MECHANISMS OF SUBSTITUTION REACTIONS OF METAL COMPLEXES

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I. Introduction

The subject of kinetics and mechanisms of substitution reactions of metal complexes was recently reviewed in some detail (*17*, *116*). Therefore the principal concern in this chapter is to summarize some of the later advances.

Substitution reactions of metal complexes include the replacement of one ligand by another, or of one metal ion by another. According to the terminology of Hughes and Ingold, developed for organic reactions, these can be called S_N and S_E to distinguish between nucleophilic and electrophilic, respectively.

$$\text{M—X} + \text{Y} \rightarrow \text{M—Y} + \text{X} \qquad S_N \qquad (1)$$

$$\text{M—X} + \text{M}' \rightarrow \text{M} + \text{M}'\text{—X} \qquad S_E \qquad (2)$$

Thus substitution reactions are generalized acid-base reactions, where the Lewis acids are the metal ions and the bases are the ligands.

Two fundamentally different reaction paths can be visualized for these reactions. For example, the S_N reaction may proceed by dissociation, the familiar S_N1 mechanism, where the rate determining step is the rupture of the metal-ligand bond.

$$\left.\begin{array}{l} M{-}X \overset{\text{slow}}{\rightleftharpoons} M + X \\ M + Y \overset{\text{fast}}{\rightarrow} M{-}Y \end{array}\right\} S_N1 \qquad \begin{array}{r}(3)\\(4)\end{array}$$

Alternatively, the reaction may proceed by displacement, the familiar S_N2 path, where the rate-determining step is the partial formation of a new metal-ligand bond plus the weakening of another such bond.

$$Y + M{-}X \rightarrow Y \cdots M \cdots X \rightarrow M{-}Y + X \qquad S_N2 \tag{5}$$

Other rather special mechanisms have been observed, but much of the effort expended in studies of substitution reactions has been concerned with attempts to classify them either as S_N1 or S_N2. At best, this is a very difficult task, since unequivocal experimental evidence in support of one over the other is hard to obtain. Seldom has it been sufficient to know the kinetic order of the reaction. No doubt the best evidence would be the detection of the reaction intermediate. Unfortunately the nature of such intermediates is generally such as to escape detection by direct means. Therefore it becomes necessary to use indirect methods in an attempt to determine which reaction path appears to predominate in any given system.

Most of the kinetic and stereochemical studies pertaining to the mechanisms of substitution reactions of metal complexes have been done on the more stable and inert compounds, particularly the Werner-type complexes. This is understandable because it is only among such systems that geometrical and optical isomers exist. Furthermore, conventional kinetic techniques are readily applicable to following these slow rates of reaction. For example, the rate of hydrolysis of $[Co(NH_3)_5Cl]^{++}$ can be followed by any one of several methods.

$$\underset{\text{purple}}{[Co(NH_3)_5Cl]^{++}} + H_2O \rightarrow \underset{\text{pink}}{[Co(NH_3)_5H_2O]^{3+}} + Cl^- \tag{6}$$

At least four methods can be used easily to determine the rate of reaction (6). They are: (i) analysis of chloride ion in solution; (ii) change in optical density at an appropriate wavelength; (iii) change in conductivity of the solution; and (iv) analysis of acid produced, the pK_a of $[Co(NH_3)_5H_2O]^{3+}$ being 5.7.

Flow techniques, relaxation spectrometry, and line-broadening nuclear magnetic resonance methods have recently been used to investigate the rates of fast reactions (*39*). This is an extremely important development because a majority of the metal complexes are labile. Kinetic studies on these systems are required to test current theories on reaction mechanisms of metal complexes and on metal-ligand bonding. One section is devoted to fast reactions in the discussion that follows. In addition sections are included on the recent developments in photosubstitution reactions of metal complexes and in reactions of organometallic and metal carbonyl compounds. Some of these developments are only in their embryonic state, but a summary of the present status of knowledge should help stimulate further research activity in these very important areas of physical-inorganic chemistry.

II. Octahedral Complexes

A. ACID HYDROLYSIS

The most common reaction of a metal complex, and the one studied to the greatest extent, is the reaction between the complex and the solvent water [see Eqs. (6) and (7)]. In acid solutions, with a pH less than about 3, such reactions are referred to as acid hydrolysis reactions. Kinetic studies show that these reactions are pseudo-first-order. Since the concentration of the solvent does not change during the reaction, the kinetic order does not show the dependence of the rate of hydrolysis on water. Attempts to determine the role played by water making use of nonaqueous solvents containing varying amounts of water have, as yet, not been successful. One difficulty arises from the fact that changes in the water concentration are also accompanied by changes in the nature of the solvent.

1. *Cobalt(III) Complexes*

Another approach has been to determine the relative rates of hydrolysis of a series of analogous compounds where the size of the ligands not being replaced increases and thus renders the central metal less accessible to nucleophilic attack. In this way a decrease in rate of reaction with increase in steric hindrance would support an S_N2 displacement process. This was tested using the reaction

$$\textit{trans}\text{-}[Co(AA)_2Cl_2]^+ + H_2O \rightarrow [Co(AA)_2H_2OCl]^{++} + Cl^- \qquad (7)$$

where (AA) is the bidentate ligand ethylenediamine and C-methyl substituted ethylenediamines (see p. 118 in Basolo and Pearson, *17*). The results of this study show a marked steric acceleration in the rates of acid hydrolysis which is not in agreement with an S_N2 mechanism. However this steric effect can be explained on the basis of an S_N1 process, where the rate-determining step involves a decrease in coordination number. In this way the increased strain in the six-coordinated system, caused by the greater size of the diamines, is diminished by dissociation of the group being replaced.

Although the hydrolyses of dichlorotetramminecobalt(III) complexes appear to involve an S_N1 reaction, this does not permit any broad generalizations regarding the mechanism of all such reactions. Not only is the metal ion expected to have an effect on the mechanism, but also the nature of the ligands may alter the reaction path. For example, the rates of hydrolysis of a series of *cis-* and *trans-*[Co(en)$_2$XCl] have been explained on the basis of a gradual change in mechanism with changes in X (p. 166 in *17*). The plot represented in Fig. 1 shows that the rate of hydrolysis of the complex [Co(en)$_2$XCl] is faster when X is OH^- and NO_2^- than when it is Cl^- and SCN^-. The accelerating effect of OH^- over Cl^- was explained by the greater basicity of OH^- and by its tendency to π-bond by donating a pair of *p* orbital electrons to Co(III). Both of these properties tend to promote an S_N1 reaction, since the effective charge on Co(III) is decreased, making

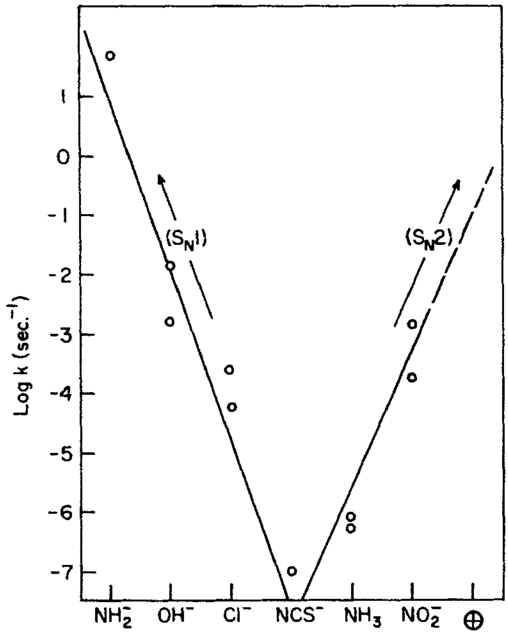
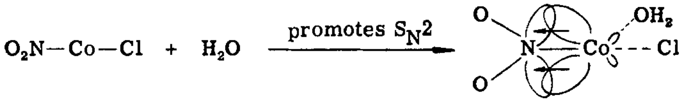


FIG. 1. Rates of acid hydrolysis of a series of [Co(en)$_2$XCl] complexes as a function of X. The ascending curves indicate increasing S_N1 character (left branch) and increasing S_N2 character (right branch) in the reaction mechanism. [See p. 166 in Basolo and Pearson (*17*).]

it easier to break the Co—Cl bond, and π-bonding tends to stabilize the five-coordinated intermediate.

(8)

Since NO_2^- tends to withdraw electrons from Co(III), the rapid hydrolysis of $[Co(en)_2NO_2Cl]^+$ cannot be explained on the basis of an S_N1 mechanism. Instead it would appear that the coordinated NO_2^- fosters an S_N2 reaction, perhaps by π-bonding with the filled nonbonding *d* orbitals of Co(III).



(9)

Tobe and co-workers have continued and extended these studies of the hydrolysis of complexes of the type *cis*- and *trans*-$[Co(en)_2XY]$. Their investigations include not only the reaction kinetics but also its stereochemistry. It is most important that the stereochemical changes accompanying substitution be investigated in order to provide some information as to the probable structure of the transition state. Unfortunately, hardly enough effort has as yet been expended in this direction (see Section II,E).

The rates of acid hydrolysis of some *cis*- and *trans*-$[Co(en)_2YX]$ complexes and the stereochemistry of the reaction products are summarized in Tables I and II. The observations on the hydrolysis of *trans*-$[Co(en)_2NH_3X]^{++}$ were explained on the basis of an S_N2 mechanism. The rates of reaction increase along the series X = Cl, Br, NO_3 in agreement

TABLE I

RATES OF ACID HYDROLYSIS OF SOME *cis*- AND *trans*-$[Co(en)_2YX]$ COMPLEXES AT 25°C[a]

Complex[b]	k_{H_2O}, sec^{-1}	E_a, kcal/mole	log PZ[c]
trans-$[Co(en)_2(NH_3)Cl]^{++}$	3.36×10^{-7}	23.6	10.9
trans-$[Co(en)_2(NH_3)Br]^{++}$	1.23×10^{-6}	24.6	12.0
trans-$[Co(en)_2(NH_3)NO_3]^{++}$	4.60×10^{-6}	25.5	13.5
cis-$[Co(en)_2(NCS)Cl]^+$	1.1×10^{-5}	20.8	10.3
trans-$[Co(en)_2(NCS)Cl]^+$	5×10^{-8}	30.4	14.9
cis-$[Co(en)_2(NCS)Br]^+$	2.3×10^{-5}	23.1	12.3
trans-$[Co(en)_2(NCS)Br]^+$	5×10^{-7}	30.1	15.3
cis-$[Co(en)_2(N_3)Cl]^+$	2.0×10^{-4}	21.7	12.3
trans-$[Co(en)_2(N_3)Cl]^+$	2.2×10^{-4}	23.1	13.3

[a] Data from Tobe *et al.* (*11, 115, 121*).

[b] Hydrolysis rate is for the replacement of the last ligand in the complex with water.

[c] From $k = PZe^{-E_a/RT}$.

with equilibrium data, although the activation energies also increase. Therefore Tobe (*121*) suggests that cleavage of the Co—X bond has not proceeded far in the transition state, but that a stereospecific interaction between the incoming water and the outgoing group, in the order Cl > Br > NO_3, lowers the activation energy, and even more markedly lowers the entropy of activation. This difference between the Cl and NO_3 complexes was attributed to the greater hydrogen bonding of Cl with the entering water than of NO_3, as diagramed in Fig. 2. Since the two terminal oxygen atoms of NO_3 are hydrogen bonded to the adjacent amine hydrogens, these are not available for hydrogen bonding to the solvent water. However it should be pointed out that these interesting results do not require a bimolecular displacement process. Unfortunately the results are not diagnostic of detailed reaction mechanism because the same effect is expected for an S_N1 path. Thus the greater solvation of Cl^- in the transition state leads to a greater tendency to pull it out of the complex and to lower the activation energy for a bond-breaking dissociation process. Because of the intramolecular hydrogen bonding, the nitrate ion can only be partially solvated in the transition state, but once completely free can be well solvated in agreement with the equilibrium data.

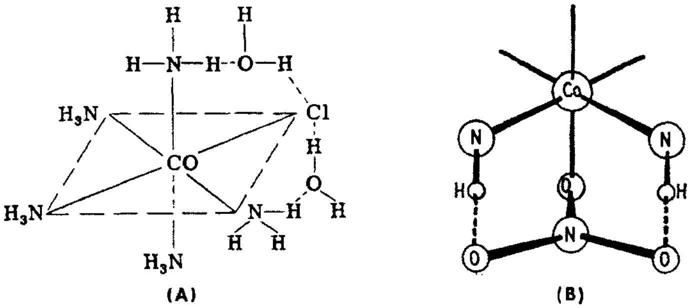
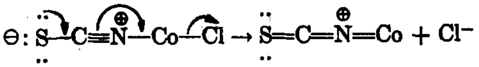


FIG. 2. Hydrogen bonding in (A) $[Co(NH_3)_5Cl]^{++}$ and (B) $[Co(NH_3)_5NO_3]^{++}$. (A) From Adamson and Basolo (*5*) and (B) from Tobe (*121*).

A comparison of the rates of acid hydrolysis of *cis*- and *trans*-$[Co(en)_2(NCS)X]^+$ shows that the *cis* isomer reacts much faster than does the *trans* form and has an activation energy of some 7–10 kcal/mole less. This "*cis*-effect," although of smaller magnitude, was previously observed for the complexes of $[Co(en)_2Cl_2]^+$, $[Co(en)_2(OH)Cl]^+$, and $[Co(en)_2F_2]^+$. This activating effect of certain *cis* groups was originally explained (*89*) by a theory of π-bonding which is stereospecific in the sense that only the ligand *cis* to the leaving group is in a position to donate electrons to an empty metal orbital. In such cases clearly the *cis* isomer should react faster than the *trans*. On the other hand, for negative ligands where π-bonding of this type is not important, the *trans* isomer will react faster than the *cis*. Recently this phenomenon has been explained in essentially the same way by Ingold, Nyholm, and Tobe (*56*).

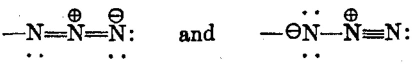
Baldwin and Tobe (*11*) have extended this π-bonding concept to account for the differences in the rates and stereochemistry of the acid hydrolysis of *cis*- and *trans*-$[Co(en)_2(NCS)X]^+$. They stress the importance of the ligand feeding the lone pair of electrons into the orbital being vacated by the outgoing group.



$$\ominus\!:\ddot{S}-C\equiv\overset{\oplus}{N}-Co-Cl \rightarrow \ddot{S}=C=\overset{\oplus}{N}=Co + Cl^- \qquad (10)$$

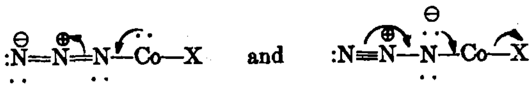
When the group is *cis* to the outgoing group there is adequate overlap without much atomic motion, resulting in a square pyramidal transition state. This is expected to lead to retention of configuration, as is shown by experiment. Instead, if the *trans* isomer is to π-bond in this manner, then a change in configuration is required, resulting in the formation of a trigonal bipyramidal or a distorted square pyramidal transition state. This distortion may be responsible for the observed high activation energy and rearrangement. It was also suggested that the distortion may result in the "release" of some of the solvating water in the transition state and account for the high entropy term. Finally an additional effect, contributing to the greater reactivity of *cis*-$[Co(en)_2(NCS)Cl]^+$ is the possibility that the NCS helps orient a water molecule such that it may hydrogen bond with Cl and assist its removal. This may account for its low activation energy and loss of entropy owing to increased ordering.

Since N_3^- is linear and resembles NCS^-, it is somewhat surprising that *cis*- and *trans*-$[Co(en)_2(N_3)Cl]^+$ react at about the same rate, and considerably faster than the corresponding NCS compounds (Table I). It is difficult to say with certainty where N_3^- should be put in Fig. 1. Does it tend to withdraw electrons as NO_2^- or does it donate electrons as OH^-? The normal state of N_3^- in the complex is perhaps a hybrid of the canonical forms



$$-N=\overset{\oplus}{N}=\overset{\ominus}{\ddot{N}}: \quad \text{and} \quad -\ominus\ddot{N}-\overset{\oplus}{N}\equiv N:$$

so that it can either accept or donate a pair of electrons, e.g.,



$$:\overset{\ominus}{\ddot{N}}=\overset{\oplus}{N}=\ddot{N}-\ddot{Co}-X \quad \text{and} \quad :N\equiv\overset{\oplus}{N}-\overset{\ominus}{\ddot{N}}-Co-X$$

The azide group, like the phenyl group, can therefore act in either direction depending on the requirements of the reaction. On the basis of the steric course of these reactions, Staples and Tobe (*115*) conclude that azide donates electrons and enhances hydrolysis by an S_N1 mechanism.

The strongest evidence for an S_N1 reaction is undoubtedly the successful detection of the active intermediate of reduced coordination number, e.g., $[Co(NH_3)_5]^{3+}$ for reactions of $[Co(NH_3)_5X]^{++}$. However, as already mentioned, the nature of the intermediate is generally such as to escape detection by direct means. Posey and Taube (*97*) have attempted this using both isotopic and chemical competition experiments. They investigated the fractionation of oxygen isotopes in the formation of $[Co(NH_3)_5H_2O]^{3+}$ from $[Co(NH_3)_5X]^{++}$ induced by metal ions. Theoretically, regardless of metal ion or of X, if the reaction involves the common intermediate $[Co(NH_3)_5]^{+}$, then it follows that the aquo product will contain the same O^{16}/O^{18} ratio. The results for complexes were X = Cl, Br, and I show that an intermediate of common properties is not formed when Ag^+ and Tl^{3+} are used to assist removal of the halide ion. However the same isotopic ratio is found for all of the halogen complexes when Hg^{++} is used, which is evidence for a common intermediate. Similar results were obtained for the competition between the formation of $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(NH_3)_5SO_4]^{+}$ (or $[Co(NH_3)_5NO_3]^{++}$) by the reaction between $[Co(NH_3)_5X]^{++}$ and metal ions in the presence of SO_4^{-} (or NO_3^{-}). These results are complicated by the formation of ion pairs, as illustrated by the rate law for the reaction of $[Co(NH_3)_5Cl]^{++}$ in the system containing Hg^{++} and $SO_4^{=}$

$$-d\sum[Co(NH_3)_5Cl^{++}]/dt = k_1[Co(NH_3)_5Cl^{++}][Hg^{++}] + k_2[Co(NH_3)_5Cl^{++}][Hg^{++}][SO_4^{=}] + k_3[Co(NH_3)_5Cl^{++}][Hg^{++}][SO_4^{=}]^2 \tag{11}$$

On the basis of these observations (that only the more reactive Hg^{++} generates a common intermediate), it was concluded that the acid hydrolysis of $[Co(NH_3)_5X]^{++}$ in the absence of metal ions to facilitate Co—X bond rupture does not involve a dissociation process. This agrees with the designation in Fig. 1 that $[Co(en)_2NH_3Cl]^{++}$ reacts predominantly by an S_N2 mechanism. It would be most interesting to apply this same technique of oxygen isotopic fractionation of induced hydrolysis to a complex presently believed to react by an S_N1 process, e.g., $[Co(en)_2Cl_2]^{+}$.

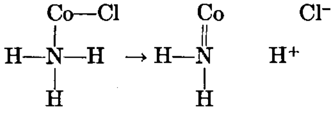
Deuterium substitution both in the complex and in the solvent slows down the rate of acid hydrolysis of $[Co(NH_3)_5Cl]^{++}$. This was visualized as being due to a hydrogen-bonded cage structure, as shown in Fig. 2A, where the solvent assists in the removal of Cl^- from the complex (*5*). Whether there was a concerted push-pull process where the oxygen of the water attacked Co(III) as well as hydrogen bonded to Cl, or whether only the latter was important in the transition state could not be established by these experiments. More recent data (*93*) on the effect of deuteration on the rate of acid hydrolysis and of solubility of $[Co(NH_3)_5Cl]^{++}$ are given in Table II. Two definite conclusions can be drawn from these data. One is that the retardation in rate on deuteration does not depend on a cooperative effect involving hydrogen bonding of water both to the chloro group and to an acidic proton in the complex. This follows from the similar retardation shown by the β-picoline complex $[Co(\beta\text{-pic})_4Cl_2]^+$ which does not contain acidic hydrogens. The other conclusion is that there is a fairly good correlation between the deuterium effect on the rate of hydrolysis and its effect on solubility. This supports the view that solvation of the complex does contribute to its rate of reaction.

TABLE II
RATES OF ACID HYDROLYSIS OF SOME CHLOROAMMINECOBALT(III) COMPLEXES AT 49.4° AND SOLUBILITIES AT 27.2°[a]

Complex	Solvent	k, min^{-1}	Solubility, mole/liter
$[Co(NH_3)_5Cl]Cl_2$	H_2O	1.91×10^{-3}	0.0224
$[Co(NH_3)_5Cl]Cl_2$	D_2O	1.34×10^{-3}	.0166
$[Co(ND_3)_5Cl]Cl_2$	H_2O	1.45×10^{-3}	.0256
$[Co(ND_3)_5Cl]Cl_2$	D_2O	1.15×10^{-3}	.0193
$[Co(ND_3)_5Cl]Cl_2$	$D_2O:H_2O = 9:1$	1.14×10^{-3}	—
$[Co(\beta\text{-pic})_4Cl_2]NO_3$[b]	H_2O	4.2×10^{-2}	.0397
$[Co(\beta\text{-pic})_4Cl_2]NO_3$[b]	D_2O	3.3×10^{-2}	.0342

[a] From Pearson *et al.* (*93*).
[b] β-pic = β-picoline.

The behavior of these inorganic complexes is very similar to that of organic halides. For both systems the rates of solvation are reduced by deuteration of the solvent and also by deuteration of the halogen compounds. In the case of isotopic substitution in the reacting molecule, the rate reduction is greater for S_N1 than for S_N2 reactions. The factor of 1.32 for k_H/k_D given by the first and third entries in Table II are in the midrange of those reported for organic halides. The factor by which the rate is reduced in going from H_2O to D_2O is not diagnostic of mechanism as it is similar for alkyl halides ranging from methyl to *tert*-butyl. The generally accepted theory for the deuterium effect when located β to the halogen in an organic compound is that of hyperconjugation in the transition state (*109*). The same explanation is certainly possible for the hydrolysis of $[Co(NH_3)_5Cl]^{++}$.



$$\begin{array}{ccccc} & \mathrm{Co{-}Cl} & & \mathrm{Co} & \mathrm{Cl^-} \\ & | & & \| & \\ \mathrm{H{-}} & \mathrm{N{-}H} & \rightarrow \mathrm{H{-}} & \mathrm{N} & \mathrm{H^+} \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array} \qquad (12)$$

Details of this method to explain lower reaction rates of deuterated molecules are given by Streitwieser (*118*).

The rates of hydrolysis of $[Co(DMG)_2H_2OX]$ (DMG = dimethylglyoximino ion, X = Cl, Br, and I) reported by Ablov and Sychev (*2*) are summarized in Table III. The reactions were followed by potentiometric determination of halide ions, changes in electrical conductivity, and pH measurements. Results by all three methods were in good agreement. Perhaps the point of chief interest in these results is that the relative rates of hydrolysis for the halogeno complexes are Cl > Br > I. This is contrary to all other known reactions of Co(III) complexes. It is also opposite to the hydrolysis of $[Co(DMG)_2NH_3X]$, which goes readily with the iodo compound, but does not occur even on prolonged heating of the chloro and bromo compounds. The slow rate of reaction in water-alcohol solvent as compared to that in water has been suggested as evidence for an S_N2 reaction, but is not justified. Such a change in rate unfortunately does not define the role played by water but may be the result of a change in solvent properties.

TABLE III
RATES OF HYDROLYSIS OF $[Co(DMG)_2H_2OCl]^b$ AT 25°C[a]

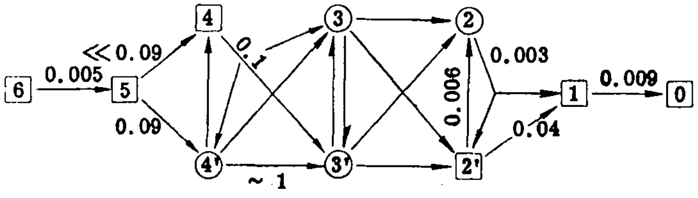
Complex	Solvent	k, sec^{-1}	E_a	log PZ
$[Co(DMG)_2H_2OCl]$	Water	100×10^{-6}	25.5	14.8
$[Co(DMG)_2H_2OBr]$	Water	70×10^{-6}	27.6	16.0
$[Co(DMG)_2H_2OCl]$	25% ethanol	48×10^{-6}	26.2	15.0
$[Co(DMG)_2H_2OBr]$	25% ethanol	39×10^{-6}	—	—
$[Co(DMG)_2H_2OI]$	25% ethanol	23×10^{-6} (35°C)	26.1	13.9

[a] From Ablov and Sychev (*2*).
[b] DMG = Dimethylglyoximine ion.

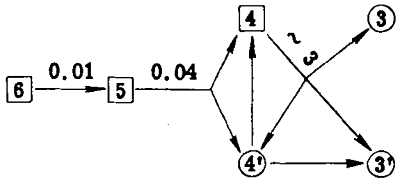
2. Chromium(III) Complexes

Most of the quantitative information on acid hydrolysis of metal complexes is for those of Co(III), but recent investigations also include compounds of Cr(III). Jørgensen and Bjerrum (*63*) studied the rather complicated stepwise hydrolysis of $[Cr(NH_3)_6]^{3+}$ to yield $[Cr(H_2O)_6]^{3+}$ as a final product. Using chromatographic techniques, it was possible to estimate the rates of reaction for most of the species both in acid and in basic solutions. The results reported are summarized in Fig. 3. It is significant that the rate of hydrolysis of $[Cr(NH_3)_6]^{3+}$ in 0.1*M* NaOH is only twice as fast as it is in 0.1*M* HNO_3. Even more surprising is the observation that $[Cr(NH_3)_5OH]^{++}$ in 0.1*M* NaOH reacts only with about half the rate of the reaction of $[Cr(NH_3)_5H_2O]^{3+}$ in 0.1*M* HNO_3. These results support the finding that hydroxide ion is not as effective a reagent toward ammine complexes of Cr(III) as it is for Co(III) compounds (p. 137 in *17*) (see Section II,B).

An even more striking example that the hydrolysis of certain Cr(III) ammines is not dependent on hydroxide ion is afforded by the observations of Mori, Ueshiba, and Yamatera (*78*) on the conversion of basic rhodochromium(III) into the basic erythro complex. This rhodoerythro system, originally believed to be composed of isomeric Cr(III) compounds, was finally characterized by Wilmarth, Graff, and Gustin (*128*) (Fig. 4). It

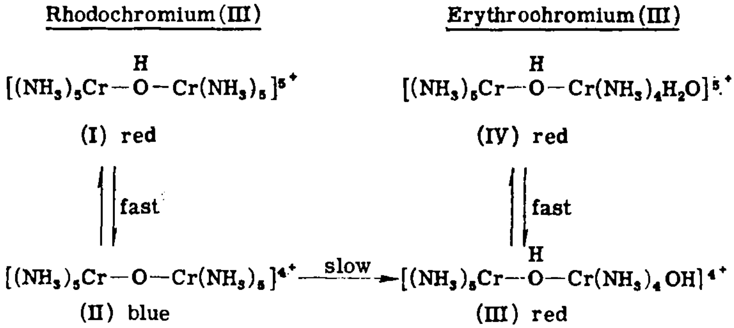


Acid Hydrolysis



Base Hydrolysis

FIG. 3. Stepwise hydrolysis of $[Cr(NH_3)_6]^{3+}$ at 40°C. Top, $>0.1M$ HNO_3; bottom, $0.1M$ NaOH; velocity constants, hr^{-1}; numbers represent n in $[Cr(NH_3)_n(H_2O)_{6-n}]^{3+}$ in acid solution and the corresponding hydroxo in basic solution; 2,3, and 4, *cis*; 2′,3′, and 4′, *trans*; □, used as solid starting materials; ○, intermediates during hydrolysis. From Jørgensen and Bjerrum (*63*).



$$\left[(NH_3)_5Cr-\overset{H}{O}-Cr(NH_3)_5\right]^{5+}$$

$$\left[(NH_3)_5Cr-\overset{H}{O}-Cr(NH_3)_4H_2O\right]^{5+}$$

$$\left[(NH_3)_5Cr-O-Cr(NH_3)_5\right]^{4+} \xrightarrow{slow} \left[(NH_3)_5Cr-\overset{H}{O}-Cr(NH_3)_4OH\right]^{4+}$$

FIG. 4. The Rhodo-Erythro-Chromium(III) system and conversion of rhodo → erythro. From Mori *et al.* (*78*) and Wilmarth *et al.* (*128*).

was observed that the reaction (II) → (III) takes place readily and does not depend on base concentration over the range 0.0001–6*M* OH^-. This rapid reaction was attributed to π-bonding by the bridged oxygen to promote Cr—N bond cleavage. At 10° in 0.07*M* NaOH the reaction has a rate constant of 2.37×10^{-3} sec^{-1}, $E_a \pm 21$ kcal/mole, and $\Delta S\ddagger = +2$ entropy units. That the rate of hydrolysis does not depend on the concentration of hydroxide ion shows that in this system the hydroxide ion is not an effective nucleophile. It also indicates that either the rhodo complex is a weak acid or that its conjugate base is not very reactive, perhaps because of the π-bonding capacity of the bridging oxygen (see Section II,B).

