Translated from *Uspekhi Khimii*, **43**, 707-726 (1974) U.D.C. 541.124:547.172.547.312.542.938

Hydrolysis of Alkyl Halides Induced by Metal Ions: M^+-S_N1 and M^+-S_N2† Reactions

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Investigations of the kinetics, mechanism, and driving forces of hydrolyses of alkyl halides and several inorganic halides, induced by metal ions M^+ in aqueous media, are summarised. Relations between the rate and the Lewis acidity of M^+ are examined, together with models of M^+-S_N1 and M^+-S_N2 reactions. A list of 163 references is included.

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I. INTRODUCTION

The ability of silver(I) and mercury(II) ions and of certain complexes to accelerate substitution in organic and inorganic halides is well known. The early work was briefly surveyed in monographs [1-3]. In 1937 Roberts and Hammett [4] suggested that a correlation, similar to the Brønsted relation [5,6] for general acid catalysis, may exist between the rates of such reactions and the Lewis acidities of the electrophiles. This question was investigated systematically [7-9] during 1967-1972 on the hydrolysis, induced by metal ions M^+, of alkyl halides of Ingold's classic α-series [1]

$$H_2O + RX + M^+ \rightarrow H^+ + ROH + XM \qquad (1)$$

(R = CH_3, C_2H_5, iso-C_3H_7, t-C_4H_9; X = F, Cl, Br, I). As a consequence of the affinity of X for M the entry of RX into the coordination sphere of M^+ promotes heterolysis of the C-X bond (M^+-S_N1 mechanism) and reactions with a nucleophile (M^+-S_N2 mechanism). The Review is concerned mainly with reactions in aqueous media. Water is more convenient than the non-aqueous and anhydrous media generally used: the kinetics is less complicated by ionic association, extrapolation to zero ionic strength is more reliable, and ample information is available on the stability of the MX complexes [10]. The present Review deals with the kinetics and the mechanism of these reactions, the role of the structure of R, X, M^+, and the medium, the validity of correlations of the Brønsted type, and fine distinctions between the correlations for M^+-S_N1 and M^+-S_N2 mechanisms. For generality reactions of inorganic halides which might have an M^+-S_N1 mechanism are also considered.

II. ROLE OF METAL IONS IN THE HYDROLYSIS OF t-BUTYL HALIDES—CORRELATION BETWEEN RATE AND LEWIS ACIDITY OF M^+

The solvolysis of t-butyl chloride is accelerated by silver salts in acetone [11] and by mercury(II)chloride in aqueous ethanol and in acetone [12-14], while hydrogen exchange between the t-butyl group and the solvent in acetic deutero-acid is accelerated by chlorides in the sequence [15]

antimony(V) > iron(III) > tin(IV) > zinc(II) > mercury(II).

Alkali-metal ions are inactive in the hydrolysis of t-butyl chloride [16]. Detailed studies have been made of the effects of other ions in the hydrolysis of t-butyl fluoride, chloride, and bromide in aqueous media [7,17-27] (Table 1). At constant ionic strength μ the kinetics of the hydrolysis is represented by the equation [18]

$$k \equiv \frac{1}{[RX]}\frac{d[RX]}{d\tau} = k_0 + k_1[M^+] \qquad (2)$$

where k_0 corresponds to the reaction with the solvent, and k_1 to that with the M^+ ion.

The activity of the ions corresponds to the concept of "hard" and "soft" acids and bases [28]. The "hard" acids—Zr^{4+}, Th^{4+}, Sc^{3+}, Al^{3+}, etc.—are active with t-butyl fluoride (detachment of the "hard" base F^-). The activity increases with decrease in the atomic number within a subgroup of the Periodic System: e.g. $In^{3+} < Ga^{3+} < Al^{3+}$; $La^{3+} < Y^{3+} < Sc^{3+}$; and $Sr^{2+} < Mg^{2+} < Be^{2+}$. "Soft" Lewis acids are active with t-butyl chloride and bromide, and k_1 increases with increase in atomic number within a subgroup: $Hg^{2+} > Cd^{2+} > Zn^{2+}$; $Tl^{3+} > Ln^{3+} > Ga^{3+} > Al^{3+}$; $Pd^{2+} > Ni^{2+}$.

