulose (28). This may be avoided by using the less powerful oxidants chlorine dioxide or sodium chlorite as efficient bleaching agents under properly selected conditions.

Thus, no appreciable drop in the degree of polymerization or  $\alpha$ -cellulose content was observed on carefully purified cotton cellulose by the action of sodium chlorite in 1 per cent solution at  $\text{pH} = 5$  and  $70^\circ\text{C}.$ ; also the copper number was unchanged (32).

The most outstanding feature of the reaction between cellulose and hypochlorite solution is the influence of the pH value. The attack reaches a maximum in the ample presence of both  $\text{ClO}^-$  and  $\text{HClO}$  ( $\text{pH} 7-8$ ) by a chain reaction, involving the transient formation of unstable OH and ClO radicals.

With respect to the action on coloring matter in the bleaching of bast fibers, Butterworth (4) found that for equivalent oxygen consumption a neutral hypochlorite bath generally gave a higher bleaching than either acid or alkaline liquors. Thus, in the concentration range of 3-10 g. of available chlorine per liter the bleaching effect quickly arrived at a maximum between 3.0 and 3.5 g. of chlorine per liter near the neutral point, whilst the attack on the fibers increased progressively in the more concentrated liquors.

In a number of interesting papers Scholefield and coworkers (44, 49, 54) have investigated the accelerated destruction of cellulose by hypochlorite in the presence of various reduced vat dyes. The leuco form of the anthraquinone dye

Cibanon Orange R was stated to be a particularly good accelerator of the hypochlorite oxidation. It appears to participate as an efficient "oxygen carrier" from hypochlorite to cellulose without undergoing any destructive oxidation, whilst blue and green vat dyes were themselves irreversibly oxidized to a considerable extent. Yellow anthraquinone dyes have also been reported to promote the oxidation of cellulose on exposure to light (1).

This accelerated oxidation of cellulose is different from the prolonged normal oxidation by hypochlorite. It appears to involve a simpler mechanism, as shown by the close connection between the oxygen consumption and the magnitude of the chemical effects produced, and these relationships were practically independent of the pH value of the bleaching solution. The primary alcohol groups should be readily oxidized via the aldehyde stage to carboxyl with a subsequent hydrolysis of the 1,4-glucoside link, giving a reducing end-group. In fact, the constant ratio between the reducing value and the carboxyl content of the oxidized cellulose in all the products of the accelerated oxidation will be explained by this mechanism. It was concluded that the intensity of the oxidation of cellulose should be proportional to the intensity of the oxidation of the leuco vat dye. This reasonable supposition would mean that the difference between the oxidation-reduction potential of the hypochlorite and that of the free leuco dye at a given pH should essentially govern the accelerated oxidation process.

For the agreement to be made obvious it was necessary to express the potential by reference to the potential of a hydrogen electrode at the same pH (44). To be sure, the potentials of a platinum electrode in hypochlorite solutions cannot be regarded as true equilibrium potentials, measuring accurately the tendency of the agent to bring about oxidation, but under suitable conditions such relatively stable and reproducible potentials may be sufficiently well-defined to characterize the oxidation power of the hypochlorite solutions in question.

The "oxidation potentials" of sodium hypochlorite in a concentration of 2.7 g. of available chlorine per liter were measured in various buffer solutions (44). These potentials were all situated on a curve a little above the potentials of the systems  $\text{HO}_2\text{--H}_2\text{O}_2$  and  $\text{O}_2\text{--H}_2\text{O}_2$  in figure 6, but distinctly below the true potential of the system  $\text{ClO}^-\text{--Cl}^-$  in figure 10.

Most probably the accelerated destruction of cellulose depends on the action of free hydroxyl radicals produced by the initial reaction of hypochlorite with the active hydrogen of the leuco vat dye. Perhaps certain substances among the numerous wood components (e.g., yellowing compounds in a reduced state) are able to cooperate in a similar attack on the fibers by hypochlorite. If this were possible, chlorine dioxide or sodium chlorite should preferably be put into some preceding stage of bleaching before the usual final whitening step.

The difficulties of obtaining reliable "oxidation potentials" are still more pronounced in solutions of hydrogen peroxide. The oxidation potential for a solution containing 1 g. of hydrogen peroxide per liter was calculated by Butterworth (4) to range from 0.705 v. at pH 3.4 to 0.835 v. at pH 13 against the hydrogen potential at corresponding pH. However, these values do not at all agree with the true potential of the system  $\text{H}_2\text{O}_2\text{--H}_2\text{O}$  ( $\text{HO}_2^-\text{--OH}^-$ ), varying from 1.78 in



acid solution to 0.87 in alkaline solution, measured against the standard hydrogen potential as zero. Conversely, the experimental values agree much better with the "reduction potential" of  $\text{H}_2\text{O}_2$  (or  $\text{HO}_2^-$ ), governing the decomposition with evolution of oxygen. These potentials are 0.68 in acid solution and  $-0.08$  in alkaline solution (referred to the standard hydrogen potential as zero). The same remarks should essentially be valid against the potentials presented in a paper by Taylor, White, and Vincent (53).

Investigating the action of hydrogen peroxide after treatment of linen with hypochlorite, and washing the material before placing it in the alkaline peroxide bath, Butterworth (4) found a minimum degradation at pH 11–12. He also reported prominent color differences in using peroxide baths of varying pH, as the acid, neutral, and slightly alkaline solutions showed poor bleaching effects, whilst above pH 10 a marked increase was obtained.

The oxidation of residual lignin in jute fibers by successive treatment with hypochlorite and peroxide has been favorably used to avoid a yellowing by light (39), but it should be borne in mind that even small amounts of hypochlorite entering the alkaline peroxide bath may cause a measurable attack on the fibers, probably due to an activating reaction of hypochlorite with hydrogen peroxide.

To get a more stable bleach effect in textile bleaching with acid sodium chlorite it has recently been proposed to use an alkaline peroxide bath in the final step (27, 46).

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