TABLE IV

RATES OF ACID HYDROLYSIS (pH = 1.1) OF $[Cr(en)_3]^{3+}$ AT 30°C[a]

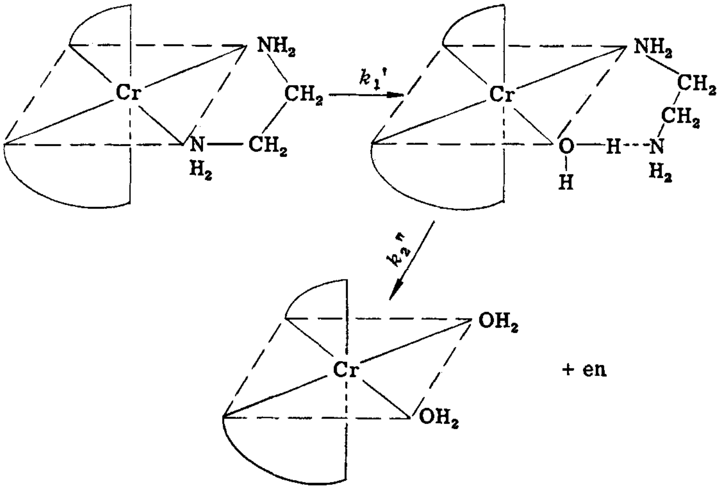
Reaction	$10^5\,k$, hr^{-1}	E_a, kcal $mole^{-1}$	ΔS,‡ entropy units
$[Cr(en)_3]^{3+} \xrightarrow{k'_1} \boxed{X_1}$	2000–3000	—	—
$\boxed{X_1} \xrightarrow{k''_1} Cis\text{-}[Cr(en)_3(H_2O)_2]^{3+}$	81.4	24.3	4.3
$Cis\text{-}[Cr(en)_3(H_2O)_2]^{3+} \xrightarrow{k'_2} \boxed{X_2}$ $Cis\text{-}[Cr(en)_3(H_2O)_2]^{3+} \xrightarrow{k_2\ (\sim k''_2)} [Cr(en)(H_2O)_4]^{3+}$	103	23.7	5.6
$\boxed{X_2} \xrightarrow{k''_2} [Cr(en)(H_2O)_4]^{3+}$	—	—	—
$[Cr(en)(H_2O)_4]^{3+} \xrightarrow{k'_3} \boxed{X_3}$	8.1	30.8	12.7
$\boxed{X_3} \xrightarrow{k''_3} [Cr(H_2O)_6]^{3+}$	1.1	28.3	0.5

[a] From Schläfer and Kollrack (*103*).

Schläfer (*102–104*) and co-workers have investigated the stepwise rates of acid hydrolysis of $[Cr(en)_3]^{3+}$ to yield $[Cr(H_2O)_6]^{3+}$. Spectrophotometric, refractometric, and polarimetric measurements were used to estimate the kinetic data shown in Table IV. The formation of *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$ was studied in some detail and it was found that this involves first the formation of an unknown intermediate, X_1, in Eq. (13).

$$[Cr(en)_3]^{3+} \xrightarrow{k'_1} \boxed{X_1} \xrightarrow{k''_1} cis\text{-}[Cr(en)_2(H_2O)_2]^{3+} \tag{13}$$

Making the assumption that the spectrum of the intermediate is similar to that of the starting material, it was found that $k'_1 = 25k''_2$ so that in a period of a few hours there is an accumulation of an appreciable concentration of the intermediate in solution. It was suggested that this unknown may have a structure in which one chelate ring is open but held in place by hydrogen bonding with the water coordinated to the site vacated by ring opening. Thus the reaction sequence is visualized as Eq. (14), shown below.



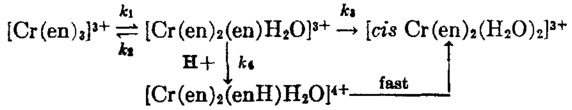
(14)

Under these same acid conditions, the loss of optical activity of a solution originally containing d-$[Cr(en)_3]^{3+}$ was investigated (*104*). It was suggested that this loss of optical activity is the result of an intramolecular rearrangement and of acid hydrolysis as shown schematically by Eq. (15).

$$\begin{tikzcd}
d\text{-}[Cr(en)_3]^{3+} \arrow[r] \arrow[d] & d\text{-}X_1 \arrow[r] & d\text{-}[Cr(en)_2(H_2O)_2]^{3+} \arrow[r] \arrow[d] & [Cren(H_2O)_4]^{3+} \\
d,l\text{-}[Cr(en)_3]^{3+} & & d,l\text{-}[Cr(en)_2(H_2O)_2]^{3+} &
\end{tikzcd}$$

(15

The studies of the acid hydrolysis of $[Cr(en)_3]^{3+}$ provide a good illustration of the fact that it is sometimes possible to give more than one interpretation to a set of kinetic data. For example, Jørgensen and Bjerrum (*64*) make the assumption that, in acid solution, the rate determining step in Eq. (13) is the formation of an intermediate which then rapidly yields *cis*-$[Cr(en)_2(H_2O_2]^{3+}$. On this basis the concentration of the intermediate in solution is never very large. It is suggested that the intermediate is an aquopentammine ion, $[Cr(en)_2(enH)H_2O]^{4+}$, stabilized by protonation of the displaced amine group. According to this interpretation, the hydrolysis may be visualized as



$$\begin{tikzcd}[Cr(en)_3]^{3+} \arrow[r, shift left, "k_1"] & \arrow[l, shift left, "k_2"] [Cr(en)_2(en)H_2O]^{3+} \arrow[r, "k_3"] \arrow[d, "k_4", "H+"'] & [cis\ Cr(en)_2(H_2O)_2]^{3+} \\ & [Cr(en)_2(enH)H_2O]^{4+} \arrow[ur, "fast"'] & \end{tikzcd} \quad (16)$$

At high acid concentration $k_4[H^+] > k_2$ so that what is being measured essentially is k_1, the opening of the chelate ring by Cr—N bond rupture. This scheme is analogous to that proposed (p. 154 in *17*) for the hydrolysis of $[Fe(bipy)_3]^{++}$ and $[Ni(bipy)_3]^{++}$, and the rate should show the same inverse dependence on hydrogen ion concentration and level off at some high acid concentration. Unfortunately the necessary pH dependence studies have not yet been made on $[Cr(en)_3]^{3+}$.

Schläfer (*100*) has studied the rate of hydrolysis of $[Cr(en)(C_2O_4)_2]^-$ in aqueous perchloric acid solution to yield $[Cr(H_2O)_2(C_2O_4)_2]^-$. Both pH and spectrophotometric measurements show a very fast first step followed by a slow second step, and in strong acidic solution a slower equilibration to an unknown species. The mechanism proposed for this hydrolysis, as represented in Fig. 5, is similar to that suggested for the acid hydrolysis of $[Cr(en)_3]^{3+}$. At 20°C it was found that $k_1 = 30k_2$, that $k_2 = 2.9 \times 10^{-2}$ hr^{-1}, and that for the second step $E_a = 19.6$ kcal/mole and $\Delta S\ddagger = -15$ entropy units. Final equilibration then occurs at a rate about 40 times slower than the formation of $[Cr(H_2O)_2(C_2O_4)_2]^-$.

Krishnamurty and Harris (*67*) report the results of kinetic studies of the hydrolysis of $[Cr(C_2O_4)_2]^{3-}$ in acid solution. The total reaction

$$[Cr(C_2O_4)_3]^{3-} + 2H_3O^- \rightarrow [Cr(H_2O)_2(C_2O_4)_2]^- + H_2C_2O_4 \qquad (17)$$

has the rate law

$$\frac{-d[Cr(C_2O_4)_3{}^{3-}]}{dt} = k'[H_3O^+][Cr(C_2O_4)_3{}^{3-}] + k''[H_3O^+]^2[Cr(C_2O_4)_3{}^{3-}] \qquad (18)$$

The mixed order with respect to $[H^+]$ is interpreted in terms of a rapid pre-equilibration of complex with one proton, followed by parallel rate-determining reaction paths involving either noncatalyzed or acid-catalyzed displacement of oxalate.

$$[Cr(C_2O_4)_3]^{3-} + H_3O^+ \rightleftharpoons [Cr(H_2O)(C_2O_4)_2(HC_2O_4)]^{=} \qquad (19)$$

$$[Cr(H_2)O(C_2O_4)_2(HC_2O_4)]^{=} + H_2O \xrightarrow{k'} [Cr(H_2O)_2(C_2O_4)_2]^- + HC_2O_4^- \qquad (20)$$

$$[Cr(H_2O)(C_2O_4)_2(HC_2O_4)]^{=} + H_3O^+ \xrightarrow{k''} [Cr(H_2O)_2(CrO_4)_2]^- + H_2C_2O_4 \qquad (21)$$

Experiments in H_2O/D_2O solvent mixtures show that the rate of hydrolysis increases as a function of deuterium atom fraction, in agreement with the Gross-Butler equation. This finding is consistent with the acid-base pre-equilibrium mechanism shown in Eqs. (19), (20), and (21). At 50°C, the values of k' and k'' are respectively 1.7×10^{-4} liter $mole^{-1}$ sec^{-1} and 5.0×10^{-4} $liter^2$ $mole^{-2}$ sec^{-1} and the activation energy for both is 22.1

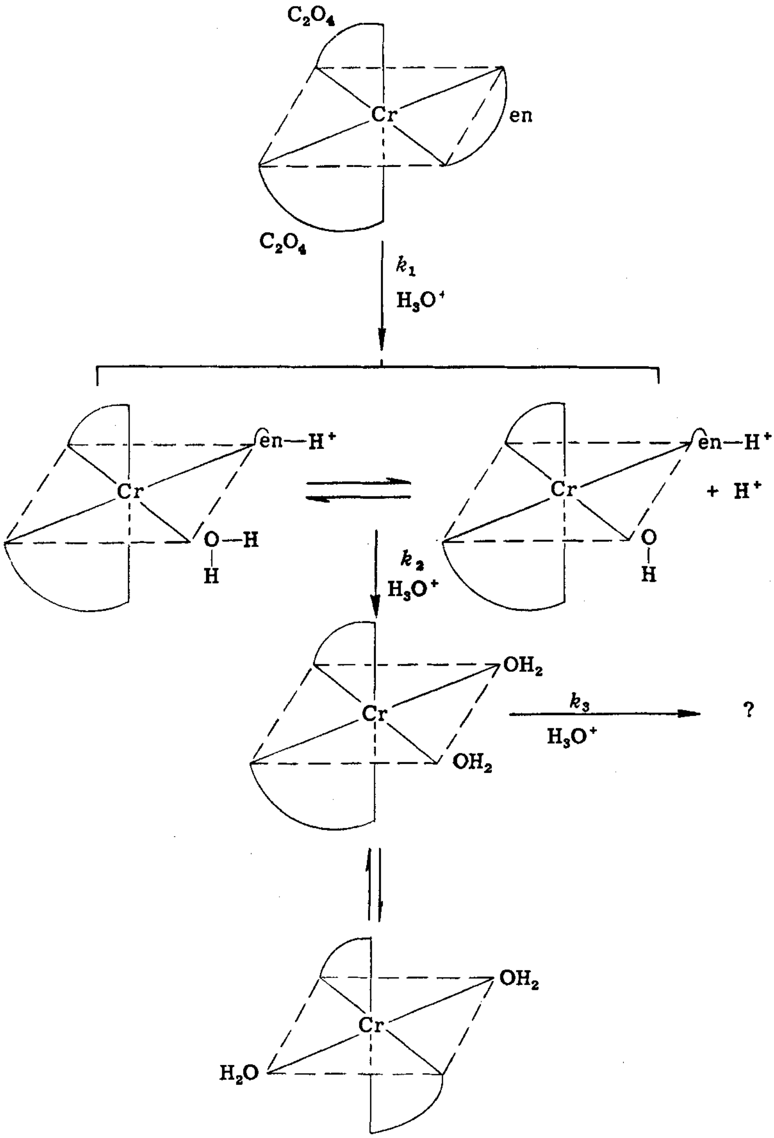


Fig. 5. Mechanism proposed for the acid hydrolysis of $[Cr(en)(CrO_4)_2]^-$. From Schläfer (*100*).

kcal/mole. This experimental activation energy is independent of $[H_3O^+]$, indicating that the activation energies for reactions (20) and (21) are equal. Assuming that ΔH for reaction (19) is similar to that for protonation of free oxalate ion (2.8 kcal/mole), it follows that E_a for reactions (20) and (21) is 19.3 kcal/mole. This is in good agreement with the value of 20 derived from exchange data and can be compared to values of 24.6 and 19.6 for the hydrolysis of $[Cr(en)_3]^{3+}$ and $[Cr(en)(C_2O_4)_2]^-$, respectively.

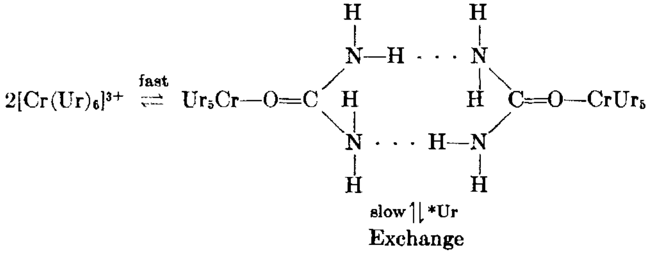
Closely related to the acid hydrolysis of $[Cr(C_2O_4)_3]^{3-}$ is its oxalate exchange. Graziano and Harris (*44*) find that, unlike $[Co(C_2O_4)_3]^{3-}$, for which the ligand exchange rate is negligible compared to that of thermal decomposition, $[Cr(C_2O_4)_3]^{3-}$ exhibits no sign of dark thermal decomposition during several weeks at 75° and $4 < pH < 6$, whereas oxalate exchange shows half-times of less than a day under similar conditions. Outside these pH limits, decomposition becomes measurable and exchange is accelerated. The rate of exchange is practically independent of $[H^+]$ in the $4 < pH < 6$ range, but becomes first-order in $[H^+]$ at lower pH. The reaction is first-order in complex and first-order in oxalate. A six-step reaction mechanism was proposed to explain the kinetic results. These results for chromium are analogous to those of $[Rh(C_2O_4)_3]^{3-}$, the chief difference being that the latter reacts at a much slower rate.

Llewellyn and Odell (*68*) report the interesting observations that the oxygen atoms of $[Cr(C_2O_4)_3]^{3-}$ exchange with oxygen in oxygen-18 enriched solvent water at a measurable rate. The reaction is acid catalyzed, and the rate is similar to that of the exchange of free oxalate ions with oxygen-18 enriched water. This rate of exchange is much faster than the rate of ligand exchange with $[Cr(C_2O_4)_3]^{3-}$, but slower than the rate of racemization. Because of this and because all twelve oxygens in the complex undergo exchange, it was concluded that there is a rapid "one-ended dissociation" of the coordinated oxalate, followed by a slow exchange of oxygen atoms with the solvent through a hydrated *ortho*-oxalate intermediate.

Mousessian and Stranks (*80*) have investigated the hydrolysis of $[Cr(OC(NH_2)_2)_6]^{3+}$ and its exchange with urea. The exchange is very slow and cannot be detected in water, wherein hydrolysis to lower complexes is very rapid and obscures any exchange. In methanol, however, the rate is readily measurable and the rate law obtained is

$$R_{\text{exch.}} = k_{\text{obs}}[Cr(Ur)_6{}^{3+}]^2[Ur], \tag{22}$$

where Ur = urea. It is suggested that this exchange may be visualized as follows:



(23)

Such a scheme is attractive because it is in agreement with the rate law, and particularly because it permits a ready explanation of a direct displacement by *Ur. For a d^3 system this is expected to be difficult, but it may well occur for a d^2 system of Cr(IV). Indeed Ogard and Taube (*84*) have shown that Cr(IV) complexes are labile—or, as the original authors put it, *liable* to substitution. The dimeric structure proposed in Eq. (23) may be effective in promoting S_N2 attack by urea owing to internal electron transfer through the H-bridges to yield a Cr(IV) and a Cr(II) species within the dimer. The kinetics of this exchange at 60°C is $k_{obs} = 6.4 \times 10^{-3}$ mole^{-2} min^{-1}, and $E_a = 35$ kcal/mole.

The exchange rate decreases markedly on adding water to the anhydrous methanol solvent; the value of $R_{exch.}$ falls to one-third of its methanol rate at 6 vol % H_2O but thereafter remains constant. This effect does not appear to be a dielectric constant effect but rather preferential hydration of the ammine groups in the complex ion, preventing effective H-bridges to form the dimer. Finally the hydrolysis of $[Cr(Ur)_6]^{3+}$ at 60° exhibits an isotope effect, $k_{14}/k_{12} = 0.961 \pm 0.005$, whereas methanolysis gives no isotope effect. This may suggest cleavage of the O—C bond in hydrolysis but cleavage of the Cr—O bond in methanolysis.

3. Ethylenediaminetetraacetate Complexes

Extensive studies and applications have been made of the coordinating properties of the multidentate chelating agent ethylenediaminetetraacetate (symbol $EDTA^{4-}$ or Y^{4-}) ion. A summary and discussion of the coordination kinetics of ethylenediaminetetraacetate metal complexes is provided by Margerum (*72*). In general the rate of formation of these complexes from the hydrated metal ion is much too fast to study by conventional kinetic techniques. However, often the exchange of metal ions in these systems and the dissociation of EDTA complexes proceed at measurable rates. On the basis of various experimental observations, some of the EDTA complexes are classified in Table V according to their reactivities. The labile complexes are those in which the changes mentioned take place within the time of mixing, and for inert complexes these changes are slow enough to be detected. Only those systems for which some kinetic data exist are shown in Table V (see also Section V). That other systems such as Ca(II), Mg(II), and Mn(II) complexes are labile can be concluded from the observations of rapid titrimetric end-points for both direct and back titration. Complexes with high charge on the metal tend to be inert. For divalent metal ions, there is a good correlation between the instability of a complex and its reactivity.

The Ni(II)—EDTA complex was studied both by direct acid dissociation and by radionickel exchange. Investigations over the acidity range of 10^{-5} to $1M$ [H^+] show that the rate of dissociation is first order with respect to complex but has a complicated high order dependence on [H^+]. Over this acidity range there is approximately a 10^8-fold increase in rate and at $0.7M$ HCl the dissociation is complete in 30 sec. Part of the apparent higher order dependence on [H^+] is due to the formation of protonated intermediates, each reacting at different rates. For example the complexes $[NiY]^{=}$, $[HNiY]^-$, $[H_2NiY]$, and $[H_3NiY]^+$ are known to exist in neutral or acid solutions. The detailed mechanism of dissociation or exchange of each individual species is not known. Presumably these may involve either an S_E1 or an S_E2 mechanism as represented by Eqs. (24) and (25). Both of

TABLE V

CLASSIFICATION OF REACTIVITY OF ETHYLENEDIAMINETETRAACETATE—METAL SYSTEMS[a]

Complex	pK[b]	Remarks
Labile complexes[c]		
$[ZnY]^{=}$	16.3	*Zn(II) exchange, pH 3–11
$[FeY]^{=}$	14.3	*Fe(II) exchange, pH 1–5
$[CdY]^{=}$	16.6	Reaction with Cu(II)
Inert complexes[c]		
$[NiY]^{=}$	18.6	*Ni(II) exchange, acid dissoc.
$[PbY]^{=}$	18.3	Formation from $[ZnY]^{=}$
$[CuY]^{=}$	18.8	Formation from $[CdY]^{=}$
$[CoY]^{=}$	16.2	*Co(II) exchange, pH 4–7
$[FeY]^-$	25.1	*Fe(II) exchange, pH 0.5–2
$[CrY]^-$	—	Formation from Cr(III)
$[CoY]^-$	36	Formation
$[AlY]^-$	16.1	Acid dissociation
$[LnY]^-$[d]	—	Exchange
[ZrY]	—	Titrimetric reactions
[ThY]	23.2	Titrimetric reactions
[IrY]	—	Formation from $[IrCl_6]^{=}$

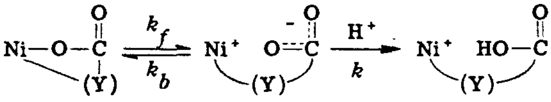
[a] For original sources see Margerum (*72*).

[b] Stability constants.

[c] Reactions too fast to measure by conventional methods are designated as labile, others as inert (see section on fast reactions).

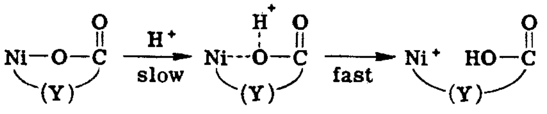
[d] Ln refers to lanthanon group.

S_E1



(24)

S_E2



(25)

these reaction paths show a dependence of the rate on the concentration of H^+ (or M^{n+}). The dependence for S_E1 is due to the competition between the reclosing (k_b) *of the chelate ring and the protonation* ($k[H^+]$) *of the free* carboxylate group.

Higginson and co-workers and Busch and co-workers have studied in some detail the kinetics of reactions of Co(III)—EDTA systems. Shimi and Higginson (*108*) investigated the kinetics of formation of $[\mathrm{CoY}]^-$ from the solvated quinquidentated complex as a function of pH. The rate of reaction increases to a maximum with an increase in pH and then decreases as shown in Fig. 6. These results are explained on the basis of the equilibria

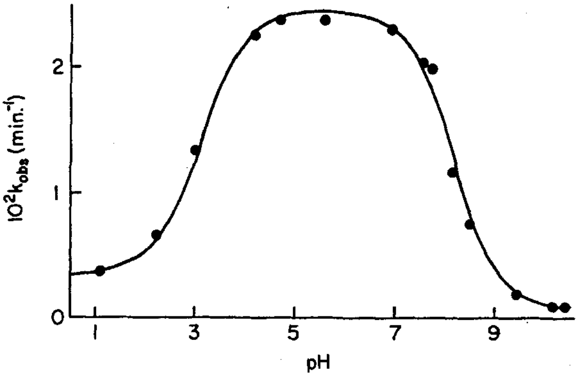


FIG. 6. The variation of k_{obs} with pH at 15° and ionic strength 0.1 for the reaction $[\mathrm{CoY(O)}] \rightarrow [\mathrm{CoY}]^-$ where k_{obs} is related to k_1, k_2, and k_3, as shown in Eq. (27). From Shimi and Higginson (*108*).

$$[\mathrm{Co(Y)OH}]^{-} \underset{\mathrm{pH}>8}{\overset{\mathrm{pH}<8}{\rightleftharpoons}} [\mathrm{Co(Y)H_2O}]^- \underset{\mathrm{pH}>3}{\overset{\mathrm{pH}<3}{\rightleftharpoons}} [\mathrm{Co(HY)H_2O}], \tag{26}$$

where *each species reacts at a fixed rate to yield* $[\mathrm{CoY}]^-$. The dependence of k_{obs} upon the hydrogen ion concentration is then given by

$$k_{obs} = \frac{k_1[H^+]^2 + k_2K_1[H^+] + k_3K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{27}$$

where

$$K_1 = \frac{[\mathrm{Co(Y)H_2O^-}][H^+]}{[\mathrm{Co(HY)H_2O}]} \tag{28}$$

and

$$K_2 = \frac{[\mathrm{Co(Y)OH^{2-}}][H^+]}{[\mathrm{CoYH_2O^-}]}. \tag{29}$$

Using the values of $pK_1 = 3$ and $pK_2 = 8$, the theoretical line constructed in Fig. 6 is in excellent agreement with the experimental values of k_{obs}.

Kinetic data for the formation of $[CoY]^-$ from each of these solvated species are collected in Table VI. The relative rates of reaction are $[Co(Y)H_2O]^- >$ $[Co(HY)H_2O] > [Co(Y)OH]^=$. This can be explained on the basis of —COO^- being more nucleophilic than —COOH and the Co—O bond in Co—OH being stronger than in Co—OH_2.

TABLE VI
KINETICS OF THE FORMATION OF $[CoY]^-$ FROM SOME COBALT(III)-ETHYLENEDIAMINETETRAACETATE COMPLEXES[a]

Complex	Temp., °C	k, min^{-1}	E_a
$[Co(HY)H_2O]$	15	3.4×10^{-3}	24.9
$[Co(Y)H_2O]$	15	2.4×10^{-2}	25.2
$[Co(Y)OH]$	15	8.4×10^{-4}	—
$[Co(HY)Cl]^-$	30	1.4×10^{-4}	24.1
$[Co(HY)Br]^-$	30	4.7×10^{-4}	20.3
$[Co(Y)Br]^=$	25	4.0×10^{-4}	—
$[Co(HY)Br]^=$—Pb^{++}	25	0.15 (liter $mole^{-1}$ min^{-1})	—
$[Co(Y)Br]^=$—Pb^{++}	25	33.8 (liter $mole^{-1}$ min^{-1})	—
$[Co(YOH)Cl]^-$[b]	30	1.9×10^{-4}	21.4
$[Co(YOH)Br]^-$[b]	30	8.1×10^{-4}	21.2

[a] From Higginson *et al.* (*51*, *108*), and Morris and Busch (*79*).
[b] (YOH) = hydroxyethylethylenediaminetriacetate ion.

Within experimental error the activation energies for the reactions of $[Co(HY)H_2O]$ and $[Co(Y)H_2O]^-$ are identical, the greater rapidity of the latter appearing in a higher temperature independent factor. It was suggested that the reaction of $[Co(HY)H_2O]$ is probably S_N1 because its temperature independent factor is near to the "normal" value for a unimolecular reaction, 10^{15}–10^{16} min^{-1}. For $[Co(Y)H_2O]^-$ this factor is unusually high, corresponding to a positive entropy of activation. This was assumed to be in accord with an S_N2 displacement where the negative charge initially on the carboxylate is partly transferred to the complex in the transition state with consequent liberation of solvated water molecules. The mechanism of the reaction of $[Co(Y)OH]^=$ is not known but it was suggested that S_N1 is more probable than S_N2, since there would be considerable electrostatic repulsion between the carboxylate and hydroxide neighboring ion in the transition state.

Morris and Busch (*79*) report the rates of formation of $[CoY]^-$ from $[Co(HY)X]^-$ (X = Cl,Br) and of formation of $[Co(YOH)H_2O]$ from $[Co(YOH)X]^-$ (YOH^{3-} = hydroxyethylethylenediaminetriacetate ion). Some of their kinetic data on these systems are shown in Table VI. The rates of reaction are first order in complex, independent of pH over the range 1–3, and essentially independent of ionic strength. Chiefly on the basis of the negative entropy of activation, the reactions are said to be S_N1.

For $[Co(HY)X]^-$, it is not known whether the dissociated species first reacts with solvent or whether it goes directly to the sexadentate product, since the rate of conversion of $[Co(HY)H_2O]$ into $[CoY]^-$ is about 80 times as fast as the rate of release of bromide from $[Co(HY)Br]^-$. However the reaction of $[Co(YOH)X]^-$ perhaps does yield $[Co(YOH)H_2O]$ because YOH is not expected to function as a sexadentate ligand.

The formation of $[CoY]^-$ from either $[Co(HY)Br]^-$ or $[CoYBr]^=$ is strongly catalyzed by Ag^+, Hg^{++} and Tl^{3+}. Other metals such as Cd^{++}, Zn^{++}, Fe^{3+} and Sr^{++} are somewhat less effective catalysts. Higginson and Hill (*51*) have investigated in some detail the catalytic effect of Pb^{++} on the reactions of these complexes. Although the uncatalyzed release of bromide from the bromo complex in the acid region does not depend on pH, the catalyzed reaction shows a pH dependence up to pH 6 which resembles that of Fig. 6. This was explained, as described previously in Eqs. (26)–(29) for the solvated species, on the basis of the catalyzed reaction for the two species $[Co(HY)Br]^-$ and $[CoYBr]^=$ being different. That the uncatalyzed reaction of $[CoYBr]^=$ is not faster than that of $[Co(HY)Br]^-$ is believed to be due to the electrostatic repulsion between the incipiently formed bromide ion in the transition state and the unbound carboxylate ion. This repulsion is overcome by the presence of the Pb^{++} in the transition state and therefore the unbound carboxylate ion can participate in the catalyzed reaction. Hence the rate of the $[CoYBr]$ —Pb^{++} reaction is expected to be greater than that of $[Co(HY)Br]^-$—Pb^{++} in which the carboxylic acid group is inactive. Finally the base hydrolysis reaction of $[CoY]^-$ to yield $[Co(Y)OH]^=$ has been investigated and is discussed in Section II,B.

4. 1,10-Phenanthroline and 2,2′-Bipyridine Metal Complexes

Wilkins and co-workers have continued and extended previous studies on the rates of dissociation or hydrolysis of these systems. The rate constants for dissociation of $[Co(phen)_3]^{++}$ and $[Co(phen)(H_2O)_4]^{++}$ were determined by Ellis and Wilkins (*34*) from exchange experiments involving $[C^{14}]$ phenanthroline and $(Co^{60})^{++}$. The values obtained are, respectively, $1.4 \times 10^{16} \exp(-20{,}600/RT)$ and $1.6 \times 10^{14} \exp(-19{,}400/RT)$ min^{-1}. It is of interest to note that $[^{14}C]$ phenanthroline was used to investigate the rate of dissociation of $[Co(phen)_3]^{++}$ which is the only species present in excess, 1,10-phenanthroline, whereas the $[Co(phen)(H_2O)_4]^{++}$ dissociation rate was determined using $(Co^{60})^{++}$, since the lowest complex is the only one present in solutions containing excess Co(II). Similar to the rates of dissociation of analogous Fe(II) and Ni(II) complexes (p. 154 in *17*) the dissociation of $[Co(phen)_3]^{++}$ is pH-independent, but that of $[Co(phen)(H_2O)_4]^{++}$ shows a marked pH dependence.

The entropies and energies of activation for the dissociation of analogous complexes of different electronic systems are summarized in Table VII. Also shown in the last column is the loss in crystal-field stabilization energy (CFSE) in going from the octahedral ground state of the complex to an assumed square pyramidal transition state. A loss of CFSE would be expected to result in a slower reaction (higher energy of activation) than that of a similar complex ion for which there is no loss of CFSE during the octahedral-square pyramid change. The CFSE changes (ΔE) given in Table VII are in units of Dq. From spectral data Dq is about 4 kcal/mole for bivalent first-row transitional cations. The Fe(II) complex is spin-paired but the Mn(II) and Co(II) systems are spin-free. It is assumed that there is a retention of spin multiplicity during the activation. These data show that the differences in activation energies for Fe(II)-, Co(II)-, and Ni(II)-phenanthroline complexes do indeed fit very well with the ΔE values. Neither a trigonal bipyramid nor a pentagonal bipyramid structure for the transition state give the required relationship. Provided that the $\Delta S‡$ term is positive or only slightly negative, the dissociation rates of $[Mn(phen)_3]^{++}$, $[Cu(phen)_3]^{++}$, and $[Zn(phen)_3]^{++}$ would be expected to be of the same order as that of $[Co(phen)_3]^{++}$. There is some evidence for the Cu(II) case suggesting that this is correct, $k \geqslant 0.25$ sec^{-1} at 0° and $E_a \leqslant 19$ kcal/mole. However, the positive value of ΔE for $[V(phen)_3]^{++}$ indicates that it should dissociate at a slower rate.