A clear relation exists between k_1 and the stability constant $K_{MX} = [MX]/[M^+][X^-]$ of the complex MX: [17,20,21]

$$\lg k_1 = A_X + \beta \lg K_{MX} \qquad (3)$$

For each X = F, Cl, Br the activity of M^+ is higher the greater the Lewis acidity of M^+. The activity series of the metals follow the variations in K_{MX}, and are different for X = F from those for X = Cl, Br. Thus Al^{3+} is active with the fluoride and relatively inactive with the chloride. The opposite situation is found for the silver ion. The independent terms A_X in Eqn. (3) are different for X = F, Cl, Br, but all the lines have roughly the same slope β. As was to be expected for reactions of acid–base type, the electronic structure (completeness of the electron shell) of the metal ions does not influence their effectiveness in the hydrolysis of alkyl halides. The acid hydrolysis ($M^+ = H^+$) of t-butyl fluoride has also been studied [21]. The nature of the anion (A = NO_3^- or ClO_4^-) does not affect the value of $k_1 = k/[H^+]$ extrapolated to $\mu = 0$ (for $\lg k_1$ varies

†Usage of the symbol "M^+" in this paper follows that of the original Russian, and does not necessarily imply "unit" positive charge: M^{n+} would have been more explicit (Ed. of Translation).

linearly with [HA])[24]. The same information is conveyed[21] by the Hammett equations: $\lg k = -1.14H_0 - 3.61$ (for perchloric acid) and $\lg k = -1.06H_0 - 3.72$ (for nitric acid), where H_0 is the acidity function. The value of k_1 for H^+ corresponds to the great stability of the complex HF, and is consistent with the general correlation (3).[26] Hydrogen chloride is significantly less stable[10]. Therefore the contribution of H^+ to the hydrolysis of t-butyl chloride becomes appreciable only in concentrated acids, e.g. perchloric acid[29].

Table 1. Stability of complexes MX and rates of M^+–S_N1 hydrolysis of t-C_4H_9X (values of K_{MX} and k_1 extrapolated to $\mu = 0$).

No.	Ion	$\lg(K_{MX}, M^{-1})$	$\lg(k_1, M^{-1}s^{-1})$ expt.	$\lg(k_1, M^{-1}s^{-1})$ calc. from Eqn.(12)
	t-butyl fluoride (aqueous solution at 25°C, effect of M^{+a}, $\lg(k_0, s^{-1}) = -6.50$) (Ref.22)			
1	Zr^{4+}	9.8±0.2	+0.7±0.3 [21]	+1.0
2	Th^{4+}	8.8±0.1	−0.2±0.3 [21]	0.0
3	Sc^{3+}	7.1±0.1	−1.16±0.1 [26]	−1.2
4	Al^{3+}	7.0±0.1	−1.70±0.1 [26]	−1.4
5	Fe^{3+}	6.1±0.1	−1.92±0.2 [26]	−2.2
6	Be^{2+}	5.6±0.1	−2.02±0.1 [26]	−2.2
7	Ga^{3+}	5.6±0.2	−2.4±0.3 [21]	−2.7
8	Cr^{3+}	5.2±0.1	<−5.0 [26]	−3.1
9	Y^{3+}	4.8±0.1	−3.7±0.3 [21]	−3.4
10	In^{3+}	4.6±0.1	−3.4±0.3 [21]	−3.6
11	H^+	3.3±0.1	−3.74±0.1 [24]	−3.9
12	La^{3+}	3.6±0.1	−4.4±0.2 [26]	−4.6
13	Mg^{2+}	1.8±0.1	−5.9±0.2 [22]	−5.9
14	Zn^{2+}	1.3±0.1	−6.1±0.2 [26]	−6.4
15	Cd^{2+}	1.1±0.1	−6.3±0.2 [26]	−6.5
	t-butyl chloride (31.9 wt.% C_2H_5OH–H_2O at 25°C, effect of M^{+b}, $\lg(k_0, s^{-1}) = -2.70$) (Ref.17)			
16	Hg^{2+}	7.6±0.2	>0	+3.7
17	Tl^{3+}	8.5±0.3	>0	+3.9
18	Ag^+	3.5±0.2	0.0±0.2	+0.2
19	Bi^{3+}	3.6±0.3	−1.0±0.1	−0.9
20	Cd^{2+}	2.3±0.2	−1.8±0.1	−1.7
21	In^{3+}	3.2±0.5	−1.5±0.1	−1.4
22	Pb^{2+}	1.8±0.2	−2.2±0.1	−2.1
23	Mn^{2+}	0.9±0.3	−3.1±0.3	−3.1
24	Tl^+	0.8±0.2	−3.0±0.3	−2.5
25	Co^{2+}	0.6±0.2	−3.0±0.2	−3.4
26	Cu^{2+}	0.6±0.4	−3.3±0.3	−3.4
	t-butyl bromide (44.6 wt.% C_2H_5OH–H_2O at 20°C, effect of M^{+c}, $\lg(k_0, s^{-1}) = -2.16$) (Ref.27)			
27	Cd^{2+}	2.7±0.2	−1.2±0.1	−0.9
28	Pb^{2+}	2.5±0.3	−1.4±0.1	−1.0
29	Zn^{2+}	0.4±0.3	−2.5±0.3	−3.2
30	Co^{2+}	0.9±0.3	−2.3±0.3	−2.7
31	Ni^{2+}	0.9±0.3	−2.7±0.3	−2.7
32	Cu^{2+}	0.5±0.2	−2.7±0.3	−3.1