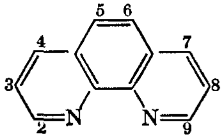
TABLE VII

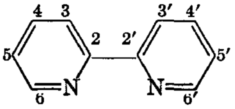
KINETIC DATA AND (CFSE) CHANGES FOR THE DISSOCIATION OF $[M(phen)_3]^{++}$ AND $[M(phen)(H_2O)_4]^{++}$[a]

Electronic system	Complex	$S‡$ (entropy units)	E_a kcal/mole	ΔE(Dq)
d^3	$[V(phen)_3]^{++}$	—	—	2
d^5	$[Mn(phen)_3]^{++}$	—	—	0
d^6	$[Fe(phen)_3]^{++}$	+28	32.1	4
d^7	$[Co(phen)_3]^{++}$	+5	20.6	0
—	$[Co(phen)(H_2O)_4]^{++}$	−4	19.4	—
d^8	$[Ni(phen)_3]^{++}$	+1	25.2	2
—	$[Ni(phen)(H_2O)_4]^{++}$	+5	26.2	—
d^9	$[Cu(phen)_3]^{++}$	← Fast	→	0
d^{10}	$[Zn(phen)_3]^{++}$	← Fast	→	0

[a] From Ellis and Wilkins (*34*).

Ellis, Hogg, and Wilkins (*33*) have determined the rates of dissociation of $[Ni(AA)(H_2O)_4]^{++}$ where AA represents various 1,10-phenanthrolines or 2,2′-bipyridines substituted in the 2-, 4-, or 5-positions.





The results of this investigation are summarized in Table VIII. These data show that the effect of substitution in the 5-position, some distance from the reaction site, parallels closely the observed behavior of ring substitution on aromatic reactivity. Compared with the parent compound, the methyl group has an opposite and smaller effect than the chloro or the nitro group. A plot of $pk_{(exch)}$ *versus* pK of the base shows an excellent linear relationship (Fig. 7, curve B). These changes in rate result mainly from changes in activation energy. Substitution of small groups in the large 1,10-phenanthroline molecule away from the reaction site might be expected only to have an electronic effect without influence on the entropy factor, leaving the form of the transition state unchanged and simply altering the M—N bond strength. Also in Fig. 7 (curve A) is shown a linear plot of $pk_{(exch)}$ *versus* Hammett's σ_m with ρ positive, the reaction being enhanced by low electron density at the reaction site. Thus it appears that the substituent effects on free-energy difference, predictable for many organic reactions, apply also to the reactivity of metal complexes.

TABLE VIII

RATES OF DISSOCIATION OF $[NiA(H_2O)_4]^{++}$ FROM $(Ni^{63})^{++}$ EXCHANGE STUDIES AT 25°[a]

Species A	pK[1]	k, min^{-1}	E_a, kcal/mole	$\log_{10}PZ$, min
2,2′-Bipyridine	4.44	3.2×10^{-3}	23.7	15.0
4,4′-Dimethylbipyridine	5.32	1.1×10^{-3}	24.0	14.7
1,10-Phenanthroline	4.96	6×10^{-4}	24.5	14.8
5-Methylphenanthroline	5.23	4.5×10^{-4}	24.4	14.6
5-Nitrophenanthroline	3.57	3.6×10^{-3}	23.5	14.9
5-Chlorophenanthroline	4.26	1.5×10^{-3}	23.9	14.9
4,7-Dimethylphenanthroline	5.94	1.1×10^{-4}	25.7	14.9
2-Methylphenanthroline	5.42	2.9×10^{-2}	20.1	13.2
2-Chlorophenanthroline	—	$\sim 7 \times 10^{-1}$	17.0	12.3

[a] From Ellis *et al.* (*33*).

[b] Acidity of AH^+.

One other substituent position of interest is position 2, which is known to markedly modify the properties of Fe(II) complexes. Likewise the effect of 2-substitution on the rates of dissociation of $[Ni(AA)(H_2O)_4]^{++}$ is very large. The ratio of rates for $[Ni(phen)(H_2O)_4]^{++}$:$[Ni(2\text{-}Mephen)(H_2O)_4]^{++}$:-

$[Ni(2\text{-}Clphen)(H_2O)_4]^{++}$ is 1:50:1000. The increased rates are the result of a lower activation energy, partly offset by a lower frequency factor. These substituents, near the reaction site, are in a position to effect the relative shapes of both the reactants and the transition states. The steric interaction is less in the transition state than the reactant state but it may be wondered why the effect of the chloro group is so much larger than that of the sterically similar methyl group. It must also be remembered that superimposed on this steric effect is the electronic effect. Relative to the 5-substituents, the chloro group in the 2 position may have a much larger effect, since this position is more sensitive judging from π-electron distribution calculations *(69)*.

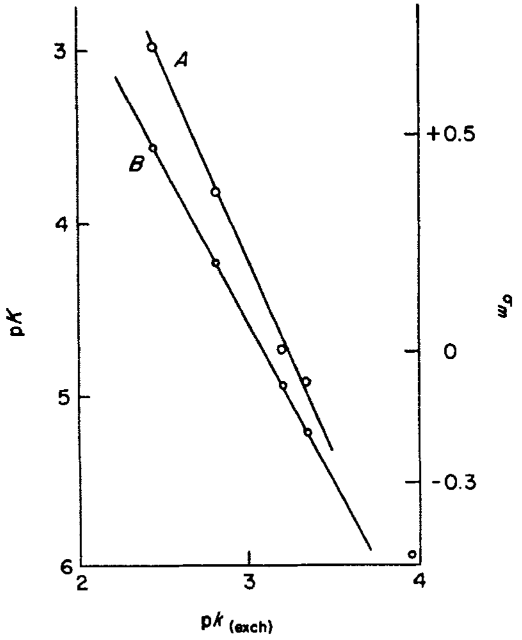


FIG. 7. Dependence of $pk_{(exch)}$ on pK (curve B) and σ_m (curve A) for the system $[NiA(H_2O)_4]^{++}$—$^{63}Ni^{++}$ at 25°C. From Ellis *et al.* *(33)*.

5. Hexacyanoferrate(II) Ion

Kinetic studies on the hydrolysis of $[Fe(CN)_6]^{4-}$ have been continued and extended. Asperger *(10)* and co-workers had observed that the reaction is catalyzed by ultraviolet light and by certain metal ions. In the absence of light the equilibrium

$$[Fe(CN)_6]^{4-} + H_2O \overset{\text{slow}}{\rightleftharpoons} [Fe(CN)_5H_2O]^{3-} + CN^- \tag{30}$$

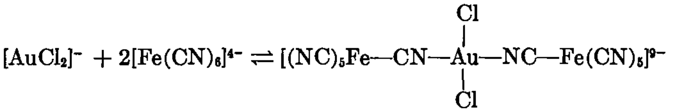
is almost completely to the left. However it is shifted to the right in the presence of excess C_6H_5NO, which rapidly reacts with the aquo product.

$$[Fe(CN)_5H_2O]^{3-} + C_6H_5NO \overset{\text{fast}}{\rightarrow} [Fe(CN)_5C_6H_5NO] + H_2O \qquad (31)$$

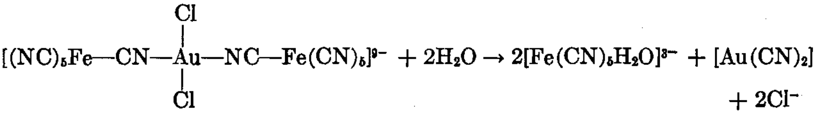
The rate of reaction (30) is strongly accelerated even by only $10^{-7}M$ Hg^{++}. The rate of the catalyzed reaction has a negative salt effect and shows a maximum at pH $\sim$ 4. The negative salt effect is consistent with a reaction between species of unlike charges. The slow rate at low pH is attributed to the formation of protonated species such as $[HFe(CN)_6]^{3-}$ and $[H_2Fe(CN)_6]^{=}$ which react more slowly. At the higher pH, the catalyst is perhaps removed by the formation of HgCNOH. It was also reported that the catalytic activity decreases in the order $Hg^{++} \sim Hg_2^{++} > Au^{3+} > Pt^{4+}$ and that Ag^+ is not effective.

Recently Yatsimirskii and Orlova (*132*) investigated in some detail the behavior of Au(III). They observed that a solution of $[Fe(CN)_6]^{4-}$ containing C_6H_5NO in the presence of $2.5 \times 10^{-6}M$ Au(III) becomes reddish violet in about three minutes. This rapid color change then stops corresponding to two equivalents of $[Fe(CN)_5C_6H_5NO]^{3-}$ per equivalent of Au(III). Thus, unlike Hg^{++}, Au^{3+} is not a catalyst but instead it reacts to yield a gold complex containing two cyanide ions per gold ion. It is suggested that the mechanism involves a rapid redox reaction and formation of a bridged intermediate which then yields the aquo product.

$$2[Fe(CN)_6]^{4-} + [AuCl_4]^- \rightleftharpoons 2[Fe(CN)_6]^{3-} + [AuCl_2]^- + Cl^- \qquad (32)$$



$$[AuCl_2]^- + 2[Fe(CN)_6]^{4-} \rightleftharpoons [(NC)_5Fe{-}CN{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Au}}{-}NC{-}Fe(CN)_5]^{9-} \qquad (33)$$



$$[(NC)_5Fe{-}CN{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Au}}{-}NC{-}Fe(CN)_5]^{9-} + 2H_2O \rightarrow 2[Fe(CN)_5H_2O]^{3-} + [Au(CN)_2]^- + 2Cl^- \qquad (34)$$

This reaction also has a maximum rate at approximately pH 4, resembling somewhat the Hg^{++} catalyzed reaction.

Emschwiller (*36*) has likewise done considerable work on these systems. Recent studies include the investigation of the second hydrolysis step to yield $[Fe(H_2O)_2(CN)_4]^{=}$ and also the hydrolysis of $[Ru(CN)_6]^{4-}$.

B. BASE HYDROLYSIS*

Whereas the term acid hydrolysis is generally used for reactions of metal complexes with water at pH < 3, the term base hydrolysis applies to reac-

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* *Note added in proof:* Tobe has recently discussed the base hydrolysis of Co(III) ammines in terms of an S_N2 mechanism [*Sci. Progr.* **48,** No. 191, 483 (1960)].

tions at pH > 10. For intermediate pH ranges the reaction is referred to just as hydrolysis. Again most of the kinetic studies to date have been done on Co(III) complexes (pp. 124–138 in *17*). For ammine complexes containing N—H bonds, the rate of base hydrolysis is often as much as 10^6 times faster than the corresponding rate of acid hydrolysis. It has long been known that the rate of base hydrolysis is second-order, being first-order in complex and first order in hydroxide ion. One interpretation is that the reaction is S_N2 involving a nucleophilic displacement by hydroxide ion on Co(III). A second interpretation is due to Garrick, who suggested a pre-acid-base equilibrium followed by a rapid rate-determining dissociation of the conjugate base (S_N1CB mechanism), which is also consistent with the observed second-order kinetics.

$$[Co(NH_3)_5Cl]^{++} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2Cl]^+ + H_2O \tag{35}$$

$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{++} + Cl^- \tag{36}$$

$$[Co(NH_3)_4NH_2]^{++} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{++} \tag{37}$$

Considerable research has been done in an attempt to determine whether the base hydrolysis of Co(III) ammines proceeds by an S_N2 or an S_N1CB mechanism. The mechanisms are sufficiently different so that, in principle, it is easy to distinguish between them. For example, clearly the S_N1CB mechanism requires an acidic proton in the complex. The facts are that complexes containing no acidic protons do not react rapidly with hydroxide ion as a rule, though, depending on the nature of the complex, certain reactions can be accelerated by the presence of base (see racemization of CoY^- below). In the area of hydrolysis reactions it is striking that the rates of release of nitrite ion in the case of *trans*-dinitro-bis(2-2′-bipyridine)-cobalt(III) and of the release of chloride ion in the case of *trans*-dichloro-(P,P,P′,P′-tetraethyl-ethylene diphosphine)Co(III) are independent of hydroxide ion concentration even at pH values of 11 to 12. The most convincing evidence for the S_N1CB mechanism is the recent demonstration (*92*) of the existence of the 5-coordinated intermediate of reaction (36). This will be discussed below.

If the conjugate base mechanism is correct, then the pre-equilibrium of Eq. (35) must be established more rapidly than the rate of base hydrolysis. Since Eq. (35) leads to hydrogen exchange, this rate can be determined by measuring the rate of isotope exchange. A direct comparison of rates was made for the complexes $[Co(NH_3)_5Cl]^{++}$, *cis*-$[Co(en)_2NH_3Cl]^{++}$, and *cis*-$[Co(trien)NH_3Cl]^{++}$ where it was found that the rates of hydrogen exchange are approximately 10^5 times faster than their rates of base hydrolysis (*16*). It is also of interest to note that the effect of chelation and of alkyl substitution on the rate of hydrogen exchange for Co(III) ammines roughly parallels the effects observed on the rates of base hydrolysis.

The rate of base hydrolysis of $[Co(NH_3)_5Cl]^{++}$ in D_2O is slower than in H_2O, having an isotope effect of $k_{D_2O}/k_{H_2O} = 0.6$ (averaged between 2.5 and 18°C). It has been pointed out (*55*) that if the mechanism does depend on a pre-equilibrium proton transfer then one might expect an increased rate in the deuterated system, as in the classical example of the base hydrolysis of diacetone-alcohol. However because of the weak acid strength of $[Co(NH_3)_5Cl]^{++}$ and the probable large isotope effect on its acid ionization constant, it is possible that in this case the deuterated system reacts slower. This is to be expected if the isotope effect on K_a is as large as it is on K_w, where K_a is the acid ionization constant for the complex and K_w is the water constant. For an S_N1CB mechanism the rate is given by

$$\text{Rate} = k(K_a/K_w)[Co(NH_3)_5Cl^{++}][OH^-] \tag{38}$$

where k is the rate constant for reaction (36). It then follows that the overall isotope effect for the three constants will be

$$\frac{k_H}{k_D} = \frac{(kK_a/K_w)_H}{(kK_a/K_w)_D} \tag{39}$$

A reasonable assumption is that the isotope effect on k will be similar to that observed for acid hydrolysis which is approximately 0.6. Since this is about the same as that for base hydrolysis, it follows that the isotope effect on K_a must be comparable to that on K_w. Because of the generalization that the smaller K_a, the larger the isotope effect, and because of the large effect observed for $[Pt(NH_3)_6]^{4+}$, it would appear justified to expect an isotope effect on K_a of $[Co(NH_3)_5Cl]^{++}$ comparable to that on K_w. These observations and the H-D exchange studies mentioned above both agree with an S_N1CB mechanism but of course do not exclude an S_N2 process.

Both of the mechanisms give rise to the same hydroxo product in water because it is a good coordinating agent and because a proton shift is very fast. However in a nonhydroxylic solvent different products are predicted for the two mechanisms in the event that an excess of some nucleophilic reagent other than hydroxide ion or water is present. The results of recent studies (*92*) using dimethylsulfoxide as a solvent are readily explained by the S_N1CB mechanism but cannot be explained by the S_N2 mechanism. For example, it was observed that reactions of the type

$$[Co(en)_2ACl] + Y \rightarrow [Co(en)_2AY] + Cl^- \tag{40}$$

where Y is nitrite, azide, or thiocyanate ion, are slow (half-life of hours) but in the presence of catalytic amounts of hydroxide ion the reaction is very fast (half-life of only a few minutes) and the product continues to be

$[Co(en)_2AY]$. Further the reaction between $[Co(en_2)AOH]$ and Y is slow which rules out a rapid S_N2 displacement path followed by a rapid reaction with Y. Instead this supports the formation of an active 5-coordinated intermediate, which then reacts rapidly with Y. This mechanism receives further support from the observation that the rate of formation of $[Co(en)_2AY]$ depends only on the concentration of base and not on the nature or concentration of Y. Hydroxide ion and piperidine were used as catalysts, while nitrite, thiocyanate, and azide ions were used as nucleophilic reagents Y. Under the same conditions all three nucleophiles reacted at the same rate. It is clear that although these results cannot be explained by an S_N2 process, they are readily accounted for by the S_N1CB mechanism.

$$[Co(en)_2ACl] + B \overset{\text{fast}}{\rightleftharpoons} [Co(en)(en{-}H)ACl] + HB^+ \tag{41}$$

$$[Co(en)(en{-}H)ACl] \xrightarrow{\text{slow}} [Co(en)(en{-}H)A] + Cl^- \tag{42}$$

$$[Co(en)(en{-}H)A] + Y \xrightarrow{\text{fast}} [Co(en)(en{-}H)AY] \tag{43}$$

$$[Co(en)(en{-}H)AY] + BH^+ \xrightarrow{\text{fast}} [Co(en)_2AY] + B \tag{44}$$

An example of base hydrolysis of a Co(III) complex which perhaps involves an S_N2 mechanism was recently reported by Cooke and Busch (*27*) for ethylenediaminetetraacetatocobaltate(III),$[CoY]^-$. This complex which does not contain any acidic hydrogens undergoes base hydrolysis at a rate which is first order in complex and first order in hydroxide ion concentration.

$$[CoY]^- + OH^- \rightleftharpoons [Co(Y)OH]^= \tag{45}$$

Furthermore the rate of racemization of d-$[CoY]^-$ in alkali is faster than the rate of base hydrolysis. At 35°, for racemization $k_{rac} = 32.5$ liter mole^{-1} min^{-1}, $E_a = 32.7$ kcal/mole, and $\Delta S\ddagger = +54.7$ whereas for base hydrolysis $k_{hyd} = 9.8$ liter mole^{-1} min^{-1}, $E_a = 25.6$ kcal/mole, and $\Delta S\ddagger = +35.5$ e.u. The authors consider three possible mechanisms and conclude that the kinetic results are best explained on the basis of bimolecular displacement by the direct attack of hydroxide ion on Co(III). This is visualized, as shown in Fig. 8, in terms of the formation of a symmetrical trigonal prism intermediate with the hydroxide ion in the face opposite the ethylenediamine chain. This can then either reform dl-$[CoY]^-$ or dissociate a carboxyl group to yield $[Co(Y)OH]^=$. Since the rate of racemization exceeds that of hydrolysis, it follows that $k_2 > k_3$.

A mechanism involving an attack on the carbonyl carbon was not believed to be very likely because it does not appear to explain the rapid racemization. However if the intermediate can undergo a rapid intramolecular rearrangement, then the scheme outlined in Fig. 9 can also explain the observed results. It seems a little unlikely that the bonding in the inter-

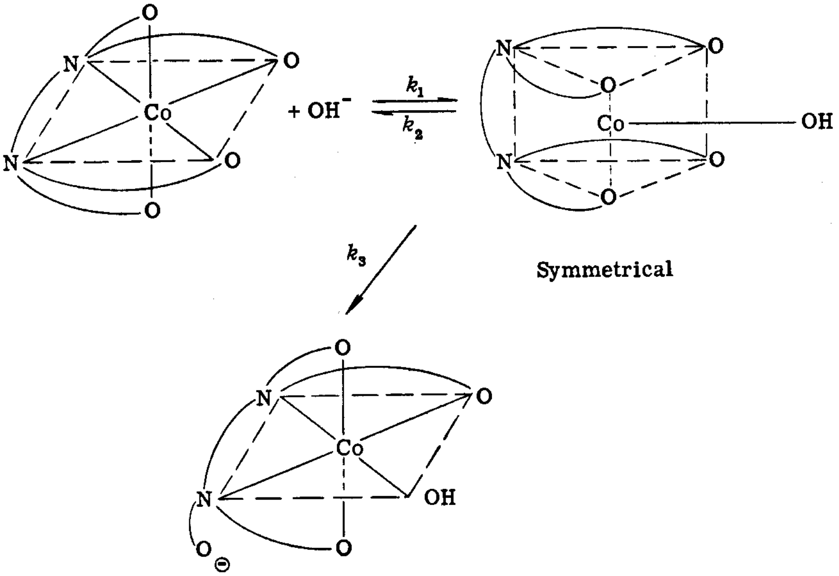


FIG. 8. Mechanism proposed for the base hydrolysis of $[CoY]^-$. From Cooke and Busch (*27*).

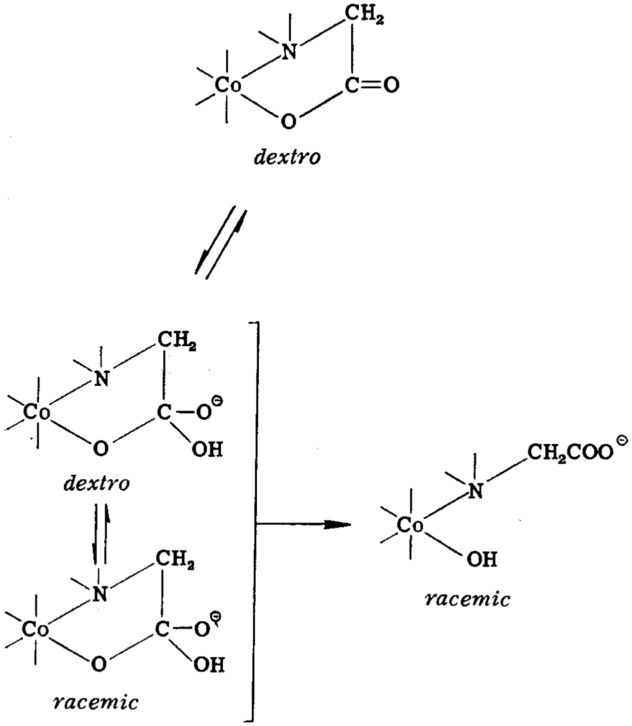


FIG. 9. Base hydrolysis of $[CoY]^-$ by means of hydroxide attack on carbonyl carbon.

mediate should be sufficiently different from that of the parent complex to permit such a racemization. Yet in order to exclude this mechanism, it would be necessary to demonstrate that racemization is not accompanied by O^{18} exchange.

Attempts to investigate the kinetics of base hydrolysis of benzoate derivatives of the type $[Co(NH_3)_5OCOC_6H_5]^{++}$ were not successful because of the complication resulting from the accompanying loss of ammonia (*54*). However Aprile, Caglioti, and Illuminati (*9*) recently prepared the more stable series of complexes of the types *cis* and *trans*-$[Co(en)_2(OCOC_6H_4X)_2]^+$ where X = *p*-CH_3O, *m*- and *p*-CH_3, H, *m*-F, *m*- and *p*-Cl, and *m*-NO_2. A plot of the relative rates of base hydrolysis of these complexes versus Hammett's σ constants is shown in Fig. 10. A very satisfactory correlation is found in the case of the *trans* series, whereas no more than a rough trend is observed in the case of the *cis* series. This is believed to be due to steric effects in the *cis* series.

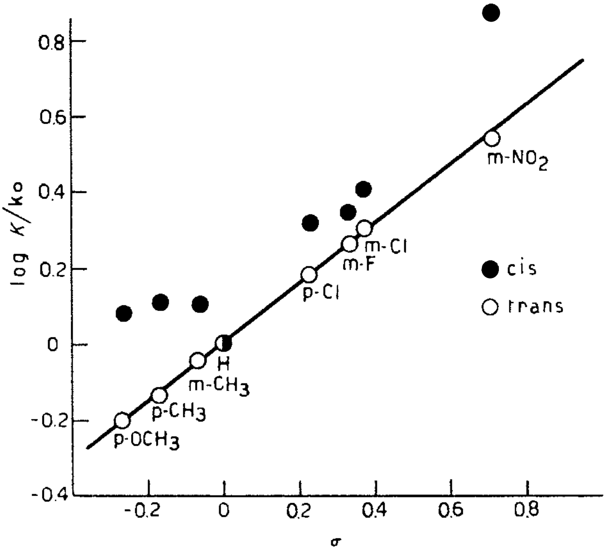


FIG. 10. Hammett relationships for the base hydrolysis of *cis*- and *trans*-$[Co(en)_2(OCOC_6H_4X)_2]^+$ in aqueous solvent. From Aprile *et al.* (*9*).

In addition to the base hydrolysis studies of cobalt(III) complexes, some work was reported on chromium(III) (see Section II,A,*2*), and research is in progress on platinum(IV) and rhodium(III) complexes. Earlier reports (*14*) on the base hydrolysis of *trans*-$[Pt(en)_2Cl_2]^{++}$ indicated that in the range 0.1–0.5M OH^- the rate does not depend on the hydroxide ion concentration. However more recent studies (*61*) show that there is in fact a slight hydroxide ion dependence. More detailed studies have now been made on this system and also on the complexes *cis*- and *trans*-$[Pt(NH_3)_4Cl_2]^{++}$, and $[Pt(NH_3)_5Cl]^{3+}$. One immediate complication is the fact that the base hydrolyses of *trans*-$[Pt(en)_2Cl_2]^{++}$ and *trans*-$[Pt(NH_3)_4Cl_2]^{++}$ are accompanied by extensive (60%) reductions, this is not true for *cis*-$[Pt(NH_3)_4Cl_2]^{++}$ and $[Pt(NH_3)_5Cl]^{3+}$. These last two complexes are acids of $pK_a^1 = 9.7$, $pK_a^2 = 12.4$ and $pK_a^1 = 8.4$, $pK_a^2 = 12.5$, respectively. Some of the kinetic data for base hydrolysis are given in Table IX. These data show that the rate dependence on hydroxide ion is not first-order. The difference between the results for the *trans*-dichloro cases and the latter two cases can be explained by the following observation: the second ionization constant of *trans*-$[Pt(en)_2Cl_2]^{++}$ is too small to detect ($pK_a > 13$). Hence the diamido complex is formed in very small amounts so that it only makes a small contribution to the rate of hydrolysis. For *cis*-$[Pt(NH_3)_4Cl_2]^{++}$ and $[Pt(NH_3)_5Cl]^+$ the second constant is large enough so that appreciable amounts of the diamido complex are formed. This leads to an increasing rate of base hydrolysis with increasing pH.

TABLE IX

RATES OF BASE HYDROLYSIS OF *cis*-$[Pt(NH_3)_4Cl_2]^{++}$ AND $[Pt(NH_3)_5Cl]^{3+}$ [a]

Complex	$[OH^-]$	Temp., °C.	$k_1 \times 10^4$, sec^{-1}
cis-$[Pt(NH_3)_4Cl_2]^{++}$	0.50	25	1.37[b]
(0.005 *M*)	0.10	25	0.57[b]
	0.05	25	0.34[b]
$[Pt(NH_3)_5Cl]^{3+}$	0.50	25	0.20
(0.005 *M*)	0.10	25	0.070
	pH = 11.0	80	9.4
	pH = 10.20	80	1.7
	pH = 9.55	80	0.68
	pH = 8.55	80	0.098

[a] From Johnson (*61*).

[b] Rate of release of first chloride.

Of course because of the rapidity of the proton transfer step, the variation of rate with pH shown in Table IX is equally explicable by displacement reactions of hydroxide ion with $[Pt(NH_3)_5Cl]^{3+}$ and $[Pt(NH_3)_4NH_2Cl]$, for example. However in this case it is not easy to see why *cis*-$[Pt(NH_3)_3(NH_2)Cl_2]^+$ reacts with hydroxide ion, whereas *trans*-$[Pt(en)(en—H)Cl_2]^+$ does not.

Anderson (*7*) has recently succeeded in preparing and characterizing salts of *cis*- and *trans*- $[Rh(en)_2Cl_2]^+$. Some of the results on the hydrolysis of these and other Rh(III) complexes are shown in Table X. The most striking observation from these data is that unlike analogous Co(III) systems, the difference between the rates of acid hydrolysis and base hydrolysis for Rh(III) complexes is rather small. If the role played by the hydroxide ion is that of nucleophilic attack on the metal ion then it is difficult to see why this should be less effective toward the larger Rh(III), which also has a larger nuclear charge than does Co(III). Since the acid strengths of $[Co(NH_3)_5H_2O]^{3+}$ and $[Rh(NH_3)_5H_2O]^{3+}$ are very similar (pK_a values of 5.7 and 5.9 respectively) it is also not readily apparent that a conjugate base mechanism can explain the observed differences. However it may be that a greater difference exists between the N—H than in the O—H acidities in these systems. Recent studies (*88*) have shown that the ratio of rates of hydrogen exchange for $[Co(NH_3)_6]^{3+}$:$[Rh(NH_3)_6]^{3+}$:$[Ir(NH_3)_6]^{3+}$ is 107:14:1. If the concentration of conjugate base is small, then its contribution to the rate of hydrolysis in the Rh(III) systems will not be large. It is of interest to note that the biggest effect is observed with the stronger acids, $[Rh(NH_3)_5Cl]^{++}$ and *cis*-$[Rh(en)_2Cl_2]^+$.

TABLE X

RATES OF HYDROLYSIS OF SOME RHODIUM(III) COMPLEXES AT 81°C[a]

Complex	pH	$k \times 10^5$, sec^{-1}
$[Rh(NH_3)_5Cl]^{++}$	1.5	4.3
	9.9	28.
trans-$[Rh(NH_3)_4Cl_2]^+$	1.5	4.7
	9.9	9.0
trans-$[Rh(en)_2Cl_2]^+$	1.5	2.7
	9.9	4.5
	13.0	5.2
cis-$[Rh(en)_2Cl_2]^+$	1.5	43.
	9.9	13.[b]

[a] From Anderson (*7*).

[b] At 55°C since reaction at 81°C is too fast to measure.

Excluding the hydroxide ion, which probably reacts by a different mechanism, it is very difficult to find good nucleophilic reagents for Co(III) complexes. Recently Nagarajaiah, Sharpe, and Wakefield (*82*) reported that cyanide ion appears to be a good nucleophile toward $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5H_2O]^{3+}$, and $[Co(NH_3)_5Cl]^{++}$. In all cases the ammonia is liberated and only five cyanides are introduced so that the product is presumed to be $[Co(CN)_5H_2O]^{=}$. Some caution should tentatively be exercised in the interpretation of these results, since Adamson (*3*) made similar observations and explained them on the basis of a redox mechanism involving catalytic amounts of Co(II). Perhaps free of such complication are the results reported by Hope and Prue (*52*) on the loss of optical activity of *d*-1,9-bis(salicylideneamino)-3,7-dithianonanecobalt(III) in the presence of potassium cyanide and sodium hydroxide. Good linear second-order kinetic plots were obtained at 25°C with $k = 7 \times 10^{-2}$ liter mole^{-1} sec^{-1} for KCN and 5×10^{-3} liter mole^{-1} sec^{-1} for NaOH. Thus cyanide is about 14 times more effective than hydroxide. This is in accord with the observation that hydroxide is not a good nucleophilic reagent toward Pt(II), but cyanide would be expected to be a good nucleophile (p. 196 in *17*).

C. REACTIONS IN NONAQUEOUS SOLVENTS

Most of the chemistry of metal complexes is aqueous chemistry. These salts are usually little soluble in organic solvents but do dissolve to some extent in the more polar solvents. Some quantitative work has been done on reactions in methanol, the *cis-trans* isomerization of $[Co(en)_2Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$ in alcohol is described in Section II,E.

Adamson (*4*) investigated the solvolysis of $[Cr(NH_3)_2(NCS)_4]^-$, the ion of Reinecke's salt, in a variety of different solvents and solvent mixtures. The results of this investigation are summarized in Fig. 11. It was found that the first step [Eq. (46)] was in general rate-determining, but was usually followed by the more rapid elimination of one [Eq. (47)] or two additional thiocyanates.

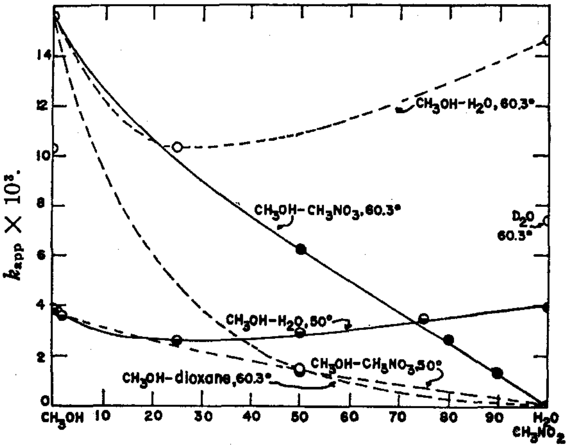


FIG. 11. Summary of rates of solvation of $[Cr(NH_3)_2(NCS)_4]^-$ for various solvents. From Adamson (*4*).

$$[Cr(NH_3)_2(NCS)_4]^- + \text{Solv.} \overset{\text{slow}}{\rightleftharpoons} [Cr(NH_3)_2(\text{Solv.})(NCS)_3] + SCN^- \quad (46)$$

$$[Cr(NH_3)_2(\text{Solv.})(NCS)_3] + \text{Solv.} \overset{\text{fast}}{\rightleftharpoons} [Cr(NH_3)_2(\text{Solv.})_2(NCS)_2]^+ + SCN^- \quad (47)$$

The extent to which these reactions occurred is about the same in water as in methanol but decreases with decreasing methanol content in the case of mixed methanol-nitromethane. The rates of solvolysis are remarkably similar for all ROH-type solvents (H_2O, CH_3OH and C_2H_5OH), and extremely small in other solvents (CH_3NO_2 and dioxane). The difference in solvent behavior appears to be related to the presence or absence of the —OH group, rather than to general solvent quality. Thus nitromethane is a better solvent than water for $K[Cr(NH_3)_2(NCS)_4]$, whereas dioxane is a much poorer solvent. The importance of the —OH function in the solvent is also demonstrated by the observation that the rate of solvolysis is affected more by replacing H_2O by D_2O than by whether R in ROH is H,CH_3, or C_2H_5 (Fig. 11). Likewise the solvation rates for $CH_3OH—CH_3NO_2$ and for CH_3OH-dioxane mixtures are approximately first order in CH_3OH concentration. The lack of importance of the nature of the R group and of general solvent quality is further borne out by the uniformity in activation energies, i.e., apparent activation energies are 27.0, 28.3, 28.5, and 31.0 kcal/mole for H_2O, CH_3OH, 75% CH_2OH–25% H_2O, and 50% CH_3OH–5% CH_3NO_2, respectively.

On this basis a simple S_N1 type mechanism was said to be unlikely. The role of the solvent is important and it cannot be attributed to general solvent effects, since, in such a case, a parallel should have been observed with the solubility of Reinecke's salt in various media.

Substitution reactions of this complex by other reagents in some of these solvent systems were also investigated. No evidence for direct bimolecular substitution could be found either in water or in methanol with added CN^-, N_3^-, or I^-. In nitromethane-ROH mixtures, CN^-, OH^-, and $C_2H_3O_2^-$, but not N_3^-, increase the rate of thiocyanate release. However the effect is very small, since 0.1 *M* KOH produces only a threefold increase in rate.

These results are said to rule out a simple S_N2 type mechanism. Reactions by such a mechanism should correlate the nucleophilic character of the displacing agent. If the solvation reaction (*46*) is occurring by virtue of the nucleophilic character of the solvent molecule, then such strongly nucleophilic ions as CN^- and N_3^- should have competed successfully with the solvation process.

Adamson (*4*) concludes from these observations that the results are best explained by a front side displacement mechanism, designated as S_N2FS (Fig. 12). In this process the hydrogen bonding solvent is visualized as serving a dual function, that of attack on the metal ion and of solvating the ligand being replaced. It would seem rather unlikely that the same solvent molecule can operate in this push-pull fashion because by its pulling action on the departing ligand the solvent becomes oriented further away from the central metal. A more plausible mechanism would seem to be one where one solvent molecule pulls on the ligand and a second solvent molecule pushes on the metal. Clearly all of the experimental results on these reactions of Reinecke's salt can also be explained by a dissociation process, aided by hydrogen-bonding solvents.

Rather extensive work has been and is being done on the exchange of water with hydrated metal ions in aqueous solution (see Section V) but very little is reported on the exchange of ammonia with metal ammines in liquid ammonia. Wiesendanger, Jones, and Garner (*126*) studied this exchange using nitrogen-15 labeled ammonia and mass spectrometric techniques. The results obtained show that at −33.5°C in the dark and with metal ion concentrations of about 0.01 *M*, the rates of exchange for $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{++}$ and $[Ni(NH_3)_6]^{++}$ are complete within the sampling time of 10 min or less. Instead 0.013 *M* $[Cr(NH_3)_6]^{3+}$ exchanges slowly at 25° giving a good MacKay type plot with a $t_{1/2}$ of 25 hrs. The exchange of $[Co(NH_3)_6]^{3+}$ was also very slow with half-lives of several hours but the results obtained were not reproducible. No detailed kinetic studies were made on these systems and there is no information on the mechanism of exchange. It is of interest to note that, as in the water systems, the d^0, d^8 and d^9 systems are labile, whereas the d^3 and d^6 are inert. The different charges on the ions must also be taken into account, however.

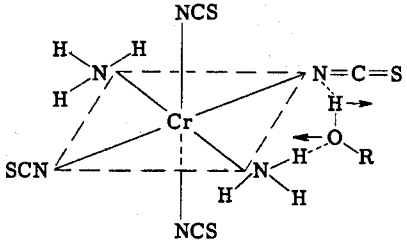


FIG. 12. Intermediate proposed for the S_N2FS mechanism. From Adamson (*4*).

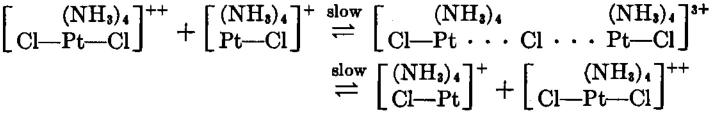
D. REACTIONS OF SOME PLATINUM(IV) COMPLEXES

The direct exchange of radiochloride with chloroammineplatinum(IV) complexes is generally extremely slow except when catalyzed by Pt(II). This catalyzed exchange has a rate law of

$$\text{Rate} = k[\text{Pt(IV)}][\text{Pt(II)}][\text{Cl}^-] \qquad (48)$$

and the mechanism proposed involves a two-electron redox reaction by means of a chloro-bridged intermediate (*14*). The rate of

$$[Pt(NH_3)_4]^{++} + Cl^- \overset{\text{fast}}{\rightleftharpoons} [Pt(NH_3)_4Cl]^+ \qquad (49)$$



$$\left[Cl-\overset{(NH_3)_4}{Pt}-Cl\right]^{++} + \left[\overset{(NH_3)_4}{Pt}-Cl\right]^{+} \overset{\text{slow}}{\rightleftharpoons} \left[Cl-\overset{(NH_3)_4}{Pt}\cdots Cl\cdots\overset{(NH_3)_4}{Pt}-Cl\right]^{3+} \overset{\text{slow}}{\rightleftharpoons} \left[Cl-\overset{(NH_3)_4}{Pt}\right]^{+} + \left[Cl-\overset{(NH_3)_4}{Pt}-Cl\right]^{++} \qquad (50)$$

chloride exchange of *trans*-$[Pt(NH_3)_4Cl_2]^{++}$ is about 2000 times faster than with the *cis* isomer and about 10,000 times faster than with $[Pt(NH_3)_5Cl]^{3+}$. This is explained (*15*) on the basis that exchange in the latter two complexes involves Pt—N bond cleavage which is of higher energy than the Pt—Cl bond rupture for the *trans* isomer (*50*). In support of this is the observation that for $[Pt(NH_3)_5Cl]^{3+}$ in hydrochloric acid solution, catalyzed exchange is accompanied by almost quantitative formation of *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$. Furthermore this mechanism requires, and it was observed, that platinum exchange takes place and that the sterically hindered system $[Pt(tetrameen)_2Cl_2]^{++}$ * cannot form a bridge and so not undergo chloride exchange. McCarley, Martin, and Cox (*70*) report a similar mechanism for the exchange of platinum between $[Pt(en)Br_4]$ and $[Pt(en)Br_2]$.

Such a mechanism suggests that substitution reactions of platinum(IV) complexes can also be catalyzed by Pt(II). The effectiveness of several reagents (X) in the reaction

$$trans\text{-}[Pt(en)_2Cl_2]^{++} + 2X^- \xrightarrow{[Pt(en)_2]^{++}} trans\text{-}[Pt(en)_2X_2]^{++} + 2Cl^- \qquad (51)$$

was tested by determining the rate of equilibration for Pt(IV)—Pt(II) exchange in these systems (*62*). This was conveniently done polarimetrically because the optical rotation of *trans*-$[Pt(l\text{-}pn)_2Cl_2]^{++}$ is approximately three times that of $[Pt(l\text{-}pn)_2]^{++}$. The results showed a very rapid exchange when X^- was Cl^-, Br^-, CNS^-, CNO^-, CN^-, and NO_2^- but very slow exchange when X^- was $SO_4^{=}$, NO_3^-, ClO_4^-, $C_2H_3O_2^-$ and F^-. These results were utilized to prepare known compounds by this different method of Pt(II)-catalyzed substitutions of Pt(IV) complexes and to prepare salts of the new compound *trans*-$[Pt(en)_2(SCN)_2]^{++}$.

The reactions of Co(III) complexes often proceed by a dissociation process and it may appear that analogous d^6 systems in which the metal has an oxidation state of two would have an even greater tendency toward S_N1 paths, whereas an analogous quadrivalent system may react by an S_N2 mechanism. This would result from the larger positive charge on the metal ion promoting nucleophilic attack while making dissociation more difficult. Such S_N2-favoring systems are found among Pt(IV) complexes. Unfortunately as described above these appear only to undergo catalyzed substitution. Preliminary observations on the reaction

$$trans\text{-}[Pt(en)_2Cl_2]^{++} + NO_2^- \rightarrow trans\text{-}[Pt(en)_2NO_2Cl]^{++} + Cl^- \qquad (52)$$

were interpreted in terms of an S_N2 process (*14*). More detailed studies by Ellison (*35*) show that this reaction too is a Pt(II)-catalyzed substitution. For example the reaction has an induction period which disappears

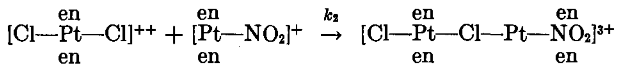
* Tetrameen = $H_2NC(CH_3)_2C(CH_3)_2NH_2$.

upon the addition of catalytic amounts of platinum(II). Similar to the chloride exchange studies described above the reaction of *trans*-$[Pt(NH_3)_4Cl_2]^{++}$ with nitrite ion is fast, but that of the *cis* isomer or of $[Pt(NH_3)_5Cl]^{3+}$ is extremely slow.

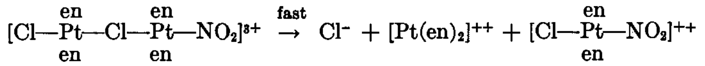
The mechanism postulated for reaction (52) is that first there is some reduction of the Pt(IV) and then the Pt(II) formed acts as the necessary catalyst.

$$\textit{trans}\text{-}[Pt(en)_2Cl_2]^{++} + NO_2^- + H_2O \xrightarrow{k_1} [Pt(en)_2]^{++} + 2Cl^- + NO_3^- + 2H^+ \qquad (53)$$

$$[Pt(en)_2]^{++} + NO_2^- \overset{\text{fast}}{\rightleftharpoons} [Pt(en)_2NO_2]^+ \qquad (54)$$



$$[Cl{-}\overset{en}{\underset{en}{Pt}}{-}Cl]^{++} + [\overset{en}{\underset{en}{Pt}}{-}NO_2]^+ \xrightarrow{k_2} [Cl{-}\overset{en}{\underset{en}{Pt}}{-}Cl{-}\overset{en}{\underset{en}{Pt}}{-}NO_2]^{3+} \qquad (55)$$



$$[Cl{-}\overset{en}{\underset{en}{Pt}}{-}Cl{-}\overset{en}{\underset{en}{Pt}}{-}NO_2]^{3+} \xrightarrow{\text{fast}} Cl^- + [Pt(en)_2]^{++} + [Cl{-}\overset{en}{\underset{en}{Pt}}{-}NO_2]^{++} \qquad (56)$$

In the presence of added $[Pt(en)_2]^{++}$, reaction (53) is essentially bypassed and k_2 can be determined directly. This then permits an estimate of k_1 from data obtained on reaction mixtures to which was added no Pt(II). That the calculated values of k_1 and k_2 and the proposed mechanism can reproduce the experimental results is shown in Fig. 13.

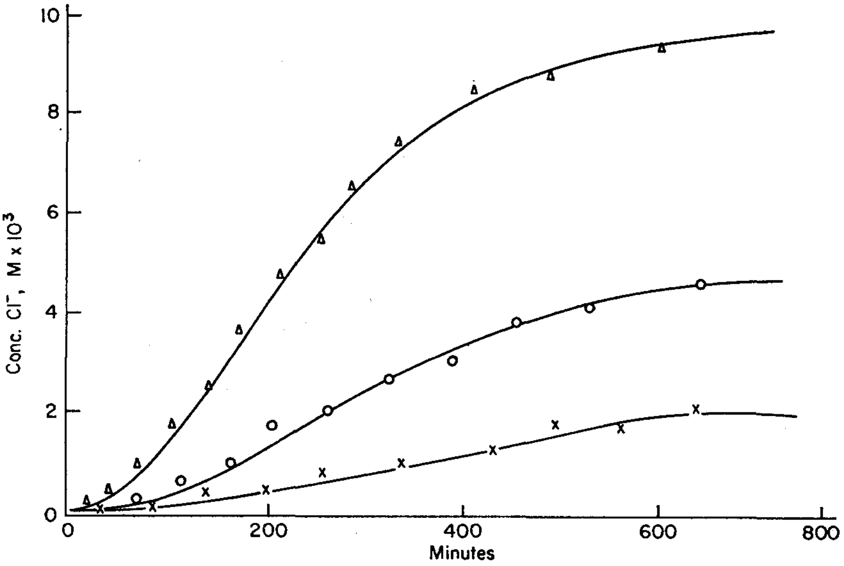


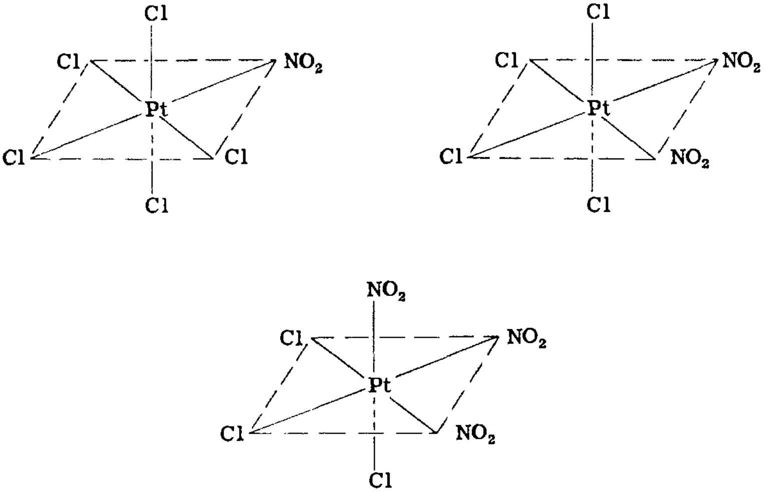
FIG. 13. Rates of reaction of *trans*-$[Pt(en)_2Cl_2]^{++}$ with nitrite ion to yield $[Pt(en)_2NO_2Cl]^{++}$ at 50°C. Lines are calculated curves based on Eqs. (53)–(56) and points are experimental. KEY: △, 0.0096*M* complex and 0.200*M* NO_2^-; ○, 0.005*M* complex and 0.200*M* NO_2^-; ×, 0.0023*M* complex and 0.232*M* NO_2^-. From Ellison (*35*).

It is further of interest to note that the reaction of *trans*-$[Pt(en)_2Cl_2]^{++}$ with nitrite ion in the absence of light yields *trans*-$[Pt(en)_2NO_2Cl]^{++}$ as the final product and not the dinitro complex. This is readily explained by the proposed mechanism if it is assumed that the nitro group is unable to form a bridge as does the chloro group.

The observations on the reaction

$$Na_2[PtCl_6] + NaNO_2 \rightarrow Na_2[Pt(NO_2)_xCl_{6-x}] \tag{57}$$

by Chernyaev, Nazarova, and Mironova (*24*) can also be explained by this mechanism. They were able to isolate all of the possible products of this reaction except $Na_2[Pt(NO_2)_6]$. It was stated that "direct replacement" can only yield the compounds shown (57a) because a chloro group *trans* to a nitro group in platinum (IV) cannot be replaced. On the basis of the Pt(II)-catalyzed mechanism, it again appears that the nitro group does not form an effective bridge. The synthesis of all the other derivatives is believed to involve reduction to Pt(II) in which complete substitution can occur and then reoxidation to Pt(IV). This readily yields *trans*-$[Pt(NO_2)_4Cl_2]^{=}$ which can then react by the bridged mechanism to give $[Pt(NO_2)_5Cl]^{=}$ but not $[Pt(NO_2)_6]^{=}$, a result which was observed experimentally.



(57a)

Although the bridged redox mechanism can explain many of the reactions of Pt(IV) complexes, it is not expected to be an all-inclusive reaction process for these systems. For example the exchange of chloride with $[PtCl_6]^{=}$ does not involve such a process (p. 207 in *17*). Furthermore, recent studies show that the absorption spectrum of *trans*-$[Pt(en)_2X_2]^{++}$ changes considerably on addition of excess X^- when it is Br^- or I^-, but not when it is chloride. These changes were accounted for on the basis of ion-pair formation with formation constants of $Br^- < 0.1$ liter mole^{-1} and $I^- \sim 2$ liter mole^{-1} at an ionic strength of $0.5M$ and room temperature of $\sim$20°. No similar evidence was observed for ion pairing between $[Pt(en)_2]^{++}$ and Cl^-, Br^-, or I^-. It was suggested (*95*) that the ion-pair formation of Pt(IV) species may result in an alternative mechanism for reactions of the bromo and iodo complexes involving only the free halogen ion and the Pt(IV) complex.

Poë and Vaidya (*96*) studied the exchange of iodine in the system $[PtI_6]^=$—$^{131}I^-$ under a variety of different conditions. In all cases the rate of exchange was immeasurably fast, even in the presence of possible inhibitors ($[IrCl_6]^=$, $[Fe(CN)_6]^{3-}$, and quinol) or in the absence of customary catalysts ($S_2O_3^=$ and light). Aged solutions of $[PtI_6]^=$ also undergo rapid iodide exchange and the equilibrium distribution of the activity is consistent with all the iodides being involved so that none are stabilized by the presence of water or hydroxide groups in the complex. Since no kinetic studies of this fast exchange were made there is no positive indication of its mechanism. However the authors (*96*) suggest that the Pt(III) mechanism proposed for the exchange of chloride with $[PtCl_6]^=$ cannot be involved because inhibitors for the chloride system do not effect the iodide system. Furthermore the bridged mechanism is believed to be unlikely because this would require the formation of quinqui-negative ion, $[I_5Pt—I—PtI_5]^{5-}$. On this basis it is concluded that the exchange takes place by a simple S_N1 or S_N2 substitution, the S_N1 mechanism not involving hydrolysis.

Preliminary studies (*96*) show that the initial rate of hydrolysis of $[PtI_6]^=$ at 25° corresponds to a rate constant of about 0.1 min^{-1}. Likewise, the reaction of $0.03M$ I^- with $0.005M$ $[PtCl_6]^=$ at 25° has a $t_{1/2} \sim 10$ min and is not light sensitive; that of $0.004M$ I^- with $0.005M$ $[PtBr_6]^=$ has a $t_{1/2} \sim 30$ sec. Independent experiments show that the Pt—I bond is weaker than Pt—Cl and Pt—Br by $\sim$12 and $\sim$5 kcal/mole, respectively.

E. STEREOCHEMISTRY

A very powerful tool for the elucidation of the reaction mechanisms of organic compounds has been the investigation of stereochemical changes which accompany substitution. Naturally if much insight is to be gained as to the structure of the transition state leading to octahedral substitution, this same type of approach will have to be utilized. However a 6-coordinated system is sufficiently more complicated than is a tetrahedral compound as to offer a variety of possible rearrangements. From elementary consideration an S_N1 reaction may involve either a tetragonal pyramidal or trigonal bipyramidal 5-coordinated intermediate (Chapter 5 in *17*). Likewise an S_N2 reaction may proceed either by *cis*-attack or *trans*-attack, also called non-edge and edge displacement, respectively. It turns out, however, that in most cases the stereochemical change alone is not diagnostic of reaction type. For example, both an S_N1 reaction via tetragonal pyramid and S_N2 by *cis*-attack are expected to lead to retention of configuration. On the basis of this approach the most unambiguous result would be where a *trans* isomer yields exclusively a *cis* product, this is predicted only by an S_N2 *trans* attack.

The elegant investigations of Tobe and co-workers (*11*, *115*) on the steric course of substitution reactions of some Co(III) complexes are summarized in Table XI. The data show that for acid hydrolysis the *cis*-isomers all yield exclusively the *cis*-aquo products. The result suggests either that for S_N1 reactions a tetragonal pyramid is involved or for S_N2 reactions there is a *cis*-attack (see Fig. 1 for probable reaction types). The *trans*-isomers of $[Co(en)_2NO_2Cl]^+$ and of $[Co(en)_2NH_3Cl]^+$ yield *trans*-aquo products. These complexes are believed to react by a predominantly S_N2 process (Fig. 1) and therefore the retention of configuration supports a *cis*-attack. Preliminary studies indicate considerable rearrangement for the acid hydrolysis of *trans*-$[Co(en)_2(OH)Cl]^+$ and *trans*-$[Co(en)_2Cl_2]^+$, both believed to react by a predominantly S_N1 mechanism (Fig. 1). It can also be seen from Table XI that the acid hydrolyses of *trans*-$[Co(en)_2(NCS)X]^+$ and *trans*-$[Co(en)_2(N_3)Cl]^+$ proceed with substantial rearrangement. These results can be explained in terms of the stereospecific π-bonding theory of Pearson and Basolo (*89*). This theory has recently been elaborated by Ingold, Nyholm, and Tobe (*56*). Reaction occurs by an S_N1 mechanism in which the transition state is stabilized by π-bonding where electrons are donated from the ligand to the metal ion. The *cis* isomer can π-bond, though inefficiently, even in the case of a square pyramidal intermediate However, the *trans* isomer must necessarily rearrange in the direction of a trigonal bipyramid in order to π-bond at all.

The *cis* isomer can π-bond more effectively if rearrangement to a trigonal bipyramid occurs. On this basis it was originally predicted (*89*) that considerable rearrangement of both *cis* and *trans* isomers would occur if π-bonding is important. The results in Table XI show that this is not so for acid hydrolysis. This may be attributed to the weak π-bonding characteristics of the group involved. In base hydrolysis the assumption of an S_N1CB mechanism leads to the prediction of extensive rearrangement both for *cis* and *trans* isomers. This is on the basis of the expected strong π-bonding characteristics of the amido group. Table XI shows that this prediction is borne out. Such an approach (p. 234 in *17*) has provided excellent agreement between the calculated and experimental base hydrolysis products of *d-cis*-$[Co(en)_2NH_3Cl]^{++}$. Application of this same method to *l-cis*-$[Co(en)_2(NCS)Cl]^+$ gives less satisfactory agreement: calculated, 39.5% *d-cis* and 12.5% *trans*; experimental, 32% *d-cis* and 20% *trans*; the remain-

TABLE XI

STERIC COURSE OF REACTIONS OF SOME COBALT(III) COMPLEXES

Reactant	Product	% *cis* in product
Acid Hydrolysis		
cis-$[Co(en)_2(NCS)Cl]^+$	$[Co(en)_2H_2O(NCS)]^{++}$	100[a]
trans-$[Co(en)_2(NCS)Cl]^+$	$[Co(en)_2H_2O(NCS)]^{++}$	50–70[a]
cis-$[Co(en)_2(NCS)Br]^+$	$[Co(en)_2H_2O(NCS)]^{++}$	100[a]
trans-$[Co(en)_2(NCS)Br]^+$	$[Co(en)_2H_2O(NCS)]^{++}$	45[a]
cis-$[Co(en)_2(NO_2)Cl]^+$	$[Co(en)_2H_2O(NO_2)]^{++}$	100[b]
trans-$[Co(en)_2(NO_2)Cl]^+$	$[Co(en)_2H_2O(NO_2)]^{++}$	0[b]
cis-$[Co(en)_2(N_3)Cl]^+$	$[Co(en)_2H_2O(N_3)]^{++}$	100[c]
trans-$[Co(en)_2(N_3Cl]^+$	$[Co(en_2H_2O(N_3)]^{++}$	20[c]
trans-$[Co(en)_2NH_3NO_3]^{++}$	$[Co(en)_2NH_3H_2O]^{3+}$	0[d]
trans-$[Co(en)_2NH_3Cl]^{++}$	$[Co(en)_2NH_3H_2O]^{3+}$	0[d]
trans-$[Co(en)_2NH_3Br]^{++}$	$[Co(en)_2NH_3H_2O]^{3+}$	0[d]
trans-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(en)_2(OH)Cl]^+$		—[e]
Base Hydrolysis		
l-cis-$[Co(en_2(NCS)Cl])^+$	$[Co(en)_2(NCS)OH]^+$	*l-cis*, 56[a] *d-cis*, 24[a] *trans*-, 20[a]
cis-$[Co(en_2(NCS)Cl]^+$	$[Co(en)_2(NCS)OH]^+$	82[f]
trans-$[Co(en)_2(NCS)Cl]^+$	$[Co(en_2(NCS)OH]$	76[f]
trans-$[Co(en)_2(NCS)Br]^+$	$[Co(en)_2(Ncs)OH]$	81[f]
cis-$[Co(en)_2(NO_2)Cl]^+$	$[Co(en)_2(NO_2)OH]^+$	66[b]
trans-$[Co(en)_2(NO_2)Cl]^+$	$[Co(en)_2(NO_2)OH]^+$	6[b]
cis-$[Co(en)_2(N_3)Cl]^+$	$[Co(en)_2(N_3)OH]^+$	51[c]
trans-$[Co(en)_2(N_3)Cl]^+$	$[Co(en)_2(N_3)OH]^+$	13[c]
cis-$[Co(en)_2(N_3)_2]^+$	$[Co(en)_2(N_3)OH]^+$	55[c]
trans-$[Co(en)_2(N_3)_2]^+$	$[Co(en)_2(N_3)OH]^+$	30[c]
d-cis-$[Co(en)_2NH_3Cl]^{++}$	$[Co(en)_2(NH_3)OH]^{2+}$	*d-cis*, 60[g] *l-cis*, 24[g] *trans*, 16[g]
d-cis-$[Co(en)_2NH_3Br]^{++}$	$[Co(en)_2(NH_3)OH]^{2+}$	*d-cis*, 59[g] *l-cis*, 26[g] *trans*, 15[g]
cis-$[Co(en)_2NH_3NO_3]^{++}$	$[Co(en)_2(NH_3)OH]^{2+}$	86[g]
trans-$[Co(en)_2NH_3Cl]^{++}$	$[Co(en)_2(NH_3)OH]^{2+}$	76[g]

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[a] From Baldwin and Tobe (*11*).

[b] From Asperger and Ingold (*10a*).

[c] From Staples and Tobe (*115*).

[d] From Tobe (*121*).

[e] Mention is made in reference *11* that preliminary experiments show considerable rearrangement.

[f] From Ingold *et al.* (*55a*).

[g] From Nyholm and Tobe (*83a*).

ing 48% is racemic. Alternatively, if it is assumed that base hydrolysis is bimolecular then the experimental results have been explained on the basis of some contribution from both edge and non-edge displacement processes.

The rates and equilibria of *cis-trans* isomerization for some Co(III) complexes are given in Table XII. No definite conclusions can be reached at present regarding the mechanism of isomerization. Presumably this is an intermolecular process involving possibly the exchange of water with solvent; it would be of interest to investigate this exchange using oxygen-18 enriched water as the solvent. One tentative piece of evidence in support of such a process is that the relative rates of isomerization somewhat correlate the relative rates of acid hydrolysis of analogous chloro complexes (where Cl takes the place of H_2O in the complex).

TABLE XII
RATES AND EQUILIBRIUM OF *cis-trans* ISOMERIZATION FOR SOME COBALT(III) COMPLEXES

Complex	Temp., °C	Rate, sec⁻¹	Equil., % *cis*
$[Co(en)_2H_2O(NCS)]^{++}$	62.6	1.6×10^{-4}	82[a]
$[Co(en)_2(H_2O)NO_2]^{++}$	90	—	31[b]
$[Co(en)_2NH_3H_2O]^{3+}$	72.8	5.6×10^{-5}	100[c]
$[Co(en)_2(H_2O)N_3]^{++}$	25	9.8×10^{-5}	73[d]
$[Co(en)_2(H_2O)Cl]^{++}$	25	9.3×10^{-5}	[e]

[a] From Ingold *et al.* (*55a*).
[b] From Asperger and Ingold (*10a*).
[c] From Tobe (*121*).
[d] From Staples and Tobe (*115*).
[e] Quoted in reference *115*.

Brasted and Hirayama (*20*) have made a detailed study of the rate of isomerization of *cis*-$[Co(en)_2Cl_2]^+$ and of *cis*-$[Co(pn)_2Cl_2]^+$ into the respective *trans* isomers in methanol, ethanol, and propanol. Some of the data collected are presented in Table XIII. The rates of isomerization of the two

TABLE XIII
RATES OF ISOMERIZATION OF *cis*-$[Co(en)_2Cl_2]^+$ AND *cis*-$[Co(pn)_2Cl_2]^+$ IN ALCOHOLS AT 30°C[a]

Complex	Alcohol	k, min⁻¹	E_a, kcal.	$\Delta S\ddagger$ entropy units
cis-$[Co(en)_2Cl_2]^+$	CH_3OH	2.4×10^{-3}	23.4	3.5
	C_2H_5OH	1.9×10^{-3}	23.5	3.4
cis-$[Co(pn)_2Cl_2]^+$	CH_3OH	2.7×10^{-3}	23.9	5.4
	C_2H_5OH	1.5×10^{-3}	24.5	5.9
	C_3H_7OH	8.9×10^{-4}	25.2	6.8

[a] From Brasted and Hirayama (*20*).

complexes are very similar as are also the rates in the three different alcohols. There is a small negative salt effect which the authors attribute to ion-pair formation. Traces of water markedly increase the rate of isomerization, which is also explained on the basis of a decrease in ion-pair formation. It was suggested that isomerization follows the reaction sequence

$$\textit{cis}\text{-}[\mathrm{Co(pn)_2Cl_2}]^+,\ \mathrm{Cl^-} \overset{\text{fast}}{\rightleftharpoons} \textit{cis}\text{-}[\mathrm{Co(pn)_2Cl_2}]^+ + \mathrm{Cl^-} \qquad (58)$$

$$\textit{cis}\text{-}[\mathrm{Co(pn)_2Cl_2}]^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Co(pn)_2Cl}]^+ + \mathrm{Cl^-} \qquad (59)$$

$$[\mathrm{Co(pn)_2Cl}]^+ + \mathrm{Cl^-} \xrightarrow{k_3} \textit{trans}\text{-}[\mathrm{Co(pn)_2Cl_2}]. \qquad (60)$$

Thus in excess chloride ion equilibrium (58) shifts to the left, which accounts for the observed decrease in rate of isomerization.

Sward and Harris (*119*) have also investigated the conversion of *cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ into the *trans* isomer in methanol and observed that added water does have an effect on the rate of isomerization. Based on the results obtained, they suggest that isomerization involves the reaction process

$$\begin{tikzcd}
 & \textit{cis}\text{-}[\mathrm{Co(en)_2H_2OCl}]^{++} + \mathrm{Cl^-} \arrow[d, shift left, "k_2"] \\
\textit{cis}\text{-}[\mathrm{Co(en)_2Cl_2}]^+ + \mathrm{H_2O} \arrow[ur, "k_1"] \arrow[dr, "k_4"'] & (61) \\
 & \textit{trans}\text{-}[\mathrm{Co(en)_2Cl_2}]^+ + \mathrm{H_2O}. \arrow[uu, shift left, "k_3"]
\end{tikzcd}$$

Thus this isomerization is believed to involve a direct *cis* to *trans* step as well as an alternate path involving water. The ratio of k_3/k_2 is small so that this equilibrium (61) is displaced far toward *trans*-$[\mathrm{Co(en)_2Cl_2}]^+$. It should also be mentioned that water has a small effect on the rate of radiochloride exchange with *trans*-$[\mathrm{Co(en)_2Cl_2}]^+$. For a twentyfold increase in water concentration, $0.033M$ to $0.66M$, the rate increases by a factor of 1.24.

Slaten and Garner (*111*) attempted to investigate the analogous isomerism of *cis*-$[\mathrm{Cr(en)_2Cl_2}]^+$ in methanol. This system turns out to be much more complicated than the Co(III) systems. The chief difficulty is that the Cr(III) complexes undergo solvolysis even in "anhydrous" methanol which contained $0.04M$ $\mathrm{H_2O}$. This still was 27 times the complex concentration. The first-order rate constant for the solvolysis of *trans*-$[\mathrm{Cr(en)_2Cl_2}]^+$ in the dark at 50° in "anhydrous" methanol is $3.8 \times 10^{-6}\ \mathrm{sec^{-1}}$ and it is $4.4 \times 10^{-6}\ \mathrm{sec^{-1}}$ for a solvent in which the $\mathrm{H_2O}$ concentration is $0.26M$. These results suggest that methanol and not water is the reactant. A solution of *cis*-$[\mathrm{Cr(en)_2Cl_2}]^+$ undergoes an initial spectral change without concurrent release of chloride ion. During this period it appears that the *cis* isomer rearranges to the *trans* form with $k = 4.1 \times 10^{-6}\ \mathrm{sec^{-1}}$, a rate that is about 100 times less than that for Co(III).

Schläfer (*101*) has reinvestigated (see p. 247 in *17*) the rate of isomerization of *trans* $[Cr(H_2O)_2(C_2O_4)_2]^-$ into the *cis* form as a function of pH over the range 0–2. The observed rate constant at an ionic strength of one, a temperature of 25°C and a pH = 0.08 is 12.5 hr^{-1}, whereas at pH = 2.97 it is 2.16 hr^{-1}. The rate law reported is

$$\text{Rate} = (k_1 + k_2[H^+]^{1.5})[trans\text{-}Cr(H_2O)_2(C_2O_4)_2^-]. \qquad (62)$$

One other observation was that the optical density of the solution, at the wavelength chosen, increases during this conversion then slowly decreases to a final equilibrium value. The latter change may be due to dissociation or acid hydrolysis of the complex.

The mechanisms of racemization of metal complexes continues to be a subject of considerable interest. Gehman and Fernelius (*41*) have investigated the kinetics of the racemization of $[Co(en)_3]^{3+}$ in the presence of ethylenediamine and of hydroxide ion. The complex is very stable optically and racemization occurs only under rather drastic conditions or by catalytic processes. For example, no racemization of aqueous solutions of *d*-$[Co(en)_3]^{3+}$ is observed after 3 months at 25°; 24 hr at 85°; 15 hr at reflux temperatures at pH < 2; 75 min. at 85° in presence of excess NO_2^-; and 24 hrs at room temperature in the presence of either excess OH^- or en. However, a solution of 0.0165M *d*-$[Co(en)_3]^{3+}$ in 1.5 M en racemizes with $k = 1.68 \times 10^{-3}$ min^{-1} at 85°C and $E_a = 24.6$ kcal $mole^{-1}$. The rate of racemization depends on the concentration of en and is about the same as that of *en exchange. On this basis it was concluded that racemization occurs by an intermolecular displacement process involving a 7-coordinated intermediate. Loss of optical activity in the presence of hydroxide ion is not due to racemization but to base hydrolysis to $[Co(en)_2H_2O(OH)]^{++}$. This is apparent because the light orange-colored solution of the original complex changes to the red color of the lower complex. That racemization in en systems is not caused by hydroxide ion was established by experiments in buffered systems.

The heterogeneous catalysis of reactions of certain metal complexes has long been known (pp. 355–359 in *17*). Sen and Fernelius (*106*) have studied the catalytic racemization of the optically active complexes $[Co(en)_3]^{3+}$, $[Rh(en)_3]^{3+}$, and $[Pt(en)_3]^{4+}$ in the presence of active carbon, platinum black and silica gel. The effectiveness of these catalysts appears to decrease in the order given. Silica gel does not catalyze the racemization of *d*-$[Co(en)_3]^{3+}$, neither silica nor platinum black are effective toward *l*-$[Pt(en)_3]^{4+}$, and none of these catalyze the racemization of *l*-$[Rh(en)_3]^{3+}$. The racemization studies of *d*-$[Co(en)_3]^{3+}$ were accompanied by *en exchange and spectrophotometric studies. When racemization is complete there is only 20% exchange. Although racemization appears to take place without decomposition, there is a definite tendency for the compound to dissociate under the conditions of these experiments. On the basis of these observations it was concluded that the reaction sequence may be visualized as follows:

$$\begin{tikzcd} \underset{\text{(optically active)}}{[Co(en)_3]^{3+}} \arrow[r, "\Delta\text{,catalyst}"] & \underset{\text{(excited)}}{[Co(en)_3]^{3+}} \arrow[r, "\text{Dissoc.}"] \arrow[dr, "\text{Rac.}"'] & \text{Hydrolysis or exchange products} \\ & & \underset{\text{(racemic)}}{[Co(en)_3]^{3+}} \end{tikzcd} \qquad (63)$$

The $[Pt(en)_3]^{3+}$ system differs in that little or no *en exchange occurs during the racemization. Therefore the mechanism is believed to be similar to (63) except for no hydrolysis or exchange. One possible alternative explanation of these results is that for the Co(III) system there may be produced catalytic amounts of $[Co(en)_3]^{++}$ which is labile and which may cause racemization by means of electron transfer.* For the Pt(IV) system it is known that reduction to $[Pt(en)_2]^{++}$ takes place fairly readily; this would result in the loss of optical activity. Such an explanation would also be consistent with *en exchange with $[Co(en)_3]^{3+}$ but not with $[Pt(en)_3]^{4+}$. In agreement with this reduction concept is the observation that $[Rh(en)_3]^{3+}$, which is difficult to reduce, does not undergo racemization at these same conditions.

Somewhat related to this discussion of heterogeneous catalysis of the racemization of certain metal complexes, is the observation that homogeneous effects are produced by large ions and by polyelectrolytes (*59*). For example the rate of racemization of *d*-$[Fe(phen)_3]^{++}$ at 25° in $0.02M$ HCl has a k_{rac} value of 4×10^{-2} min^{-1}, whereas under the same conditions but containing $0.3M$ quinine hydrochloride the value is 14×10^{-2} and with $0.3M$ camphor sulfonate, the value is 6.2×10^{-2}. The k_{rac} for this system in 0.1% sodium polystyrenesulfonate is 1.7×10^{-2}. Dialysis and spectrophotometric measurements provide independent evidence for association between these large ions and the complex (58). The effect on the rate of racemization is then attributed to the formation of these associated species in solution. The decrease in rate observed for the polyelectrolyte may be due to its rigidity which tends to retard the rate of intramolecular racemization.

The rates of racemization and of dissociation of $[Fe(bipy)_3]^{++}$ and $[Fe(phen)_3]^{++}$ in methanol and in water–methanol mixtures were determined (*105*). It was found that the rates of racemization increase continuously with increasing methanol content of the solvent, while the rates of dissociation display a maximum. The differences in the two rates suggest that in alcohol-rich solvents racemization takes place essentially by an intramolecular process.

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* *Note added in proof:* Recent studies by F. P. Dwyer and A. M. Sargeson [*Nature* **187,** 1022 (1960)] seem to support this view.

III. Square Complexes

Kinetic studies of substitution reactions of square complexes continue to deal primarily with reactions of Pt(II) compounds. Some investigations have also been made on certain Pd(II) and Ni(II) systems. On the basis of the information now available, it would appear that these reactions proceed by a displacement process involving either the solvent or the entering ligand as the nucleophilic agent.

Elleman, Reishus, and Martin (*32*) have studied the kinetics of hydrolysis and of chloride exchange in $[Pt(NH_3)Cl_3]^-$ and its hydrolysis product, $[Pt(NH_3)H_2OCl_2]$. The reversible acid hydrolysis was described by the reactions

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)H_2OCl_2] + Cl^- \qquad (64)$$

and

$$[Pt(NH_3)H_2OCl_2] + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Pt(NH_3)(H_2O)_2Cl] + Cl^-, \qquad (65)$$

where for 25°C

$$k_1 = 3.6 \times 10^{-5}\ \text{sec}^{-1},\ \Delta H\ddagger = 18.9\ \text{kcal},$$
$$k_{-1} = 2.5 \times 10^{-3}\ \text{liter mole}^{-1},\ \text{sec}^{-1},\ \Delta H\ddagger = 16.8\ \text{kcal},$$
$$k_2 = 1 \times 10^{-5}\ \text{sec}^{-1},\ \text{and}\ k_{-2} = 0.2\ \text{liter mole}^{-1}\ \text{sec}^{-1}.$$

For each complex the exchange of chloride occurs by the observable acid hydrolysis and by additional chloride-independent processes. It was proposed that the nonequivalent chlorides in each complex undergo separate acid hydrolyses. Although all such hydrolysis reactions have roughly the same rate constant and $\Delta H\ddagger$, there is considerable variation in $\Delta F°$. In support of this proposal, the substitution of chloride by hydroxide in $[Pt(NH_3)H_2OCl_2]$ is found by a tracer technique to be unsymmetric, indicating the presence of the *cis*-isomer. These results suggest that reaction (64) is not stereospecific, as might be expected if the *trans*-effect of chloride ion were much greater than that of ammonia. Instead reaction (64) yields an equilibrium mixture of *cis-trans*-$[Pt(NH_3)H_2OCl_2]$ in which the *cis* isomer is approximately 3 kcal more stable than the *trans* form.

This observation is of interest in connection with the well-known reaction of $[Pt(NH_3)Cl_3]^-$ with ammonia to yield predominantly *cis*-$[Pt(NH_3)_2Cl_2]$. This reaction is almost the classical example cited to illustrate the greater *trans*-effect of chloride ion relative to ammonia. It has been felt that this reaction yields the less stable isomer, since it is known that the *cis*- form upon heating in the solid state is converted into the *trans*-isomer (*83*). However it may just be that the formation of *cis*-$[Pt(NH_3)_2Cl_2]$

in high yield reflects the relative competition of chloride and ammonia to replace H_2O in *cis*- and *trans*-$[Pt(NH_3)H_2OCl_2]$, both of which exist in the solutions in their equilibrium concentrations. It is also possible that there is a direct displacement of chloride ion in $[Pt(NH_3)Cl_3]^-$ by ammonia.

Grinberg (*45*) and co-workers do find that the reactions of this and other Pt(II) complexes with ammonia and with pyridine follow second-order kinetics. Similar reactions with hydroxide ion are first order. Some of the data reported are summarized in Table XIV. It is of interest to note that the hydroxide ion is not a very effective reagent, its rate of reaction being the same as that for acid hydrolysis. Grinberg further calls attention to the observation (Table XIV) that the relative rates of reaction are $[Pt(NH_3)X_3]^- > [PtX_4]^{=}$ and refers to this as a *cis*-effect. Thus for these systems the relative *cis*-effect is py > NH_3 > Cl, and NH_3 > Br.

TABLE XIV

RATES OF REACTION OF SOME PLATINUM(II) COMPLEXES AT 25°C[a]

$$[PtX_4] + Y \xrightarrow{k_Y} [PtX_3Y] + X$$

Complex	k_{OH^-}, sec^{-1}	k_{NH_3}, liter $mole^{-1}$ sec^{-1}	k_{py}, liter $mole^{-1}$ sec^{-1}
$[PtCl_4]^{=}$	3.9×10^{-5}	4.2×10^{-4} (16.6)[b]	1.7×10^{-3} (15.7)
$[Pt(NH_3)Cl_3]^-$	6.0×10^{-5}	1.1×10^{-3} (15)	3.3×10^{-3}
$[Pt(py)Cl_3]^-$	—	1.7×10^{-3}	5.7×10^{-3}
$[PtBr_4]^{=}$	1.6×10^{-4}	3.1×10^{-3} (17.9)	—
$[Pt(NH_3)Br_3]^-$	—	fast[c]	—

[a] From Grinberg (*45*).

[b] Values in parentheses are E_a in kcal/mole.

[c] At 15°C k_{NH_3} for $[Pt(NH_3)Br_3]^-$ is 7.0×10^{-2}, that for $[PtBr_4]^{=}$ is 1.7×10^{-3}.

No serious attempt has yet been made to explain this effect, nor is it at all certain that it will be as general a phenomenon as the *trans*-effect. The suggestion is made that for the present the *cis*-effect may be regarded as either a strengthening or weakening of the *trans*-effect. For example under the influence of NH_3 or py in a *cis* position, the reactivity of Br—Pt—Br and of Cl—Pt—Cl is enhanced, while the presence of a *cis* NO_2^- would decrease the reactivity. This may result from NO_2^- tending to remove electrons from the system and thus decrease the polorization or *trans*-effect. Instead NH_3 and py tend to keep electrons in the system and thus to emphasize the *trans*-effect. In general it may develop that ligands with a small *trans*-effect will have a large *cis*-effect and vice versa.

A. SOLVENT EFFECT

It was reported earlier that a division of nucleophilic reagents (ligands) into two classes is possible for substitution reactions of Pt(II) complexes

(p. 196 in *17*). In one class were good reagents, whose reaction rates were high and depended on the concentration of the reagent; in the other class were poor reagents, where the solvent is believed responsible for the rate-determining step. Recent studies by Gray (*43*) support this view and show that for a reaction of the type

$$[Pt(A)_3X] + Y \rightarrow [Pt(A)_3Y] + X, \tag{66}$$

the rate law is given by the general expression

$$\text{Rate} = k_1[Pt(A)_3X] + k_2[Pt(A)_3X][Y], \tag{67}$$

where k_1 is a first-order rate constant for solvent-controlled reaction and k_2 is a second-order rate constant for reaction with Y. Therefore the experimental first order rate constant, k_{obs}, is related to the individual rate constants by the equation

$$k_{obs} = k_1 + k_2[Y]. \tag{68}$$

This is supported by the observation that for reactions of the same complex with different reagents, linear plots of k_{obs} *versus* [Y] are obtained having the same intercepts, k_1, but different slopes, k_2 (Fig. 14). Without attempt-

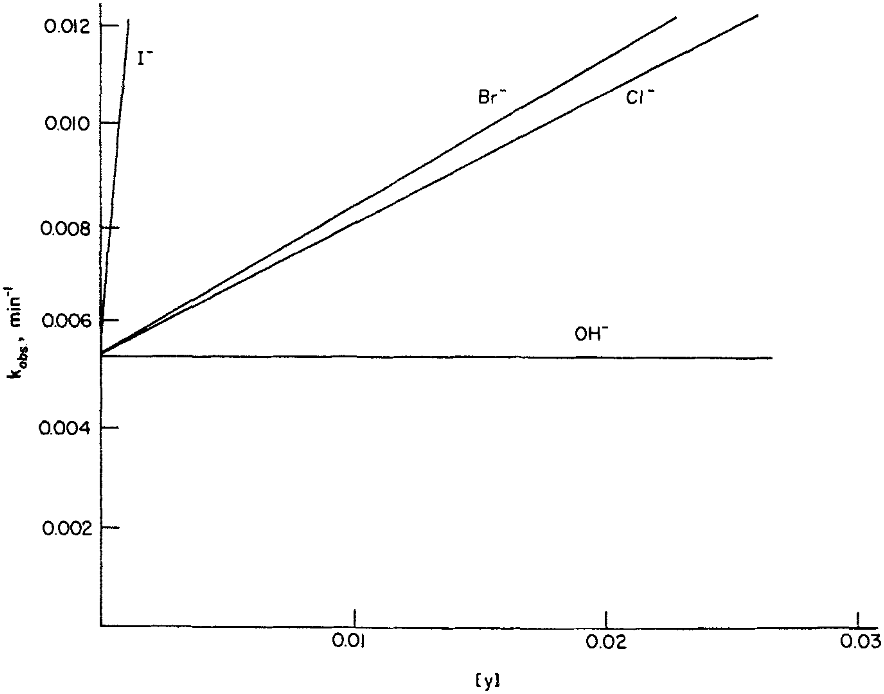


FIG. 14. Rates of reaction of [Pt(dien) Cl]$^+$ with different reagents, Y, as a function of reagent concentration [see Eq. (68)]. (dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$.) From Gray (*43*).

ing to define in detail the course of these reactions, it does appear that there is a competition between a solvent path(I) and a reagent path(II). Thus reaction (66) may be visualized as follows:

$$\begin{tikzcd}[\mathrm{Pt(A)_3X \cdots S_2}] \arrow[r, shift left, "\text{slow, }+\mathrm{Y}"] \arrow[d, shift left] & \text{[Intermediate (II)]} \arrow[l, shift left] \arrow[d, "\text{fast}", "-\mathrm{X}"'] \\ \text{[Intermediate (I)]} \arrow[u, shift left, "\text{slow}"] \arrow[r, "\text{fast}", "+\mathrm{Y}"'] & [\mathrm{Pt(A)_3Y \cdots S_2}].\end{tikzcd} \tag{69}$$

Because of the solvent participation postulated by path(I) in Eq. (69), an extensive study (*90*) was made of the effect of solvent on the rate of chloride exchange in the system *trans*-$(\mathrm{Pt(py)_2Cl_2}]$-${}^{36}\mathrm{Cl}^-$. Some of the results reported are tabulated in Table XV. The solvents investigated fall essentially into two categories: (1) those where the rate of exchange does not depend on chloride ion concentration, $k_1 \gg k_2$, and (2) those where it does depend on the concentration of chloride, $k_1 \ll k_2$. In general it appears that good coordinating solvents such as H_2O and ROH are in group (1) while poor coordinating solvents such as CCl_4 and C_6H_6 are in group (2). However it is also clear that the usual kind of coordinating ability will not explain the extreme reactivity of the solvents CH_3NO_2, $(CH_3)_2SO$, CH_3COOH and solutions of H_3BO_3. These solvents all have available potentially vacant orbitals of a type capable of bonding with the filled d_{yz} and d_{xz} orbitals of Pt(II). As shown in Fig. 15, such π-bonding may permit these solvent molecules to approach so that their basic oxygen atoms are very close to Pt and in a favorable position to displace Cl^- from the complex. Alternately, the transition state for exchange is stabilized. These solvents have the same properties as those reagents that are good nucleophiles for

TABLE XV

EFFECT OF SOLVENT ON THE RATE OF CHLORIDE EXCHANGE IN *trans*-$[\mathrm{Pt(py)_2Cl_2}]$—$\mathrm{Cl^{36-}}$ AT 25°C AND $[\mathrm{R_4NCl^{36}}] = 0.001$[a]

Solvent (A)[b]	k_{obs}, min^{-1}	Solvent (B)[b]	k_{obs}, min^{-1}
H_2O	2.1×10^{-3}	CCl_4	1×10^{-4}
C_2H_5OH	8.5×10^{-4}	C_6H_6	2×10^{-4}
m-C_3H_7OH	2.5×10^{-4}	*m*-cresol	2×10^{-4}
$(CH_3)_2SO$	2.3×10^{-2}	*tert*-C_4H_9OH	1×10^{-3}
CH_3NO_2	1.9×10^{-3}	CH_2ClCH_2Cl	7×10^{-4}
$CH_3NO_2(2.2M\,CH_3COOH)$	2.4×10^{-2}	$CH_3COOC_2H_5$	4×10^{-5}
$C_2H_5OH(0.075M\,H_3BO_3)$	3.1×10^{-3}	$(CH_3)_2CO$	4×10^{-4}
		$HCON(CH_3)_2$	9×10^{-4}
		CH_3CN	1×10^{-3}

[a] From Pearson *et al.* (*90*).

[b] For solvents (A) the rate of exchange does not depend on $[Cl^-]$, but for solvents (B) it does. See text.

Pt(II), such as NO_2^-, $CS(NH_2)_2$, and R_3P. That is they can both donate electrons to the metal atom and accept electrons from the metal atom. The name "biphilic" reagent is suggested to describe such ions and molecules.

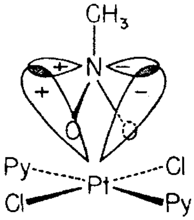
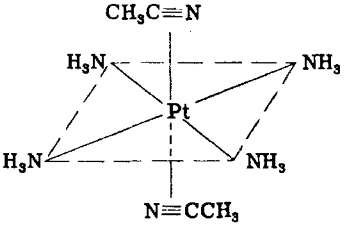


FIG. 15. π-Bonding (metal to ligand) in the interaction of solvent molecules with platinum(II) complexes. From Pearson *et al.* (*90*).

Somewhat surprising is the observation that CH_3CN is not an effective solvent for exchange although it is known to coordinate and form stable complexes of the type $[Pt(NH_3)_4(CH_3CN)_2]Cl_2$. The structure of this species, as determined by X-ray analysis (p. 186 in *17*), was used to explain the solvent behavior of CH_3CN. The complex has the structure shown (70)



(70)

where the distance between CH_3CN and the plane of the platinum axis is ~3Å. This parallel arrangement of the CH_3CN molecules above and below the $[Pt(NH_3)_4]^{++}$ plane does not permit a closer approach because of steric repulsion between the CH_3 group and the groups in the plane. Hence the close approach required for a solvent induced exchange by path(I) reaction (69) is not possible. It then becomes necessary to assume that $(CH_3)_2CO$ and $HCON(CH_3)_2$ also coordinate to the complex through their carbonyl double bonds.

B. STERIC EFFECT

The importance of solvation above and below the plane in determining the rates of certain reactions of Pt(II) complexes has also been verified by blocking these positions by groups attached to the ligands in the plane (*12*). This was done by using complexes containing *ortho*-substituted phenyl or pyridine ligands. As shown in Fig. 16, the aromatic ring is forced out of the plane of the complex and the group in the *ortho* position lies above and below the plane. The results of these studies are given in Table XVI. It is apparent that this steric shielding of the platinum(II) is accompanied by a decrease in rate of reaction. Even a more pronounced effect is observed for analogous Pd(II) and Ni(II) complexes.

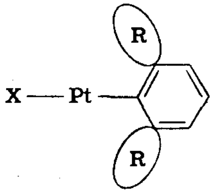


Fig. 16. Steric effect of *ortho*-substituted phenyl or pyridine ligands. Only x-axis of plane shown, y-axis is perpendicular to the paper.

It is of interest to note that the steric effect is greater for *cis* than for *trans* isomers. Thus for [Pt(PEt$_3$)$_2$(R)Cl] where R = phenyl, *o*-tolyl and mesityl, the relative rates of reaction for the *cis* isomers are 100,000:200:1, while for the *trans* isomers it is only 30:6:1, respectively. Scale molecular models suggest that the formation of a square pyramidal intermediate by the approach of nucleophilic groups along the *z* axis of either isomer is difficult, if not impossible. Furthermore, the same steric effect would be expected for either isomer. However, a nucleophilic approach at a slight angle in the direction of the departing chloro group is possible in either case, but the steric effect is expected to be much less for the *trans* than for the *cis* isomer. These results, therefore, suggest a displacement process

TABLE XVI[a]

STERIC EFFECT ON THE RATES OF REACTION OF SOME PLATINUM(II) COMPLEXES AT 25°C IN ETHANOL

Complex	Reactant	k_1, min^{-1}
cis-[Pt(4-ampy)$_2$Cl$_2$][b]	R$_4$NCl[36]	6.5×10^{-4}
cis-[Pt(α-pic)$_2$Cl$_2$][c]	R$_4$NCl[36]	2.9×10^{-5}
trans-[Pt(PEt$_3$)$_2$(phenyl)Cl]	pyridine	2×10^{-3}
trans-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl]	pyridine	4×10^{-4}
trans-[Pt(PEt$_3$)$_2$(mesityl)Cl]	pyridine	7×10^{-5}
cis-[Pt(PEt$_3$)$_2$(phenyl)Cl]	pyridine	2.3[d]
cis-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl]	pyridine	5.2×10^{-3}[d]
cis-[Pt(PEt$_3$)$_2$(mesityl)Cl]	pyridine	2.5×10^{-5}[d,e]

[a] Data from Basolo *et al.* (*12*).

[b] 4-ampy = 4-amyl pyridine.

[c] α-pic = α-picoline.

[d] At 0°C.

[e] Value for bromo compound which differs only slightly from analogous chloro compound.

involving a trigonal bipyramidal intermediate for such sterically hindred *cis*-complexes.

C. Trans-Effect

The rates of reaction of complexes of the type *trans*-[Pt$(A)_2$(R)Cl] with pyridine in ethanol solution are given in Table XVII, along with a few *cis* isomers for comparison (*12*). The effect on the rates of reaction of different R groups *trans* to Cl being replaced shows that the *trans*-labilizing abilities of these ligands decrease as follows: $PMe_3 > PEt_3 \sim H \geq PPr_3 >$ Me > phenyl ~ *p*-methoxyphenyl ~ *p*-chlorophenyl > biphenyl > Cl. Both the electrostatic (polarization) and π-bonding theories are necessary in order to explain these results.

TABLE XVII

Trans-Effect on the Rates of Reaction of Some Platinum(II) Complexes with Pyridine at 25°C[a]

trans-Ligand	Complex	k_1, min^{-1}[b]	k_2, liter mole^{-1} min^{-1}[b]
Cl	*trans*-[Pt$(PEt_3)_2Cl_2$]	6×10^{-5}	2.4×10^{-2}
Biphenyl	*trans*-[Pt$(PEt_3)_2$(biph)Cl]	1×10^{-3}	5.8×10^{-1}
p-Methoxyphenyl	*trans*-[Pt$(PEt_3)_2$(meoph)Cl]	1.7×10^{-3}	7.8×10^{-1}
p-Chlorophenyl	*trans*-[Pt$(PEt_3)_2$(Clph)Cl]	2×10^{-3}	9×10^{-1}
Phenyl	*trans*-[Pt$(PEt_3)_2$(ph)Cl]	2×10^{-3}	9.5×10^{-1}
Methyl	*trans*-[Pt$(PEt_3)_2$(Me)Cl]	1×10^{-2}	4
H	*trans*-[Pt$(PEt_3)_2$(H)Cl][c]	1.1	2.5×10^2
PPr_3	*cis*-[Pt$(PPr_3)_2Cl_2$][c]	5×10^{-1}	1×10^2
PEt_3	*cis*-[Pt$(PEt_3)_2Cl_2$][c]	1	2.3×10^2
PMe_3	*cis*-[Pt$(PMe_3)_2Cl_2$][c]	5	—

[a] From Basolo *et al.* (*12*).

[b] k_1 and k_2 as defined by Eqs. (67) and (68).

[c] Reaction is too fast to measure at 25°C so the rate constants reported are for 0°C.

The relative rates of reaction for complexes with *trans* groups H, Me, phenyl, and Cl are approximately 100,000:200:30:1. Since π-bonding is not expected to be very important in binding these groups to the metal, this rapid decrease in rate must be mainly electrostatic in origin. This is supported by several other observations. For example, there is a rapid decrease in dipole moment along the series of compounds *trans*-[Pt$(PEt_3)_2$(R)Cl] whose moments for different R groups are H = 4.2 debye, Me = 3.4 debye, phenyl = 2.6 debye, and Cl = 0 debye. Recent studies show that both hydride ion and methide ion cause large ligand field splittings of the *d*-energy levels in Ru(II) complexes (*23*). Finally in *trans*-

[$Pt(PEt_3)_2(H)Br$], the Pt—Br bond distance is 2.56Å instead of the radius sum of 2.43Å (*85*).

By comparison with the *trans* isomers, it is seen (Table XVI) that the reactivity of *cis*-[$Pt(PEt_3)_2(R)Cl$] varies only slightly with changes in R. Thus for R = Cl, phenyl, and Me the relative rates are only 1, 2.3, and 3.6. Although in the same direction, the effect is much smaller than for the *trans* isomers. This clearly shows the directional nature of the effect of these groups which activate almost entirely by induction and agrees with Grinberg's theory of the *trans*-effect (p. 178 in *17*).

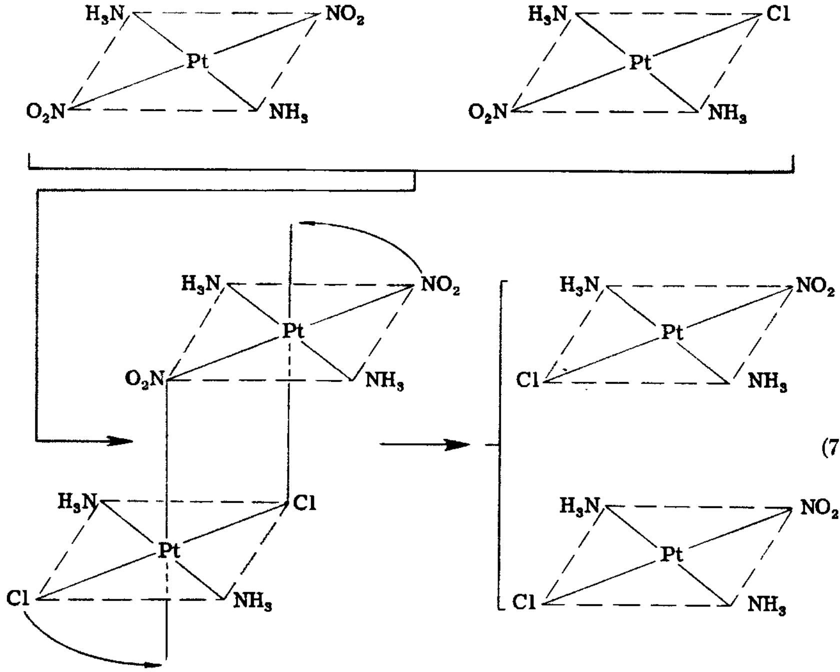
However, the large *trans*-labilizing ability of groups like PR_3 and C_2H_4 is in agreement with the Chatt-Orgel π-bonding theory (p. 183 in *17*) of the *trans*-effect. It is of interest to note that in *trans*-[$Pt(C_2H_4)(NHMe_2)Cl_2$] the $NHMe_2$ is very readily replaced by other groups because of the high *trans*-effect of C_2H_4, yet, in contrast to the bromohydride compound mentioned above, the Pt—N bond is of normal length (*21*). Similarly, inductive effects alone cannot account for the observation that phenyl, biphenyl, *p*-methoxyphenyl, and *p*-chlorophenyl have approximately the same *trans*-activating ability. However, this can be explained if both inductive and π-bonding influences are important. The larger the electron density on the ring, the smaller the back donation of electrons from the metal. This means that substitution on the ring alters the inductive and π-bonding contribution in different directions so that these opposing effects may result in the observed similar reaction rates.

Summarizing, it now appears possible to distinguish two different mechanisms of the *trans*-effect: (i) strong polarization of the metal ion by electrostatic forces as exemplified by hydride ion; and (ii) strong polarization of the metal ion by dative π-bonding as exemplified by ethylene. There is also the possibility of cases where both effects operate somewhat weakly but add to give a strong *trans*-effect as exemplified by iodide ion.

The attempt to explain the *trans*-effect by a mechanism involving a trigonal bipyramidal intermediate was recently challenged by Dyatkina and Syrkin (*30*). This was done on the basis of theoretical grounds which indicate that a tetragonal pyramidal path would require less energy. Thus the change of a square hybrid ($d_{xy}sp_xp_y$) into a trigonal bipyramidal hybrid ($d_{z^2}sp_xp_yp_z$) requires the addition of a p_z orbital and the change from d_{xy} to d_{z^2}. Instead the rearrangement from square planar to tetragonal pyramidal ($d_{xy}sp_xp_yp_z$) is of lower energy because it requires only the addition of the p_z orbital. Using this structure for the intermediate, an interesting mechanism is postulated to account for reactions of the type

$$[Pt(NH_3)_2Cl_2] + [Pt(NH_3)_2(NO_2)_2] \rightarrow 2[Pt(NH_3)_2NO_2Cl]. \qquad (71)$$

Reaction (71) is visualized as shown in (72).



(72)

D. Effect of Ligand on Its Replacement

The rate of exchange of X in systems of the type $[PtX_4]^{=}$—$^*X^-$ is known to decrease in the order $CN^- > I^- > Br^- > Cl^-$, which is also the decreasing order of stability of these complexes (see p. 192 in *17*). More recently Grinberg and Borzakova (*46*) report very rapid thiourea exchange with $[Pt(SC(NH_2)_2)_4]^{++}$, and Grinberg and Inkova (*47*) find no exchange of ethylamine with $[Pt(C_2H_5NH_2)_4]^{++}$. That the most labile complex is also the most stable has been explained on the basis of the relative *trans*-effects of these ligands, which also decrease in the above order. Data are now available (*13*) which permit a comparison of the reactivity of different X groups in analogous compounds of the type $[Pt(A)_3X]$ where the only change is the change in X. The results given in Table XVII show that the rate of reaction of $[Pt(NH_2(CH_2)_2NH(CH_2)_2NH_2)X]^+$ with pyridine decreases for changes in X in the order $NO_3^- > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$. This parallels both the order of increasing bond strength and the position of X in the *trans*-effect series. For these examples, strongly *trans*-activating groups are difficult to replace. It is also of interest that, except for the halide ions, the order of reaction rates is similar to that for $[Co(NH_3)_5X]^{++}$. In both cases the reaction rates are slower for the more stable systems. Reversal of the order for the halogeno complexes in the two systems is consistent with the view that π-bonding is more important for Pt(II) than for Co(III) complexes. The general order of reactivity appears to be the same for analogous Pd(II) compounds, but the spread in rates is smaller than for Pt(II). This may result from the smaller tendency to π-bonding of Pd(II) relative to that of Pt(II).

TABLE XVIII

RATES OF REACTION OF SOME $[Pt(dien)X]^+$ AND $[Pd(dien)X]^+$ COMPLEXES WITH PYRIDINE AT 25°C[a]

$[M(dien)X]^{+}$[b]	M = Pt k_{obs}, min^{-1}[c]	M = Pd k_{obs}, min^{-1}[c]
NO_3^-	fast[d]	—
Cl^-	2.1×10^{-3}	fast[d]
Br^-	1.4×10^{-3}	fast[d]
I^-	6.0×10^{-4}	2.0[e]
N_3^-	5.0×10^{-4}	—
SCN^-	1.8×10^{-5}	2.5
NO_2^-	3.0×10^{-6}	2.0
CN^-	1.0×10^{-6}	—

[a] From Basolo *et al.* *(13)*.

[b] dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$.

[c] k_{obs} as defined by Eq. (67). For reactions of Pt(II) the values of k_{obs} are for 0.006 *M* pyridine and for Pd(II) these are for 0.001 *M* pyridine.

[d] Reactions are too fast to measure.

[e] For 0°C.

E. EFFECT OF THE METAL ON RATES OF SUBSTITUTION

Data in Tables XVIII and XIX afford a unique quantitative comparison of rates of reaction of analogous Ni(II), Pd(II), and Pt(II) compounds. The ratio of rates for the reactions

$$trans\text{-}[M(PEt_3)_2(o\text{-tolyl})Cl] + py \rightarrow [M(PEt_3)_2(o\text{-tolyl})py]^+ + Cl^- \qquad (73)$$

is approximately 5,000,000:100,000:1, where M is Ni(II), Pd(II), and Pt(II), respectively. This large difference in lability between Pt(II) and Ni(II) complexes is consistent with a displacement mechanism, since Ni(II) is known to expand its coordination number more easily than Pt(II). Additional support for this is provided by the observation that *trans*-$[Ni(PEt_3)_2(mesityl)Cl]$ reacts only about 20,000 times faster than does the corresponding Pt(II) compound. For comparison, the relative rates of acid hydrolysis of $[M(NH_3)_5Br]^{++}$ are about 4,000 to 1 for Co(III) and Ir(III), respectively. Thus, by tending to block the positions above and below the planar complex with a mesityl group, Ni(II) becomes much less labile relative to Pt(II), and the rate differences more nearly resemble those between octahedral Co(III) and Ir(III) complexes.

Banerjea and Tripathi (*11b*) determined the kinetics of the reactions of several different Pd(II) complexes with a variety of different reagents. They found that the rates of reaction were too fast to measure for several Pd(II) compounds, but in a few cases about the same reactivity is reported for corresponding Pd(II) and Pt(II) systems. The rates of reaction of certain Pd(II) complexes with a variety of reagents are reported to decrease in the order $OH^- > SC(NH_2)_2 > C_5H_5N > NH_2CH_2COOH > C_6H_5NH_2 > H_2O$. On the basis of these results it was concluded that the reactivity of different reagents toward Pd(II) correlates the reagents' nucleophilic character and not their π-bonding ability. Since the reaction of $[Pd(en)Cl_2]$ is faster by several powers of ten than that of *trans*-$[Pd(NH_3)_2Cl_2]$, it was further concluded that the *trans*-effect is insignificant in these systems. However it should be pointed out that some of these results are at variance with the general observations reported before that reactions of Pd(II) are of the order of 10^5 times faster than reactions of analogous Pt(II) complexes.

TABLE XIX

RATES OF REACTION OF SOME ANALOGOUS (Ni(II), Pd(II) AND Pt(II) COMPLEXES WITH PYRIDINE AT 25°[a]

Complex	k_1, min^{-1} [b]
trans-$[Ni(PEt_3)_2(o\text{-tolyl})Cl]$	2×10^{3} [c]
trans-$[Pd(PEt_3)_2(o\text{-tolyl})Cl]$	3.5×10 [c]
trans-$[Pt(PEt_3)_2(o\text{-tolyl})Cl]$	4×10^{-4}
trans-$[Ni(PEt_3)_2(mesityl)Cl]$	1.2
trans-$[Pt(PEt_3)_2(mesityl)Cl]$	7×10^{-5}
cis-$[Ni(PEt_2CH_2CH_2PEt_2)(mesityl)Br]$	2×10 [c]
cis-$[Pt(PEt_3)_2(mesityl)Br]$	3×10^{-4}

[a] From Basolo *et al.* (*12*).

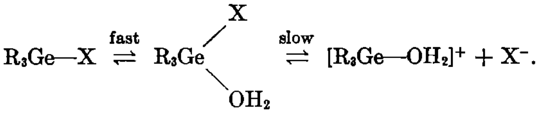
[b] k_1 as defined by Eqs. (66) and (67).

[c] Rate constants estimated from data at temperatures ranging from −80 to 0°C.

IV. Tetrahedral Complexes

Tetrahedral metal complexes are generally labile, so that kinetic-mechanistic studies on these systems are few (p. 209 in *17*). The exchange of carbon monoxide with nickel carbonyl and the reactions of phosphines with phosphine nickel carbonyls are described in the next section. Quantitative studies are reported on some Group IV organometallic halides. Although substitution at a saturated carbon atom is known to proceed either by an S_N1 or S_N2 mechanism, depending on the system, this does not appear to be the case for other members of the carbon family. For example, reactions of organosilicon halides appear to involve a quinquecovalent intermediate and a synchronous mechanism in which bond making between silicon and the attacking nucleophile is dominant. Recent studies indicate the same mechanism for reactions of organogermanium and organotin halides. All of these halides are much more rapidly solvolyzed than are carbon halides of analogous structure, presumably because of the ease of expansion of their coordination number.

Johnson and Schmall (*60*) determined the rate constants for the hydrolysis of several triarylgermyl halides by conductance measurements. The pseudo-first-order rate constants k, $\sec^{-1}$, for solvolysis in dioxane-water (4:1) at 30°C are 0.0111, 0.0102, 0.0098, and 0.0096 for $(C_6H_5)_3GeBr$, $(C_6H_5)_3GeCl$, $(C_6H_5)_3GeF$, and $(CH_3C_6H_4)GeF$ respectively. For dioxane-water and acetone-water solvent mixtures, it was observed that the rate of solvolysis increases with increasing ionizing power of the solvent. In some cases a salt retardation effect was observed. These results are interpreted in terms of the reaction scheme

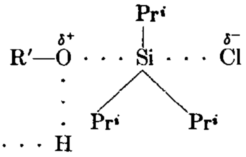


$$R_3Ge{-}X \overset{\text{fast}}{\rightleftharpoons} R_3Ge\begin{smallmatrix}X\\ \\ OH_2\end{smallmatrix} \overset{\text{slow}}{\rightleftharpoons} [R_3Ge{-}OH_2]^+ + X^-. \tag{74}$$

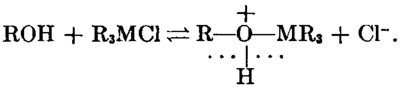
It was suggested that such a mechanism is consistent with the salt retardation effect and with the observation that $(C_6H_5)_3GeF$ hydrolyzes faster than $(CH_3C_6H_4)_3GeF$. Since in the transition state in reaction (74) the germanium is less positive than it is in the reactant, the reaction is inhibited by electron-release to germanium in the reactant, as is expected for the case for tolyl relative to phenyl.

Prince (*99*) has investigated the solvolyses of organotin chlorides [R_3SnCl where R is ethyl (Et), isopropyl (Pr^i), *tert*-butyl (Bu^t), or phenyl (Ph)] in ethanol, propan-2-ol and water-dioxane. These reactions are rapid to positions of equilibrium which depend upon the medium and the nature of the alkyl group. When the latter is isopropyl and in the solvent propan-2-ol rates are measurable; when the alkyl group is *tert*-butyl, solvolysis rates are measurable in ethanol and in propan-2-ol, but solvolytic equilibrium lies further in favor of the undissociated halide. These two facts on rates and equilibria are cited to support a synchronous type substitution at tin.

The characteristics of the solvolysis of $(Pr^i)_3SiCl$ in propan-2-ol and propan-2-ol-water mixtures were found to differ from those of the corresponding tin compound. For hydrolysis a second-order reaction is observed which is not catalyzed by pyridine, whereas alcoholysis is subject to pyridine catalysis. This was explained in terms of the transition state



where S is a proton acceptor, either propan-2-ol or pyridine. In hydrolysis where R′ is H, it is probably as easy for a propan-2-ol molecule to accept a proton as it is for a pyridine molecule in alcoholysis. Where R′ is Pr^i it may be easier for the more basic and less hindered pyridine to approach the proton. Finally, conductivity data suggest that the chief difference between the solvolysis of R_3SiCl and R_3SnCl can be ascribed to the differing extents of fission of the O—H bond in the scheme:



$$ROH + R_3MCl \rightleftharpoons R{-}\underset{\cdots|\cdots\atop H}{\overset{+}{O}}{-}MR_3 + Cl^-. \qquad (75)$$

When M = Si, fission is essentially complete, when M = Sn, fission is very limited.

In this connection it should be noted that Sommer and Frye (*114*) have recently been able to prepare optically active organosilicon compounds having reactive groups bonded to asymmetric silicon, e.g., R_3Si^*Br, R_3Si^*OH and $R_3Si^*OCH_3$. They observed that certain substitution reactions at asymmetric silicon proceed with pure retention and others with pure inversion of configuration. This supports the mechanism mentioned above in which such reactions involve an expansion of coordination number rather than being of the S_N1 type, in which some racemization is expected. The availability of optically active organosilicon compounds in sufficient quantities should be most helpful in the elucidation of their reaction mechanisms.

Dipole moment measurements indicate that *bis*(cyclopentadienyl)-titanium(IV) halides have a distorted tetrahedral structure. A spectrophotometric kinetic study (*58*) was made of the reaction

$$(C_5H_5)_2TiBr_2 + 2RCl \rightleftharpoons (C_5H_5)_2TiCl_2 + 2RBr \qquad (76)$$

in a variety of different solvents and where R was either a large quaternary ammonium ion or lithium ion. The rate of reaction with the quaternary ammonium chloride in the solvents tetrahydrofuran and benzene shows a first-order dependence on the concentration of chloride. This suggests that the reaction takes place by an S_N2 displacement process. Instead the reaction with lithium chloride, under the same experimental conditions in tetrahydrofuran, is only about one-twentieth as fast and the rate of reaction does not depend upon the concentration of lithium chloride. It is presumed that in this case the rate-determining step involves a nucleophilic displacement by the solvent. The lithium chloride is believed to exist chiefly as an ion pair. The same reaction of $(C_5H_5)_2ZrBr_2$ was much too fast to study by the techniques employed. It was suggested that the greater reactivity of the Zr(IV) relative to the Ti(IV) compound is due to the larger size of Zr(IV), which makes it more susceptible to nucleophilic attack and also probably makes the Zr—Br bond strength less than that of Ti—Br.

V. Fast Reactions

One of the important recent developments in chemical kinetics is a great interest in the study of very rapid reactions. Chemical events with half-lives as short as 10^{-7} seconds have been studied with reasonable accuracy. It is obvious that rather special methods must be used to investigate systems as labile as this. In fact a large part of the interest in rapid reactions results from the availability of electronic methods of measuring times in the millisecond, microsecond, and even millimicrosecond ranges.

Even though short times can be easily measured, there is still the difficult problem of detecting a change in the system because reaction takes place in this time interval. Furthermore, the problem of mixing together the reagents to initiate reaction is a severe limitation in that a finite time of at least 1 msec is required for homogeneous mixing even in the best circumstances. For shorter times it is necessary to start with the reactants already uniformly distributed and in a state of equilibrium. The equilibrium may then be disturbed and subsequent events followed, or alternatively the consequences of the dynamic nature of a chemical equilibrium may be utilized. A favorite technique is to invoke some other time-dependent phenomenon, with a characteristic time of the same order as that of the half-life of the chemical reaction. The interplay of these two times then produces observable results which depend on their relative values.

It is indeed fortunate that methods for studying rapid reactions are becoming available, since the majority of substitution reactions of the metal ions are too fast to follow by ordinary means. Until a few years ago, in fact, it was impossible to even estimate the rates of most such reactions. Now enough work has been done so that a feeling, at least, for the order of magnitudes of the rates can be developed. In what follows no attempt will be made to describe the methods used in detail, since this has been done elsewhere (*39*). Instead the emphasis will be on results and their interpretation.

Perhaps the best examples to start with are some solvent exchange studies done by means of nuclear magnetic resonance methods. It has been known for some time that paramagnetic ions will shorten the measured transverse (T_2) and longitudinal (T_1) relaxation times in NMR spectra

(*71*). Recently it has been shown that the changes enable rate constants for exchange reactions of the following kind to be measured:

$$[Cu(H_2{*}O)_6]^{++} + H_2O \rightleftharpoons [Cu(H_2O)_6]^{++} + H_2{*}O. \qquad (77)$$

The asterisk is used to indicate a solvent molecule bound initially to a paramagnetic ion to distinguish it from bulk solvent molecules. In general one can measure either the lifetime, τ_B, of a water molecule bound to the ion or the lifetime, T_{2B}, of a nuclear spin state in a water molecule bound to the ion (*91*). Whichever time is the longer will correspond to the rate-determining step and will be measured. The reciprocal of τ_B is the first-order rate constant for the forward step of reaction (77).

TABLE XX
LOWER LIMITS TO EXCHANGE RATE CONSTANTS, $1/\tau_B$,
FOR PARAMAGNETIC IONS IN WATER AND METHANOL AT 25°C[a]

Ion	$CH_3O\underline{H}$[b]	$\underline{CH_3}OH$[b]	$\underline{H_2}O$[c]	$H_2\underline{O}$[d]
Cr^{3+}	2.1×10^4	7.0×10^3	1×10^5	slow
Fe^{3+}	3.2×10^4	2.2×10^4	2×10^5	1×10^6
Mn^{++}	2.5×10^5	1.8×10^4	5×10^6	7×10^7
Co^{++}	1.1×10^4	1.7×10^3	5×10^3	2×10^5
Ni^{++}	2.6×10^3	2.2×10^3	6×10^3	4×10^4
Cu^{++}	1.0×10^4	1.0×10^4	8×10^3	6×10^5
Ce^{3+}	2.5×10^2	0.8×10^2	8×10^2	—
Gd^{3+}	1.2×10^5	2.1×10^4	1×10^4	—

[a] All rates constants in sec^{-1}.

[b] The underlined atoms are the nuclei whose exchange rate (or rate of relaxation)is being measured Pearson *et al.* (*91*).

[c] Rounded off values from Morgan and Nolle (*77a*), except Fe^{3+} and Ce^{3+} (Conger and Selwood, *24a*).

[d] From Connick and Poulson (*25a*).

Table XX presents some exchange data obtained in water and in methanol solutions of some paramagnetic ions. In most cases only lower limits can be put on the rate constants because of the possibility that T_{2B} is rate controlling. Even so the data are tremendously valuable in that for the first time it is possible to get some idea of the permanance of a solvent molecule bound to the simpler ions. For some cases, such as Cu(II) and Ni(II) in methanol, it is clear that the rate of solvent exchange is being measured, since the rates are the same for the methyl protons and for the hydroxyl protons. This would not be true if T_{2B} were being measured.

It is of considerable interest that methyl alcohol molecules are exchanged more slowly than water molecules. This is either because they are held more firmly or because the methyl group offers steric hindrance to an incoming solvent molecule in an S_N2-like process. The very high lability of solvent attached to Fe(III) is noteworthy. The results are probably complicated by the fact that, even in the acid solutions where the spectra were taken, some $[Fe(H_2O)_5OH]^{++}$ will exist and it is known that the hydroxy group is usually strongly labilizing for substitution reactions (pp. 124–138 in *17*). Even so the water exchange rate constant is clearly very much greater than for an ion such as $[Cr(H_2O)_6]^{3+}$ where τ_B is about 10^6 sec (53) instead of 10^{-6}. This is an extreme example of crystal field stabilization in the latter ion (see Chapters 2 and 3 in *17*).

Crystal field effects are also demonstrated by the lability order Mn(II) > Co(II) > Ni(II) < Cu(II). This order is predicted by crystal field theory as a result of the loss of crystal field stabilization energy (CFSE) in passing from the ground state to the transition state. It has been amply verified in a number of less reactive systems (see *34*; also Chapters 2 and 3 in *17*).

Table XXI presents some data on the sulfation reaction obtained by Eigen (*31*)using ultrasonic relaxation spectroscopy. It is strongly indicated by the results that the process of forming a sulfato complex from an aquo complex consists of several stages. The first of these are concerned with the diffusion controlled formation of an ion pair or outer-sphere complex

TABLE XXI

RATE CONSTANTS AT 25°C[a] FOR REACTION

$$[M(H_2O)_n]^{++}, A^{=} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_{n-1}A] + H_2O$$

M	A	k_1 sec^{-1}	k_2, sec^{-1}
Be^{++}	$SO_4^{=}$	1×10^2	1.3×10^3
Mg^{++}	$SO_4^{=}$	1×10^5	8×10^5
Ca^{++}	$SO_4^{=}$	(10^7)[b]	(10^8)[b]
Mg^{++}	$S_2O_3^{=}$	1×10^5	1.5×10^6
Mg^{++}	$CrO_4^{=}$	1×10^5	1.5×10^6
Cu^{++}	$SO_4^{=}$	(10^4)[b]	1×10^6
Ni^{++}	$SO_4^{=}$	1×10^{-4}	1×10^5
Co^{++}	$SO_4^{=}$	2×10^5	2.5×10^6
Mn^{+}	$SO_4^{=}$	4×10^6	2×10^7

[a] Data from Eigen (*31*).

[b] The numbers in parentheses are relatively uncertain.

$$[M(H_2O)_6]^{++} + SO_4^{=} \rightleftharpoons [M(H_2O)_6]^{++},SO_4^{=}. \tag{78}$$

The last stage, and the one of chemical interest, is the rearrangement of this ion pair to the true complex

$$[M(H_2O)_6]^{++},SO_4^{=} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_5SO_4] + H_2O. \tag{79}$$

The table shows values of k_1 and k_2 for a number of metal ions. Some data for anions other than sulfate are also given.

The results show the expected dependence on electrostatic factors since small cations react more slowly than similar but larger ions. The transition metal ions show the expected order Mn(II) > Co(II) > Ni(II) < Cu(II). Two other features are especially noteworthy: one is that the rate constant k_1 is apparently independent of the anion associated with the cation, and the other is that the value of k_1 is remarkably similar to the rate constants for water exchange given in Table XX. This seems to be very powerful evidence for an S_N1 or dissociation mechanism operating in all these cases, so that the rate step is the loss of a water molecule from the first coordination shell of the cation. Apparently the anion gives very little assistance in pushing off the leaving group. The detailed mechanism presented elsewhere seems appropriate (p. 99 in *17*).

Table XXII gives some data on the reaction of the trivalent anion of EDTA with several metal ions, e.g.,

TABLE XXII

RATES OF $M^{++} + HY^{3-} \xrightarrow{k} [MHY]^-$

M^{++}	k, mole^{-1} sec^{-1}	Temp.	Ref.
Ni^{++}	1.8×10^5	25°C	*a*
Co^{++}	4×10^6	25°C	*b*
Cd^{++}	1×10^9	25°	*c*
Cu^{++}	1×10^9	0°	*d*
Pb^{++}	1×10^{11}	0°	*d*

Note: H_4Y is ethylenediaminetetraacetic acid.

[a] Cook and Long (*26a*).

[b] F. A. Long, private communication quoted in Eigen (*31*).

[c] Koryta and Zabransky (*66a*).

[d] Tanaka and Sakuma (*119a*).

$$Ni^{++} + HY^{3-} \xrightarrow{k} [NiHY]^-. \tag{80}$$

The rate constant k is not the same as k_1 in Table XXI since it includes the equilibrium constant for the formation of the ion pair as in Eq. (78). The interest in Table XXII lies in the fact that the nickel ion rate is again the slowest and the rates for the copper ion, cadmium ion and lead ion are very high. This would be expected for the latter two ions because of their large size and because they lack CFSE. The data on the last three ions were obtained by polarographic means, and are probably of low accuracy for Cu(II) and Pb(II).

Table XXIII gives some better polarographic data for the dissociative

TABLE XXIII

RATE CONSTANTS AT 25°C[a] FOR $[MX]^- + H^+ \rightarrow M^{++} + HX^{2-}$ [b]

M^{++}	k, mole^{-1} sec^{-1}
Cd^{++}	3.0×10^5
Pb^{++}	9.6×10^5
Mn^{++}	9.2×10^6

[a] Data from Koryta *et al.* (*66b*).

[b] X = nitrilotriacetate ion.

rate constants of complexes of nitrilotriacetic acid. The dissociating species is probably $[MHX]^-$, but the rates are calculated as if for the reaction

$$[MX]^- + H^+ \xrightarrow{k} M^{++} + HX^=. \tag{81}$$

To get true rate constants the acid dissociation constant of $[MHX]^-$ must be known. In any event the second-order rate constants of Table XXIII again show high lability for Cd(II), Pb(II) and the noncrystal-field stabilized Mn(II). As is well known, ions that have large CFSE usually do not give reversible polarographic waves, and this may sometimes be related to the slowness of removing a ligand from the metal ion before reduction can occur (*42*).

Flow methods have been used by Connick and his co-workers (*25*) to study the anation of $Fe(H_2O)_6{}^{3+}$ with chloride ion and thiocyanate ion.

$$[Fe(H_2O)_6]^{3+} + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(H_2O)_5X]^{++} + H_2O. \tag{82}$$

The pH dependence of the reaction shows that an important contribution comes from the reaction

$$[Fe(H_2O_5OH]^{++} + X^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Fe(H_2O)_4OHX]^{+} + H_2O. \tag{83}$$

Table XXIV shows the values of k_1, k_2, and k_3 computed from the rate

TABLE XXIV

REACTIONS OF FERRIC ION WITH CHLORIDE, THIOCYANATE, AND FLUORIDE IONS AT 25°C[a]

Complex	Reactant	k_1, mole^{-1} sec^{-1}	k_2, sec^{-1}	k_3, mole^{-1} sec^{-1}
$[Fe(H_2O)_6]^{3+}$	Cl^-	9.4	2.3	—
$[Fe(H_2O)_6]^{3+}$	CNS^-	127	0.87	—
$[Fe(H_2O)_6]^{3+}$	F^-	1800	—	—
$[Fe(H_2O)_5OH]^{++}$	Cl^-	—	—	1.1×10^4
$[Fe(H_2O)_5OH]^{++}$	CNS^-	—	—	1.0×10^4

[a] Data from Connick *et al.* (*25*) and Smith (*113*).

data at 25°C and the K_a of the aquo iron ion. The rate constant at 0°C for reaction (82) with fluoride ion has been measured by Smith (*113*) and is included in Table XXIV after a rough correction to 25°C using an activation energy of 12 kcal, which is similar to that for the other two anions. Independent of this value, fluoride ion certainly reacts the fastest of the three, which correlates with its greater basicity and greater coordinating power for ferric ion.

The rates of all these anation reactions are first order in the anion. However this does not distinguish between an S_N1 and an S_N2 mechanism (see pp. 138–141 in *17*). The S_N1 mechanism would require an intermediate which is five-coordinated and which can either react again with water or react with an anion.

$$[Fe(H_2O)_6]^{3+} \underset{k_r}{\overset{k_d}{\rightleftharpoons}} [Fe(H_2O)_5]^{3+} + H_2O \tag{84}$$

$$[Fe(H_2O)_5]^{3+} + X^- \xrightarrow{k_a} [Fe(H_2O)_5X]^{++} \tag{85}$$

The relation $k_r \gg k_a[X^-]$ is necessary to agree with the observed dependence on the anion concentration. The rate equation becomes, for the steady state,

$$\text{Rate} = \frac{k_d k_a [C][X^-]}{k_r + k_a[X^-]} \tag{86}$$

where C is either $[Fe(H_2O)_6]^{3+}$ or $[Fe(H_2O)_5OH]^{++}$. The rate constant k_d would be the same as for solvent water exchange which is reported in Table XX. The necessary requirement is that the rate of exchange of solvent be greater than the rate of anation. From the data it can be seen that this is so.

It is of considerable interest to compare k_2 and E_a for the acid hydrolysis of the thiocyanato complex of Fe(III) with the corresponding figures for Cr(III).

$$H_2O + [M(H_2O)_5CNS]^{++} \xrightarrow{k_2} [M(H_2O)_6]^{3+} + CNS^- \tag{87}$$

From Table XXIV the value of k_2 is 0.87 sec^{-1} and E_a is 14.6 kcal for iron(III) (*25*). For chromium the corresponding figures (*98*) are 0.90×10^{-8} sec^{-1} and 28 kcal. The difference in rate is almost entirely due to difference in the energy barrier for loss of thiocyanate ion. On the other hand, the overall energy change for reaction (87) is the same within 0.5 kcal for both metal ions. The equilibrium favors greater aquation of the Fe(III) complex by a factor of no more than ten.

Some data on the reactions of Cd(II) with bromide ion have been obtained by Hertz (*48*). The method used is an NMR line-broadening technique in which advantage is taken of the fact that a halide ion coordinated to a metal ion has a very high rate of nuclear magnetic relaxation (very broad line). This high rate is due to a coupling of the nuclear quadrupole moment of the halide ion with the asymmetrical electric field produced at the halide nucleus by the metal ion. The figures in Table XXV are the rate constants for the following reactions

TABLE XXV
RATE CONSTANTS FOR THE REACTION OF CADMIUM(II) WITH BROMIDE IONS AT 25°C[a]

$Cd^{++} + Br^-$	$k_1 = 1.4 \times 10^9$ mole^{-1} sec^{-1}	$k_2 = 1 \times 10^7$ sec^{-1}
$CdBr^+ + Br^-$	$k_3 = 1 \quad \times 10^8$ mole^{-1} sec^{-1}	$k_4 = 1 \times 10^6$ sec^{-1}
$CdBr_2 + Br^-$	$k_5 = 2.8 \times 10^7$ mole^{-1} sec^{-1}	$k_6 = 6 \times 10^6$ sec^{-1}

[a] Data from Hertz (*48*).

$$Cd^{++} + Br^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [CdBr]^+ \tag{88}$$

$$[CdBr]^+ + Br^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [CdBr_2] \tag{89}$$

$$[CdBr_2] + Br^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [CdBr_3]^-. \tag{90}$$

It is necessary to know the equilibrium constants for the three reactions to get all the rate constants.

The high rates of the cadmium ion are noteworthy in comparison to those of ferric ion. For example, the reaction which we may write as

$$H_2O + [Cd(H_2O)_3Br]^+ \xrightarrow{k_2} [Cd(H_2O)_4]^{++} + Br^- \tag{91}$$

has k_2 equal to 1×10^7 sec^{-1}, whereas the corresponding aquation of $[Fe(H_2O)_5Cl]^{++}$ has k_2 equal to only 2.3 sec^{-1}. This is an example of the electrostatic influence, both size and charge playing a role.

Some line-broadening data for chloride ion under the influence of paramagnetic ions have been presented by Wertz (*125*). From the data it is possible to say that at least some of the chloro complexes, present at $3M$ chloride ion, of Mn(II), Cu(II), Ti(III) and Fe(III) must be very labile. An estimate can be made that the rate of hydrolysis

$$FeCl_3 + H_2O \xrightarrow{k_1} [Fe(H_2O)Cl_2]^+ + Cl^- \tag{92}$$

has a constant k_1 equal to about 3×10^6 sec^{-1}. This greater rate of hydrolysis compared to $[FeCl]^{++}$ is reasonable in terms of electrostatic theory. It is therefore surprising that the effect of charge does not show up in the hydrolysis reactions of the bromocadmium complexes of Table XXV. These numbers for cadmium are best viewed with some reservation since the extraction of six rate constants from the available data is not an easy task.

From the fact that separate resonances are observed in the fluorine NMR spectra, it is possible to set lower limits for the exchange time of fluorine between two environments (*39*). Thus exchange of fluorine between SnF^+—SnF_2, $SiF_6^=$—F^- and ZnF^+—F^- occurs in a time longer than a few tenths of a millisecond. For exchange between AlF_2^+ and AlF^{++}, a time of greater than about 8 msec is required. The exchange time in the systems SbF_6^-—F^-, is greater than 10^{-4} sec, for PF_6^-—F^- and AsF_6^-—F^-, is greater than 10^{-2} sec, and for $SiF_6^=$—F^- greater than 10^{-3} sec (*81*).

A study of the ^{17}O magnetic resonance spectrum of water in the presence of various diamagnetic cations leads to the conclusion that water molecules bound to Be(II), Al(III) and Ga(III), have an exchange time greater than 10^{-4} sec (*57*). Magnesium(II), Sn(II), Ba(II), Hg(II), and Bi(III) show τ_B less than 10^{-4} sec. From the effect of aluminum(III) on the proton resonance in water, an exchange lifetime of about 5–10 msec has been estimated for the reaction (*110*)

$$[Al(H_2{}^*O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_6]^{3+} + H_2{}^*O \tag{93}$$

This corresponds to a value of $1/\tau_B$ equal to 100–200 sec^{-1}. Comparing this to the figures in Table XX, it seems very likely that the high rate constant of 1×10^6 sec^{-1} for Fe(III) must be due to $[Fe(H_2O)OH]^{++}$ acting as the labile species. The rate constant for $[Fe(H_2O)_6]^{3+}$ is more likely of the order of 10^3 sec^{-1}.* The large trivalent gadolinium ion would be expected to be more labile than ferric ion. Table XX indicates that the rate constant is greater than 1×10^5 sec^{-1} for $[Gd(H_2O)_6]^{3+}$.

For the final examples of rapid reactions we may take the elegant work of Ahmed and Wilkins (*107*) on the reactons of Ni(II) with ethylenediamine and related diamines. These reactions were studied in water at 25°C by means of the stopped flow method, though some of the reactions were also studied at 0°C by other techniques. The data are presented in Table XXVI in terms of the rate constants for the dissociation reaction of the mono, bis, and tris complexes. The activation energies, frequency factors, and equilibrium constants are also given. From the equilibrium constants it is possible to calculate the rates of the reverse reaction, for example,

$$[Ni(en)_3]^{++} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Ni(en)_2]^{++} + en \tag{94}$$

the ratio k_2/k_1 is equal to K_3, the third formation constant of nickel(II)en which is equal to 1×10^5. The rate constant for dissociation, k_1 is equal to 89 sec^{-1} at 25°C, whence k_2 is equal to 8.9×10^6 $mole^{-1}$ sec^{-1}.

The most interesting conclusion from Table XXVI is that differences in successive formation constants reside almost entirely in the different

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* *Note added in proof:* H. Taube (private communication) finds a value of 10^4 sec^{-1} in $1M$ acid.

rates of dissociation of the complexes, since the rates of formation are all about the same. It is also of interest that the racemic butylenediamine complexes, which dissociate more slowly than the ethylenediamine complexes, do so because of a low probability or entropy factor and not because of a higher activation energy. This is probably related to solvation effects.

It is of interest to compare the en rates with nickel ion with those obtained for Cu(II) and Co(II) by an NMR technique involving direct measurement of T_1 and T_2 of water protons in solutions containing excess en and the metal ions (*77*). The mechanism for changing the relaxation times is that of exchange of coordinated en with free en in solution. The protons of the newly released en molecule then exchange rapidly with the protons of water. In the case of nickel ion it has been shown (*107*) that the rate of en exchange is the same as the rate of dissociation given in Table XXVI. These rates of exchange are independent of the en concentration in the case of nickel.

TABLE XXVI

KINETIC DATA FOR FIRST-ORDER DISSOCIATION OF NICKEL COMPLEXES IN 0.2M ACID AT 25°C[a]

Species[b]	k_1, sec^{-1}	E_a, kcal	log pZ, sec^{-1}	log K_n
$Ni(en)_3^{++}$	86.6	18.0	15.2	5.0
$Ni(en)_2^{++}$	5.2	19.8	15.3	6.5
$Ni(en)^{++}$	0.15	20.5	14.3	7.6
$Ni(bn)_3^{++}$	8.25	14.6	11.6	4.3
$Ni(bn)_2^{++}$	0.26	16.1	11.2	6.5
$Ni(bn)^{++}$	0.02	18.4	11.8	7.7
$Ni(gly)_3^-$	230[c]	—	—	3.6
$Ni(gly)_2$	21[c]	—	—	4.8
$Ni(gly)^+$	0.5[c]	—	—	5.8

[a] Data from Ahmed and Wilkins (*107*).

[b] en = ethylenediamine, bn = *dl*-butylenediamine, gly = glycine.

[c] At 20°C.

In the case of cobalt(II) the NMR studies (*76*) give a rate of dissociation of 1.3×10^3 sec^{-1} at 25°C for $[Co(en)_3]^{++}$. This is the rate of exchange also and is independent of the en concentration. The number may be compared to that of 86.6 sec^{-1} shown in Table XXVI for $[Ni(en)_3]^{++}$. The case of Cu(II) is quite different in that the exchange reaction is a bimolecular process, the rate being given by

$$\text{Rate} = 2.4 \times 10^7 \text{ mole}^{-1} \text{ sec}^{-1}[\text{en}][\text{Cu(en)}_2^{++}] \tag{95}$$

At reasonable ethylenediamine concentrations, this is much more rapid than either the nickel or cobalt rates. The activation energy for process (95) is 4.5 kcal, which is very low.

The different behavior of copper ion is clearly associated with the lower coordination number and tetragonal structure of copper complexes. The water molecules above and below the plane of $Cu(en)_2^{++}$ can easily be displaced by en molecules acting as unidentate ligands. A rearrangement process then occurs which makes the added en molecule identical with one or both of the en molecules in the plane. Reversal of the process leads to a random loss of en equivalent to exchange. There is a close similarity of this process to the postulated reaction mechanisms of square planar complexes in general (see Section III). Such an S_N2 path probably always accounts for the high lability of Cu(II) complexes.

VI. Metal Carbonyls

In recent years there has been considerable interest in the chemistry of metal carbonyls and substituted metal carbonyls. These compounds are of importance because of the role that some play as catalysts (*124*) and because of their relation to the transition metal organometallics and hydrogen compounds (*38*, *127*). Of primary interest here is the fact that these compounds afford an excellent opportunity for the study of analogous systems having a variety of different coordination numbers and structures. Often it is also possible to study the reactivity of nonequivalent carbon monoxides in the same compound.

A. PHOSPHINE NICKEL CARBONYLS

Nickel tetracarbonyl readily reacts with a variety of reagents, such as phosphines, arsines, pyridine, etc., with the release of two CO's and the formation of $[NiL_2(CO)_2]$. Replacement of the remaining two CO's is possible but much more difficult. Meriwether and Fiene (*73*) have investigated the phosphine exchange kinetics with $[Ni(PR_3)_2(CO)_2]$ and also to a lesser extent the phosphine replacement of carbon monoxide in $[Ni(PR_3)(CO)_3]$. Some of the results reported are shown in Table XXVII. These results show that the reactions

$$[Ni(PR_3)_2(CO)_2] + PR'_3 \underset{k_4}{\overset{k_1}{\rightleftharpoons}} [Ni(PR_3)(PR'_3)(CO)_2] + PR_3 \qquad (96)$$

and

$$[Ni(PR_3)(PR'_3)(CO)_2] + PR'_3 \underset{k_3}{\overset{k_2}{\rightleftharpoons}} [Ni(PR'_3)_2(CO_2] + PR_3 \qquad (97)$$

are first order in complex and zero order in attacking phosphine. Furthermore reactions in acetonitrile as a solvent are only 2–3 times faster than the same reactions in cyclohexane, so that the solvent effect is rather small. It therefore appears that this reaction goes by on S_N1 mechanism.

However, the rate of dissociation of the phosphine ligand from the complex $[Ni(PR_3)_2(CO)_2]$ does depend on the nature of PR_3. Assigning a value of 1 to $P(n\text{-}C_4H_9)_3$, the order of dissociation from the complex decreases as follows: PCl_3 (> 300) $\gg$ $P(CH_2CH_2CN)_3(18.7)$ $\sim$ $P(C_6H_5)_3(17.1)$ $>$ $P(n\text{-}C_4H_9)_3(1.0)$ $\gg$ $P(OC_2H_5)_3$ (< 0.003) $\sim$ $P(OC_6H_5)_3$ (< 0.003). This closely parallels the order of increasing basicity of the phosphines with the exception of the two phosphite complexes, which would be expected to follow PCl_3. Such a result suggests that σ-bonding is relatively more important than is π-bonding to the strength of the Ni—P bond. This is consistent with the observation of Woodward and Hall (*131*) that the force constant for the Ni—P bond in $[Ni(PF_3)_4]$ is in the range expected for single bonds and with the recent conclusions of Chatt and Hart (*22*) based on dipole moment measurements of phosphine nickel carbonyls.

TABLE XXVII

RATES OF REACTION OF SOME PHOSPHINE NICKEL CARBONYLS AT 25.0°C[a]

Complex	PR'_3	Solvent[b]	10^4k_1, sec^{-1} [c]	10^4k_2, sec^{-1} [c]
$[Ni(PCl_3)_2(CO)_2]$	$P(n\text{-}C_4H_9)_3$	C	>100	>100
$[Ni(P(CH_2CH_2CN)_3)_2(CO)_2]$	$P(OC_6H_5)_3$	A	14.2	—
$[Ni(P(CH_2CH_2CN)_3)_2(CO)_2]$	$P(n\text{-}C_4H_9)_3$	A	11.6	2.9[d]
$[Ni(P(C_6H_5)_3)_2(CO)_2]$	$P(n\text{-}C_4H_9)_3$	C	5.3	4.0
$[Ni(P(n\text{-}C_4H_9)_3)_2(CO)_2]$	$P(C_2H_4CN)_3$	A	1.2	—
$[Ni(P(n\text{-}C_4H_9)_3)_2(CO)_2]$	$P(C_6H_5)_3$	C	0.4	<0.01
$[Ni(P(OC_2H_5)_3)_2(CO)_2]$	$P(n\text{-}C_4H_9)_3$	C	<0.001	—
$[Ni(P(OC_6H_5)_3)_2(CO)_2]$	$P(n\text{-}C_4H_9)_3$	C	<0.001	—
$[NiP(C_6H_5)_3(CO)_3]$	$P(C_6H_5)_3$	A	13.4[e]	—
$[NiP(C_6H_5)_3(CO)_3]$	$P(C_6H_5)_3$	C	5.7[e]	—
$[NiP(OC_2H_5)_3(CO)_3]$	$P(n\text{-}C_4H_5)_3$	C	2.8[e]	—

[a] From Meriwether and Fiene (*73*).

[b] A = acetonitrile, C = cyclohexane.

[c] k_1, and k_2 for reactions (95) and (96).

[d] $E_a = 25.5$ kcal/mole and $\Delta S\ddagger = +10.5$ e.u.

[e] k_1 for replacement of CO and formation of $[Ni(Pr_3)_2(CO)_2]$.

B. METAL CARBONYLS

Discounting kinetic studies related to the oxo reaction (*124*), which is not to be discussed here, the relatively few investigations on substitution reactions of metal carbonyls deals with the exchange of carbon monoxide in these systems. Keeley and Johnson (*65*) were the first to make a systematic and extensive study of the rates of exchange of various metal carbonyls and their derivatives with isotopically labelled carbon monoxide in benzene solution. Some of the results they report are shown in Table XXVIII. Also in this table are given the preliminary data on $V(CO)_6$ obtained by Pajaro, Calderazzo, and Ercoli (*86*) and the gas phase exchange they report for $Cr(CO)_6$ (*87*). In addition the exchange measured by Wojcicki (*18*) for the lactone derivative $[Co_2(CO)_7(C_7H_8O_2)]$ is included.

The exchange of radiocarbon monoxide with the simplest first row transition metal carbonyls in solution in the dark is extremely slow at room temperature for $Cr(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$, moderately slow for $V(CO)_6$, and very fast for $Co_2(CO)_8$ and $Ni(CO)_4$. Both $V(CO)_6$ and $CO_2(CO)_8$ are perhaps special cases, the former being paramagnetic (*37*) and the latter having two bridging carbon monoxides. Thus $V(CO)_6$ may exchange more rapidly than $Cr(CO)_6$ because d^5 systems are generally more labile than d^6 and/or because it has only five electrons to contribute in dative π-bonding with carbon, e.g., M=C=O. On the other hand, the reactivity of $Co_2(CO)_8$ may be due to the ease with which bridged cobalts can provide a low-energy exchange path. Except for these two compounds it would appear that the reactivity of these metal carbonyls is related to their coordination number: four-coordinated $Ni(CO)_4$ exchanges rapidly while five- and six-coordinated $Fe(CO)_5$ and $Cr(CO)_6$ exchange very slowly. It is also of interest to note that much the same trend was

TABLE XXVIII
RATES OF CO EXCHANGE WITH SOME METAL CARBONYLS IN BENZENE SOLUTION IN THE DARK AT 25°C[a]

Compound	Concentration (mmole/liter) Carbonyl	CO	Rate, $t_{1/2}$
$V(CO)_6$	22	2 atm.	Slow[b]
$Cr(CO)_6$	—	—	Very slow[c]
$Mn_2(CO)_{10}$	11	2.1	>10 yrs.
$Fe(CO)_5$	49	3.4	>4 yrs.
$Co_2(CO)_8$	5.0	1.4	<5 min.[d]
$Ni(CO)_4$	61	2.3	<4 min.[e]
$CoNO(CO)_3$	28	1.8	19 hr.
$Fe(NO)_2(CO)_2$	78	3.2	325 hr.
$Fe_3(CO)_{12}$	5.8	2.8	350 hr.
$Co_4(CO)_{12}$	5.2	3.0	80 hr.
$Co_2(CO)_7(C_7H_8O_2)$	15	3.0	Fast[f]
$Co_2(CO)_6(C_6H_5CCC_6H_5)$	15	2.3	240 hr.

[a] From Keeley and Johnson (*65*), except as indicated.

[b] At 10° in heptane $t_{1/2}$ — 7 hr, (Pajaro *et al.*, *86*).

[c] Gas phase at 117°C $k = 2 \times 10^{-5}$ sec.$^{-1}$ (Pajaro *et al.*, *87*).

[d] At 0° in toluene $k = 1.5 \times 10^{-3}$ sec^{-1}, $E_a = 16$ kcal/mole and all 8 CO's exchange at the same rate (Basolo and Wojcicki, *18*).

[e] At 0° in toluene $k = 7.5 \times 10^{-4}$ sec^{-1}, $E_a = 13$ kcal/mole.

[f] At 0° in toluene $k = 9 \times 10^{-4}$ sec^{-1}. $E_a = 19$ kcal/mole and all 7 CO's exchange at the same rate (Basolo and Wojcicki, *18*).

observed for the exchange of cyanide with transition metal cyanide complexes (p. 105 in *17*), e.g., $[Cr(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, and $[Co(CN)_6]^{3-}$ exchange slowly, whereas $[Ni(CN)_4]^{=}$, $[Pd(CN)_4]^{=}$, and $[Hg(CN)_4]^{=}$ exchange rapidly. The rapid exchange of $Ni(CN)_4^{=}$, $Pd(CN)_4^{=}$, and $Hg(CN)_4^{=}$ has been attributed to a low-energy bimolecular displacement process. This seems plausible since species of high coordination number such as $[Ni(CN)_5]^{3-}$ and $[Ni(CN)_6]^{4-}$ have been reported (*19*). Still it would be of interest to determine the rate of exchange as a function of cyanide ion concentration by some fast reaction technique.

The results of kinetic studies by Wojcicki (*18*) on the exchange of radiocarbon monoxide with nickel tetracarbonyl in toluene solution show that the exchange rate does not depend on the concentration of carbon monoxide. The first-order rate constant at 0°C is $k = 7.5 \times 10^{-4}$ sec^{-1}. This supports a dissociative path for exchange

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO. \tag{98}$$

Such a process is in accord with the kinetic studies of Garratt and Thompson (*40*) on the thermal decomposition of $Ni(CO)_4$ in the gas phase. They report an activation energy of "somewhat greater than 12 kcal" in good agreement with the value of 13 kcal obtained for exchange in toluene solution. It is also of interest to note that the nickel-phosphine-carbonyls were found to react by a dissociation mechanism.

One can speculate as to why these tetrahedral compounds react by an S_N1 rather than an S_N2 process. First, it should be remembered that unlike tetrahedral carbon compounds, the Ni(0) compounds are d^{10} systems and the filled d orbitals may offer appreciable repulsive interaction to any attacking nucleophilic reagent. Second, the geometry of the d orbitals is such that for a tetrahedral structure only the $d_{x^2-y^2}$ and the d_{z^2} orbitals can efficiently π-bond with the vacated p orbitals on the ligand atom. This means that in $Ni(CO)_4$ there is a total of two π-bonds to distribute among four Ni-C bonds. Kimball (*66*) calculated that there are three strong π-orbitals available for overlap with the ligand atoms in a triangular planar structure (sp^2). Thus the driving force for a dissociative exchange path may be the stabilization effect of π-bonding in the transition state.

Cotton, Fischer, and Wilkinson (*28*) report the enthalpies of the reaction

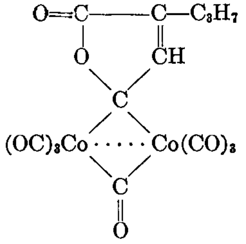
$$M(CO)_{n(g)} \rightarrow M_{(g)} + n(CO)_{(g)} \tag{99}$$

for M = Cr, Fe, and Ni. They calculated average bond energies of 27.1, 27.7, and 35.2 kcal for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ respectively. These values are inconsistent with the observation that the dissociative exchange of $Ni(CO)_4$ is fast whereas that of $Fe(CO)_5$ and $Cr(CO)_6$ is extremely slow. However the above thermochemical data for Eq. (99) are for the ground states of $M_{(g)}$ and $CO_{(g)}$, which means $3d^54s^1$ for Cr, $3d^64s^2$ for Fe and $3d^84s^2$ for Ni. For an S_N1 exchange process, the metal in the transition state is perhaps in about the same valence state as it is in the compound. On this basis values of average bond energies of 57, 60, and 44 kcal for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ respectively were estimated (p. 63 in *17*) assuming valence states of d^6, d^8, and d^{10}, respectively. Because of the uncertainties in these values they should be given only qualitative significance. However this treatment does show that the Ni—C bond is weaker than either the Fe—C or Cr—C bonds in these metal carbonyls. This then is in agreement with their rates of carbon monoxide exchange.

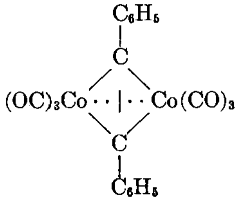
The estimated average bond energy of 44 kcal for the Ni—C bond in $Ni(CO)_4$ is much larger than the activation energy of 13 kcal for carbon monoxide exchange. This can only be understood if the energy required for the rupture of the first Ni—C bond is much less than the average bond energy. There is some chemical evidence to support this. For example, it is known that two of the CO's in $Ni(CO)_4$ are readily replaced to form $Ni(CO)_2L_2$ but that the last two are much less reactive. Such behavior has been explained on the basis that the two π-bonds available to these tetrahedral compounds become largely localized on the Ni—C bonds of the last two CO's. Thus each Ni—C bond in $Ni(CO)_2L_2$ contains essentially a complete π-bond and is stronger than the Ni—C bond in $Ni(CO)_4$, which has only effectively half of a π-bond.

This same π-bonding phenomenon may also explain why the relative rates of the isoelectronic carbonyls decrease in the order $Ni(CO)_4 \gg CoNO(CO)_3 > Fe(NO)_2(CO)_2$. This is the same order as the increase in electron density at the metal which means more dative π-bonding resulting in a greater M—C bond strength.

Data in Table XXVIII show that the rate of carbon monoxide exchange with $Co_2(CO)_8$ and with its lactone derivative $Co_2(CO)_7(C_7H_8O_2)$ is rapid, and recent studies (*18*) show that exchange does not depend on the concentration of CO. This suggests that the exchange proceeds by a dissociative rate-determining path. Such a result is in agreement with the dissociation process proposed (*74*) to account for the absorption of 1 mole of CO by 1 mole of $Co_2(CO)_8$. It was previously suggested (*65*) that exchange in the system $Co_2(CO)_8$-*CO may involve first a rapid equilibration to form two equivalents of the free radical $Co(CO)_4\cdot$, which in turn undergoes a rate-determining S_N2 exchange with *CO. Such a mechanism can be ruled out on two accounts. First, the rate of exchange was found not to depend on the concentration of CO. Second, even if the radical $Co(CO)_4\cdot$ should undergo exchange by a dissociative process, the rate would be proportional to the square root of the concentration of $Co_2(CO)_8$, and not its first power, as was found. Additional evidence against a possible initial dissociation of the dimer into monomer comes from the observation that $Co_2(CO)_7(C_7H_8O_2)$ undergoes exchange at about half the rate of $Co_2(CO)_8$ exchange, and with about the same energy of activation. Mills and Robinson (*75*) have shown that these compounds have only one carbonyl bridge and are lactone derivatives with the structure

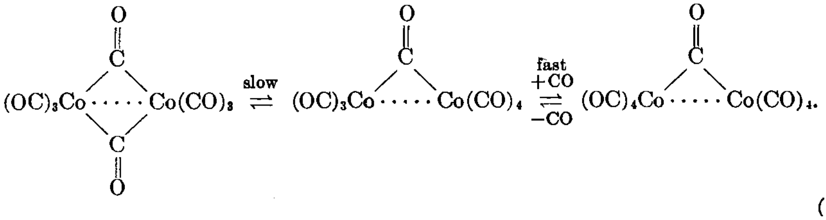


It is difficult to see how such a compound could undergo cleavage to yield reactive monocobalt species. Unlike either of these two cobalt compounds, $Co_2(CO)_9(C_6H_5CCC_6H_5)$ undergoes exchange of $^*CO$ at an extremely slow rate. Sly (*112*) has found that this acetylene derivative has the structure



Therefore it would appear that at least one carbonyl bridge is required for the rapid exchange of CO in these systems.

In keeping with these observations, a possible mechanism may be the following



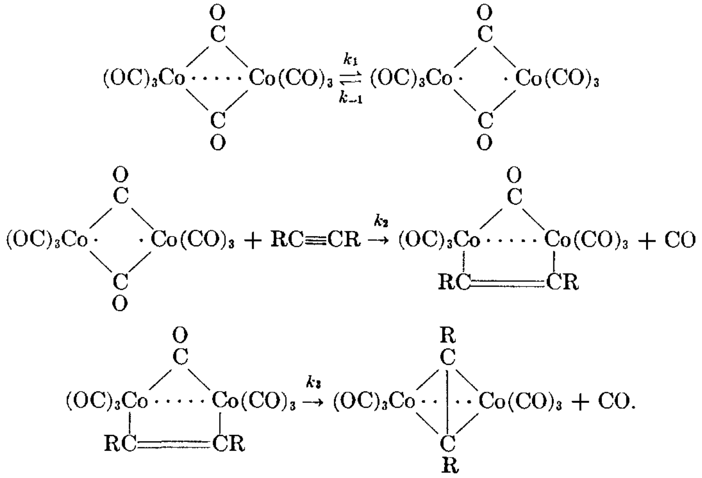
(100)

Since all eight CO's exchange at the same rate, it is necessary that free rotation about the cobalts in the active intermediates be assumed possible.

Somewhat related to this is the reaction of $Co_2(CO)_8$ with hexyne-1 and with hexyne-2,

$$Co_2(CO)_8 + RC\equiv CR \rightarrow Co_2(CO)_6(RCCR) + 2CO. \qquad (101)$$

Tirpak, Wotiz, and Hollingsworth (*120*) investigated the kinetics of this reaction and obtained evidence that in solution the stable form of $Co_2(CO)_8$ is in equilibrium with a less stable form which is the reactive species. Several reaction mechanisms were considered but a mathematical analysis of the kinetic data was in best accord with the scheme



(102)

(103)

(104)

For hexyne-1 the kinetics at 25°C are $k_1 = 1.1 \times 10^{-2}$ sec^{-1}, $(k_{-1} + k_1)/k_2 = 3.6 \times 10^2$ mole liter^{-1}, $k_3 = 8 \times 10^{-3}$ sec^{-1} and E_a for k_1 of 23 kcal mole^{-1}; for hexyne-2 these values are 1.1×10^{-2}, 5.4×10^2 and 5×10^{-3}, respectively. That the value of k_1 is the same for the two reactions is also in agreement with the proposed mechanism. A similar mechanism may likewise be used to explain the exchange of CO with $Co_2(CO)_8$.

Keeley and Johnson (*65*) also report that all twelve CO's in $Co_4(CO)_{12}$ exchange at the same rate. This is said to be in agreement with the observation that the reaction

$$2Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + 4CO \tag{105}$$

occurs at elevated temperatures. However the exchange for $Fe_3(CO)_{12}$ shows that about half the CO's exchange at a rate approximately 5 times faster than the other half. This agrees with the structure assignment of Mills in which there are six terminal CO's and six bridging CO's. It is impossible, of course, to decide from the kinetic data which group of six CO's is exchanging more rapidly. Finally the photochemical reaction

$$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO \tag{106}$$

was investigated in the presence of radiocarbon monoxide. The results show that the incorporation of labeled carbon monoxide into $Fe_2(CO)_9$ is exceedingly small. This suggests that a photodissociation process is not a major reaction path but instead that the reaction sequence is best represented by Eqs. (107) and (108).

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_5^* \tag{107}$$

$$Fe(CO)_5^* + Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO \tag{108}$$

Assuming that the exchange of carbon monoxide with $Fe(CO)_5^*$ is slow, it is apparent that such a process would not introduce $C^{14}O$ into $Fe_2(CO)_9$.

C. Cyclopentadienyl Metal Carbonyls

The exchange of radiocarbon monoxide with cyclopentadienyl metal carbonyls follows the same trend as that with the simplest first row transition metal carbonyls (*129*). The nickel and cobalt compounds, $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$, exchange much faster than the other cyclopentadienyl metal carbonyls investigated, i.e., $(C_5H_5)_2Fe_2(CO)_4$, $C_5H_5Mn(CO)_3$, $(C_5H_5)_2Mo_2(CO)_6$, and $C_5H_5V(CO)_4$ (Table XXIX). The qualitative agreement between the two classes of metal carbonyls with respect to their CO exchange stops, however, at this point. Whereas the exchange in $Ni(CO)_4$ and $Co_2(CO)_8$ was shown to proceed by a dissociative path, the data for $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$ (Table XXX) clearly indicate first-order dependence on the carbon monoxide concentration. Thus a bimolecular, S_N2 mechanism is proposed for the latter reactions.

TABLE XXIX

Rates of CO Exchange with Cyclopentadienyl and Metal Carbonyls[a]

	Concentration (mmole/liter)				
Metal carbonyl	Carbonyl	CO	Solvent	Temp.	Exchange
$(C_5H_5)_2Ni_2(CO)_2$	21–23	0.7–6	Toluene	25°C	Fast[b]
$C_5H_5Co(CO)_2$	26	8	Toluene	0°	Very fast[b]
$(C_5H_5)_2Fe_2(CO)_4$	24	0.5	Chlorobenzene	32°	Slow[c]
$C_5H_5Mn(CO)_3$	45	6	Toluene	32°	Very slow[d]
$CH_3C_5H_4Mn(CO)_3$	66	6	Toluene	32°	Very slow[d]
$(C_5H_5)_2Mo_2(CO)_6$	22	6	Toluene	32°	Very slow[d]
$CH_3C_6H_5Cr(CO)_3$	45	5	Toluene	25°	Very slow[d]
$C_5H_5V(CO)_4$	23	6	Toluene	25°	Very slow[d,e]

[a] From Wojcicki and Basolo (*129*).

[b] For specific rates, see Table XXV.

[c] Solution decomposes slowly. Very slight exchange observed in 4 days.

[d] No detectable exchange in 3 weeks.

[e] Extreme caution is necessary in handling solutions of $C_5H_5V(CO)_4$. Presence of even small traces of air and/or moisture leads to an apparent exchange through decomposition.

It was mentioned earlier that possibly one reason for the dissociative mechanism for the exchange in $Ni(CO)_4$ may be the absence of vacant low-energy orbitals on the nickel. This would render nucleophilic attack of carbon monoxide energetically unfavorable and thus lead to dissociation. In cyclopentadienyl metal carbonyls, the nature of the bonding between carbon monoxide and the metal is essentially similar to that in simple metal carbonyls (*29*). The only difference between the two classes of compounds is a partial replacement of carbon monoxide by the π-cyclopentadienyl ring. Thus any difference in lability and/or mechanism of exchange may perhaps be accounted for in terms of electronic changes resulting from such replacement.

TABLE XXX

RATES OF CO EXCHANGE WITH $C_5H_5Co(CO)_2$ AND WITH $(C_5H_5)_2Ni_2(CO)_2$ IN TOLUENE[a]

Concentration (mmole/liter)				
$C_5H_5Co(CO)_2$	CO	Temp, °C	k, liter mole^{-1} sec^{-1}	E_a, kcal mole^{-1}
25.5	8.5	−33.4	4.1×10^{-4}	16
25.5	2.1	−33.4	4.9×10^{-4}	—
$(C_5H_5)_2Ni_2(CO)_2$	CO	Temp, °C	k, liter mole^{-1} sec^{-1}	E_a, kcal mole^{-1}
22.9	6.2	25	5.3×10^{-2}	20
22.3	2.8	25	6.1×10^{-2}	—

[a] From Wojcicki and Basolo (*129*).

In terms of the simple valence bond treatment of cyclopentadienyl metal carbonyls, the cyclopentadienyl ring is essentially a tridentate ligand, the metal being in the +1 oxidation state (*38*, *127*). All of the π-electrons from the ring interact with vacant 3*d*, 4*s*, and 4*p* orbitals of the metal, thus resulting in an inert gas configuration of the latter. Therefore, according to this theory, the metals in $(C_5H_5)_2Ni_2(CO)_2$ and $Co_2(CO)_8$, as also in $C_5H_5Co(CO)_2$ and $Fe(CO)_5$, are isoelectronic. Such an approach immediately causes some concern in explaining the CO exchange results. Whereas both $Co_2(CO)_8$ and $(C_5H_5)_2Ni_2(CO)_2$ exchange rapidly, the former reacts by dissociation and the latter by a nucleophilic displacement. An even more striking difference is observed with the "isoelectronic" $C_5H_5Co(CO)_2$ and $Fe(CO)_5$. The cobalt compound exchanges very rapidly and by an S_N2 path, the iron compound extremely slowly by an unknown mechanism. These two sets of results are difficult to interpret if one assumes identical electronic structures for the metals.

The results can be explained more readily on the basis of the molecular orbital theory (*38, 127*). Thus the low-lying metal orbitals, i.e., 3*d*, 4*s*, and 4*p*, make some contribution to the bonding, but the extent of this bonding varies somewhat from one compound to another. This then gives rise to empty antibonding orbitals which may be of lower energy and hence more readily accessible to the attacking nucleophile than are the corresponding orbitals in the simple metal carbonyls. Regardless of the electronic structure of the activated complex, the important conclusion that the CO experiments point to is that metal atoms in simple metal carbonyls and those in the corresponding cyclopentadienyl compounds do not appear to be isoelectronic in the true sense of the word. Thus the results support the view that the "inert gas" rule is merely a useful formalism for the prediction of new compounds but it does not always predict their reactivities.

The lability trend shown in Table XXIX can be explained on the basis of a bimolecular mechanism proposed for these compounds. Unfortunately, no quantitative theoretical calculations are available for the bonding in cyclopentadienyl metal carbonyls, so it is possible to offer only a reasonable qualitative explanation. In going from $C_5H_5Co(CO)_2$ to $C_5H_5V(CO)_4$ along the first transition series, the number of carbon monoxide groups increases, thus rendering the central metal ion sterically less accessible. Although such an explanation is plausible, it may deal only with a secondary effect. It is possible that with an increase in the coordination number of the metal, the energy of its lowest available vacant orbital also increases. Finally, the relative strength of the M—CO bond may also be an important factor. It has been shown that the Cr—CO and Fe—CO bonds in the respective carbonyls are stronger than the Ni—CO bond in $Ni(CO)_4$ (*28*). Should this trend also hold for M—CO bonds in cyclopentadienyl metal carbonyls, then a possible explanation for lack of lability in higher-coordinated cyclopentadienyl carbonyls may be sought in terms of the relative bond strengths. In order to evaluate the importance of each of these contributing factors, more thermodynamic and spectroscopic work is required.

D. METAL CARBONYL HALIDES

The metal carbonyl halides that have been investigated by Wojcicki (*130*) are believed to have three different types of structure. The compounds $Mn(CO)_5X$ and $Fe(CO)_4I_2$ are octahedral, $C_5H_5Fe(CO)_2X$ compounds are distorted tetrahedra, and the Rh(I) and Pt(II) compounds are square planar. It is not possible to make a quantitative comparison of rates of exchange for these systems but qualitatively the rates decrease in the order Rh(I) and Pt(II) carbonyls $\gg Fe(CO)_4X_2 \sim Mn(CO)_5X > C_5H_5Fe(CO)_2X$ (Table XXXI). The rapid rate of exchange for the square complexes may suggest a low energy bimolecular displacement path. Unfortunately the exchange was much too fast to permit kinetic studies by this technique so that there is no information on the reaction process. The slow exchange of $C_5H_5Fe(CO)_2X$ may indicate that it behaves more like a six-coordinated system than a sterically accessible distorted tetrahedron.

Three definite conclusions were drawn from the exchange studies on $Mn(CO)_5X$: (i) one CO exchanges more slowly than do the other four; (ii) the rate of CO exchange does not depend on the concentration of CO; and (iii) the rate of CO exchange does depend on ligand X. That four CO's exchange more rapidly than does the fifth is clearly shown in Fig. 17. One possible explanation for this is that the Mn—C bond *trans* to X is stronger than the M—C bond *trans* to CO. This may result from the greater amount of π-bonding of CO compared to X. In d^6 octahedral systems of this type the d_{xy}, d_{xz} and d_{yz} pairs of electrons back donate *via* π-bonding into vacated *p* orbitals of the carbonyl carbons, e.g., M=C=O. Because of the geometry of these orbitals, ligands *trans* to each other compete for the same sets of *d* orbitals. Therefore, the CO *trans* to X is in competition with X and as a result is more π-bonded than it would be if in competition with CO for the *d*-orbital electrons.

TABLE XXXI
RATES OF CO EXCHANGE WITH SOME METAL CARBONYL HALIDES IN TOLUENE AT 31.8°C[a]

	Concentration (mmoles/liter)		
Compound	Compound	CO	k, sec^{-1}
$Mn(CO)_5Cl$	12.6	6.2	3.0×10^{-3} [b]
$Mn(CO)_5Br$	13.3	6.6	1.1×10^{-4} [b]
	15.2	0.85	1.5×10^{-4} [b]
$Mn(CO)_5I$	16.6	6.2	1.3×10^{-5} [b]
$Fe(CO)_4I_2$	23.7	6.6	1.4×10^{-2} [c]
	15.8	0.32	1.8×10^{-2} [c]
$C_5H_5Fe(CO)_2Cl$	33.3	0.28	1×10^{-4} [d]
$C_5H_5Fe(CO)_2Br$	33.3	0.28	5×10^{-6} [d]
$C_5H_5Fe(CO)_2I$	33.3	0.28	2×10^{-7} [d]
$C_5H_5Fe(CO)_2CN$	33.3	0.28	1×10^{-7} [d]
$Rh_2(CO)_4Cl_2$	16.7	2.4	Fast[e]
$Rh(P(C_6H_5)_3)_2COCl$	15.9	0.75	Fast[f]
$Pt_2(CO)_2Cl_4$	18.0	1.2	Fast[g]

[a] From Wojcicki and Basolo (*130*).

[b] Calculated on the basis of the exchange of 4 CO's (Fig. 15).

[c] Second-order reaction so k is in liter $mole^{-1}$ sec^{-1}.

[d] Values are for k apparent.

[e] Exchange complete in less than 3 min at 0°C.

[f] Exchange complete in less than 3 min at −20°C.

[g] Exchange complete in less than 3 min at 25°C.

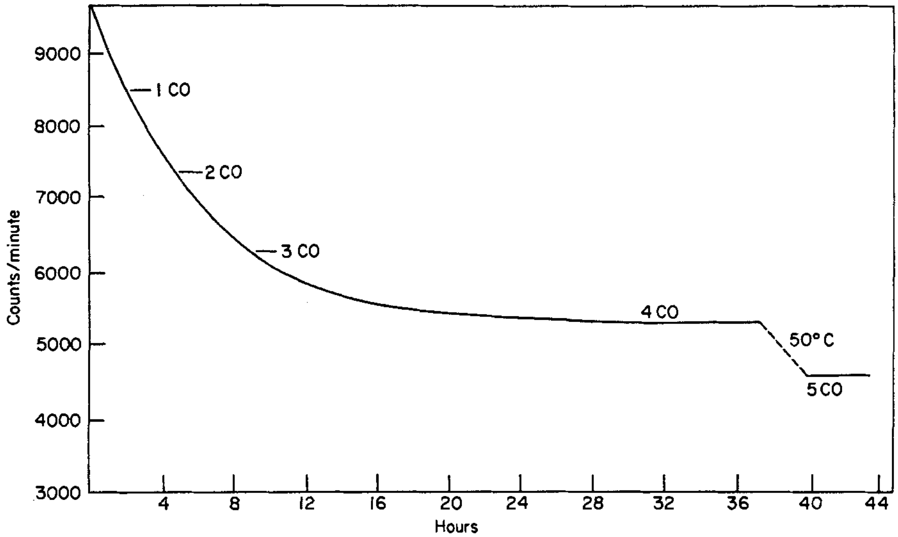
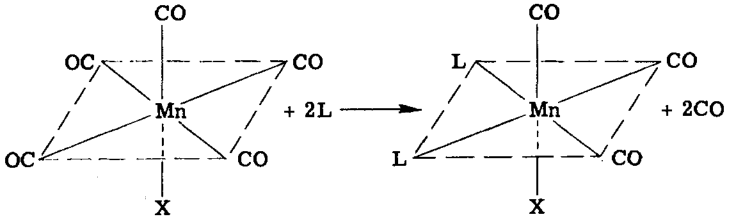


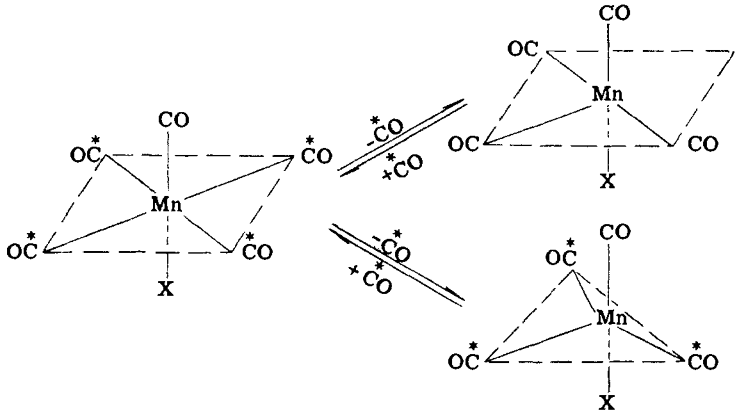
Fig. 17. Rate of CO (6.6 mmole/liter) exchange with $Mn(CO)Br$ (13.3 mmole/liter) in toluene solution at 31.8°C. From Wojcicki and Basolo (*130*).

That there are four reactive CO's in these systems is in agreement with the recent observations of Abel and Wilkinson (*1*). They find that the reaction between $Mn(CO)_5X$ and excess L (where L = amines, phosphines and arsines) takes place as shown in Reaction (109).

 (109)

The *cis* structures were assigned $Mn(CO)_3L_2X$ on the basis of the similarity of the infrared spectra of $Mn(CO)_3(py)_2X$ and $Mn(CO)_3(bipy)X$ (where py = pyridine and bipy = 2,2′-bipyridine). That only two CO's are replaced by L is said to be due to the weaker π-bonding tendency of L compared to CO. Thus the *cis* structure results and the CO's then *trans* to L are more strongly bonded and not readily replaced.

The second point, as shown by the data in Table XXXI, is that the rate of CO exchange does not depend on the concentration of CO. This then means that a dissociation or S_N1 mechanism is involved. The configuration of the 5-coordinated active intermediate is not known, but whatever its structure the inactive CO retains its identity and does not become identical with the other three CO's. This can happen with either a tetragonal pyramid or a trigonal bipyramid intermediate [see Reaction (110)].



(110)

The final point to make on these systems is that the ratio of rates of exchange for $Mn(CO)_5X$ for I:Br:Cl is 1:8:200. This reactivity order may be explained on the basis of the polarizability and/or electronegativity of the halide ions. The bond strength of Mn—C is greater, the greater the π-bonding by back donation of *d* Mn electrons into vacated *p* orbitals of C. This flow of electron density away from Mn is enhanced by a smaller effective positive charge on Mn. Since I^- has the greatest polarizability and smallest electronegativity it renders the Mn least positive and promotes Mn=C=O bonding. Thus, in agreement with experiment, the CO exchange of $Mn(CO)_5I$ is the slowest and that of $Mn(CO)_5Cl$ the fastest. Were it possible to decrease the charge on Mn to zero while maintaining a d^6 octahedral system, the exchange would be expected to be markedly slower. It is of interest to note that the isoelectronic $Cr(CO)_6$, with zero valent Cr, does indeed exchange CO very slowly.

In order to determine further the effect of oxidation state of the metal on the rate of CO exchange in isoelectronic systems, the compound $Fe(CO)_4I_2$ was investigated. This compound is assigned a *cis* structure on the basis of dipole moment measurements (*123*). It is also known (*50*) to react with phosphines, arsines and stibines to yield $Fe(CO)_3LI_2$. In view of the findings with $Mn(CO)_5X$, these results tentatively suggest that the two CO's *trans* to each other will exchange more rapidly than the two *trans* to I.

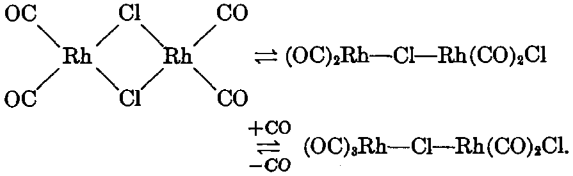
Instead it was found that all four CO's in $Fe(CO)_4I_2$ exchange at the same rate and that the rate of exchange depends on the CO concentration (Table XXXI). These results support a bimolecular, S_N2, exchange process,

$$Fe(CO)_4I_2 + CO \rightleftharpoons Fe(CO)_5I_2 \tag{111}$$

The S_N2 exchange for $Fe(CO)_4I_2$ compared to S_N1 for $Mn(CO)_5I$ may result from the greater positive charge on Fe tending to promote nucleophilic attack. It is significant that $Fe(CO)_5I_2$ has been isolated from the reaction of iodine with iron pentacarbonyl at moderately low temperatures (*49*).

The CO exchange data for $C_5H_5Fe(CO)_2X$ compounds are given in Table XXXI. Because of some decomposition only approximate apparent rate constants are reported. No attempt was made to determine the dependence of rate on the CO concentration. Therefore nothing can be said as to the mechanism of exchange. Since the concentrations of $C_5H_5Fe(CO)_2X$ and of CO were kept constant, it is possible to compare the relative rates of exchange. The data show that for the different X groups CN:I:Br:Cl the ratio of rates are 1:2:50:1000. This is the same order of rate observed for the $Mn(CO)_5X$ compounds but it need not mean that the mechanisms of exchange are the same. A decrease in positive charge on M due to the polarizabilities of X is expected to result in a decrease in rate of CO exchange by either S_N1 or S_N2 mechanism. Since the compounds $C_5H_5Fe(CO)_2X$ are more like $Fe(CO)_4I_2$ than $Mn(CO)_5X$, there is some reason to favor a bimolecular displacement process. Furthermore the CO exchange of some other cyclopentadienyl metal carbonyls has been found to involve an S_N2 process.

Finally the data in Table XXXI also show that the CO exchange in the three square planar compounds investigated is much too fast to study by the technique used. Two of these compounds are dimeric with chloro-bridged structures. The presence of one or more such bridges in a molecule seem to provide a reactive cite. Therefore a possible exchange process may involve the scheme



(112)

Depending on which reaction step is rate determining, the rate of exchange may or may not depend on the CO concentration.

Since $Rh(P(C_6H_5)_3)_2(CO)Cl$ also undergoes CO exchange very rapidly, it is clear that a bridged structure is not required for fast reaction in square planar compounds. In keeping with current theories on substitution reactions in square complexes, it would appear that the rapid rate is due to extensive π-bonding in this system which greatly stabilizes the 5-coordinated transition state. Recent observations (*8*) show that chloride and phosphine exchange are also very rapid. Since the compound

$Rh[P(C_6H_5)_3]_2(CO)(Cl)$ is known to be extremely stable (*122*), these results provide an excellent example of an extremely thermodynamically stable but extremely labile system.

VII. Photochemistry of Metal Complexes*

As a result of the current emphasis on the nature of the metal-ligand bond, according to crystal(ligand) field and molecular orbital theories, considerable information on the absorption spectra of metal complexes has been accumulated and interpreted (see Chapter 2 and pp. 368–375 in *17*). In most cases these systems show two distinct kinds of light absorption. The high-intensity bands in the ultraviolet region are attributed to electron transfer and it might therefore be expected that light absorption in this region should lead to oxidation-reduction processes. On the other hand, the low-intensity bands, usually in the visible region for the first row transition metal complexes, involve transitions between 3*d* levels whose degeneracy has been partially removed by the ligand field. For an octahedral field, the d_{xy}, d_{xz} and d_{yz} orbitals, whose electron density is directed away from the ligand positions, are lowered in energy relative to the d_{z^2} and $d_{x^2-y^2}$ orbitals, whose electron density is directed toward ligand positions. Thus, the light absorption in this region is believed to involve promotion of an electron from a T_{2g} to an E_{2g} state. Since this places an electron nearer a ligand positon, it is expected to lead to a repulsion between the ligand and the metal ion and therefore to enhance a substitution process.

Although the general photosensitivity of metal complexes has long been known, only a scattering of quantitative observations had been reported. Recently, both Adamson (*6*) and Plane (*94*) and their respective co-workers have commenced a systematic investigation of the photochemistry of metal complexes. It is as yet too early to attempt any definitive interpretation of their findings, but it is of interest to present some of the experimental results and the different mechanisms proposed to explain them.

Some of the results reported for the photochemical reactions of aqueous solutions of certain Co(III) complexes are given in Table XXXII, and for complexes of Cr(III) in Table XXXIII. It is immediately apparent that the two systems differ markedly; photochemical reactions of Co(III) complexes are often redox processes, whereas for Cr(III) complexes only substitution reactions are observed. This difference is probably due to the greater ease of reduction of Co(III) to Co(II) relative to the reduction of Cr(III) to Cr(II). There is some evidence in the case of Co(III) complexes

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* *Note added in proof:* The photochemical dissociation of $[Mo(CN)_8]^{4-}$ $[W(CN)_8]^{4-}$ and $[Fe(CN)_6]^{4-}$ in aqueous solution have been studied in some detail by V. Carassiti *et al.* [*Ann. chim.* **49,** 1697 (1959); **50,** 630, 645, 782, 790 (1960).]

that absorption in the electron transfer band region leads to redox reactions, whereas absorption in the ligand field band leads to substitution reactions. For example, the ratio of substitution/redox for $[Co(NH_3)_5NCS]^{++}$ is 0.47 for light of 370 mμ and 4.1 for light of 550 mμ. However, redox reactions do result from light absorption in the ligand field band region provided that an easily oxidizable ligand is attached to the metal ion, e.g., $[Co(NH_3)_5I]^{++}$.

TABLE XXXII

PHOTOCHEMICAL REACTIONS OF SOME COBALT(III) COMPLEXES[a]

Complex	Wavelength irrad., mμ	Product	Quantum yield, ϕ
$[Co(NH_3)_6]^{3+}$	370	No reaction	—
$[Co(NH_3)_5Cl]^{++}$	370	$[Co(NH_3)_5H_2O]^{3+}$	0.05
	550	$[Co(NH_3)_5H_2O]^{3+}$	0.007
$[Co(NH_3)_5I]^{++}$	370	Co(II), I_2	3.0
	550	Co(II), I_2	0.5
$[Co(NH_3)_5NCS]^{++}$	370	$[Co(NH_3)_5H_2O]^{3+}/Co^{++} = 0.47$	0.3
	550	$[Co(NH_3)_5H_2O]^{3+}/Co^{++} = 4.1$	0.003
$[Co(CN)_6]^{3-}$	370	$[Co(CN)_5H_2O]^-$	0.9
$[Co(CN)_5Cl]^{3-}$	370	$[Co(CN)_5H_2O]^-$	0.3
$[Co(CN)_5Br]^{3-}$	370	$[Co(CN)_5H_2O]^-$	0.7
$[Co(CN)_5I]^{3-}$	370	$[Co(CN)_5H_2O]^-$	0.95
	550	$[Co(CN)_5H_2O]^-$	0.7
$[Co(C_2O_4)_3]^{3-}$	370	Co(II), CO_2	1.0
	550	Co(II), CO_2	0.007
l-$[Co(C_2O_4)_3]^{3-}$	550	No photoracemization	—

[a] From Adamson and Sporer (*6*).

For the series $[Co(CN)_5X]^{3-}$, the quantum yields for hydrolysis decrease in the order I > CN > Br > Cl. This is not the order of the spectrochemical series, as might be expected if the primary act were an ionic fission, but is the order of increasing difficulty of oxidation of the ligand. This suggests that the primary act is a homolytic fission, even though the final product is an aquo complex and light absorption is of the ligand field type.

Adamson and Sporer (*6*) explain these observations on the basis of a three-stage process. For the first stage, it is supposed that the immediate consequence of light absorption is a homolytic fission.

$$[M(III)A_5X] + h\nu \rightarrow\rightarrow [M(II)A_5 \cdot X] + \Delta. \quad (113)$$

In Eq. (113), Δ represents excess energy and the double arrow is used to indicate that there may be intervening states between the primary excited state and that in which bond fission occurs, the essential assumption being the $[M(II)A_5{\cdot}X]$ is the common precursor to species formed subsequently.

In the second stage it is suggested that the precursor can either return to the original complex

$$[M(II)A_5 \cdot X] \rightarrow [M(III)A_5X] + \Delta' \tag{114}$$

or interact with the solvent water

$$[M(II)A_5 \cdot X] + H_2O \rightarrow [M(III)A_5(H_2O) \cdot X]. \tag{115}$$

Reaction (114) is favored if Δ is small, whereas the partial M—X separation of (115) is favored if Δ is large. The third stage then has to do with the fate of $[M(II)A_5(H_2O) \cdot X]$ and determines the course of the net chemical reaction. If electron transfer is energetically favorable and can take place with high frequency, then the electron is returned from $M(II) \rightarrow \cdot X$ and hydrolysis occurs.

$$[M(II)A_5(H_2O) \cdot X] \rightarrow [M(III)A_5H_2O] + X^- \tag{116}$$

However, if the separation of the homolytic fission products continues then this leads to a redox reaction.

$$[M(II)A_5(H_2O) \cdot X] \rightarrow M(II) + 5A + X^- \tag{117}$$

Although photochemical redox reactions were not observed for Cr(III) complexes, Adamson suggests that the first and second stage processes are still involved but that the third stage goes entirely by reaction (116).

TABLE XXXIII
PHOTOCHEMICAL REACTIONS OF SOME CHROMIUM(III) COMPLEXES[a]

Complex	Wavelength irrad. mμ	Product	Quantum yield, ϕ
$[Cr(H_2O)_6]^{3+}$	254	O^{18} exchange	0.03
	540–730	O^{18} exchange	0.02
$[Cr(NH_3)_6]^{3+}$	254	$[Cr(NH_3)_5H_2O]^{3+}$	0.49
	320–600	$[Cr(NH_3)_5H_2O]^{3+}$	0.32
$[Cr(NH_3)_5H_2O]^{++}$	320–600	$[Cr(NH_3)_4(H_2O)_2]^{3+}$	0.25
$[Cr(NH_3)_5NCS]^{++}$	560	$[Cr(NH_3)_5H_2O]^{3+}$	0.013
	360	$[Cr(NH_3)_5H_2O]^{3+}$	0.018
$[Cr(NH_3)_5H_2O]^{3+}$	560	$[Cr(NH_3)_5NCS]^{++}$	0.075
$[Cr(H_2O)_6]^{3+}$	575	$[Cr(H_2O)_5NCS]^{++}$	0.002
	400	$[Cr(H_2O)_5NCS]^{++}$	0.0024
$[Cr(H_2O)_5NCS]^{++}$	575	$[Cr(H_2O)_6]^{3+}$	0.0001
	400	$[Cr(H_2O)_6]^{3+}$	0.003
$[Cr(H_2O)_6]^{3+}$	370	$[Cr(H_2O)_5Cl]^{++}$	0.006

[a] From Adamson and Sporer (*6*), and Plane *et al.* (*94*).

Alternatively, Plane and Hunt (*94*) and Edelson and Plane (*94*) explain the photosubstitution reactions of Cr(III) complexes in terms of a mechanism involving reaction while the species is in its lowest spin-forbidden (doublet) electronic state. That the species in the doublet state should be more reactive than in the ground state is consistent with the observation that complexes having at least one vacant d_{2g} orbital are labile. The importance of the available orbital compared to the repulsion owing to a single electron in a d_{eg} orbital can be seen by comparing the photochemical behavior of $[Cr(NH_3)_6]^{3+}$ with that of $[Co(NH_3)_6]^{3+}$. In the latter case, despite the presence of a low-lying spin-forbidden (triplet) state, there is no appreciable photochemical hydrolysis.

The quantum yields for the photochemical hydrolysis of $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5H_2O]^{3+}$ are higher, and do not show the temperature dependence for water exchange, compared to $[Cr(H_2O)_6]^{3+}$. This difference in quantum yield was explained on the basis that the spacing of the doublet is relatively close to the lowest quartet state for $[Cr(H_2O)_6]^{++}$, thus thermal energy may return the molecule to the quartet state from which internal conversion can take it to the ground state prior to chemical reaction. The ammines differ in that there is a wide enough separation so that the doublet state persists until the molecule is deactivated by collisions with solvent molecules.

Adamson (*6*) has investigated, in some detail, the photosubstitution reactions

$$[Cr(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Cr(H_2O)_5NCS]^{++} + H_2O \qquad (118)$$

and

$$[Cr(NH_3)_5H_2O]^{3+} + SCN^- \rightleftharpoons [Cr(NH_3)_5NCS]^{++} + H_2O. \qquad (119)$$

Some of the results reported are shown in Table XXXIII. The forward reactions (118) and (119) are second order and it was suggested that the reactions involve formation of ion pairs followed by a photochemical outer-inner sphere exchange of ligands.

Stranks and Weston (*117*) report that the exchange of urea (Ur) with $[Cr(Ur)_6]^{3+}$ is photocatalyzed. The photoexchange has quantum yields, ϕ, of 0.020 at 254, 436, and 589 mμ and E_a for ϕ is 19 kcal/mole at all three wavelengths. Photosolvolysis of $[Cr(Ur)_6]^{3+}$ to $[Cr(Ur)_5S]^{3+}$ in methanol exhibits $\phi \sim 0.15$ at the three wavelengths but the temperature dependence does not seem to exceed 5 kcal/mole.

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