[a]The theoretical equation for this system is $\lg(k_1/k_0K_{MX})_{theor} = -3.1Z_M/(4.5 + r_M)$, where Z_M and r_M are the charge and the radius of M^+ (in Å)(see Section III).
[b]Theoretical equation $\lg(k_1/k_0K_{MX})_{theor} = -4.1Z_M/(5.4 + r_M)$.
[c]Theoretical equation $\lg(k_1/k_0K_{MX})_{theor} = -4.6Z_M/(5.7 + r_M)$.

An important exception to the correlation (3) has been established[26] for the Cr^{3+} ion, which is inert in the hydrolysis of t-butyl fluoride despite the great stability of CrF^{2+}. Since $[Cr(H_2O)_6]^{3+}$ has an abnormally low rate of exchange of the aquo-ligands $k_{exch} = 10^{-6}$ s^{-1},[28,30] this exception indicates inner-sphere coordination in the interaction of RX with M^+, and hindrance to M^+–S_N1 reactions, when the ion is not accessible to direct contact with the substrate. Rates of exchange are high in the case of other metal ions[28,30], and departures from correlations (3) are not observed.

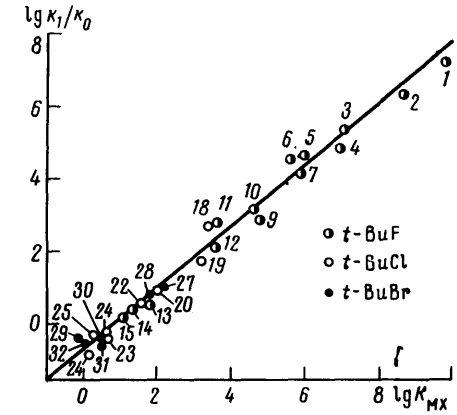


Figure 1. Dependence of $\lg(k_1/k_0)$ on $\lg K_{MX}$ for the hydrolysis of t-butyl halides in the presence of aquo-ions of metals. The numbering and the characteristics of the systems are given in Table 1.

Table 2. Effect of composition of aqueous ethanolic solvent on rate of reaction between t-C_4H_9Cl and Cd^{2+} at 25°C.[8]

C_2H_5OH, wt.%	D	$\lg K_{MX}$	$\lg k_1$, expt.	$\lg k_1$* calc. from Eqn.(12)
30.0	61.1	2.5	−1.7±0.1 [19]	−1.3
35.0	58.1	2.6	−2.0±0.1 [19]	−1.6
40.0	55.0	2.7	−2.2±0.1 [19]	−1.9
49.7	49.2	2.9	−2.4±0.1 [27]	−2.3
64.7	40.9	3.4	−3.0±0.2 [27]	−2.9

*Theoretical equation $\lg(k_1/k_0K_{MX})_{theor} = -76/D$.

Plots of k_1/k_0 against K_{MX}, both taken at zero ionic strength, merge into a single line for different t-butyl halides (Fig. 1). This leads to a correlation of great generality

$$\lg k_1/k_0 = -0.7 + 0.84 \lg K_{MX} \quad (4)$$

which allows for the effects of both M^+ and X.[7,23] Equation (4) represents also the effects of the solvent for the reactions of t-butyl chloride with Cd^{2+} in aqueous alcohol (Table 2) and is applicable to the reaction in nitromethane[23]

$$t\text{-}C_4H_9Cl + HCl \rightarrow t\text{-}C_4H_9^+ + HCl_2^-.$$

In the latter case the electrophile is an uncharged hydrogen chloride molecule, and values of k_1, k_0, and $K_{MX} = [HCl_2^-]/[HCl][Cl^-]$ were estimated[23] from published data[31]. Catalysis is clearly developed in aprotic media: the lithium ion accelerates heterolysis of triphenylmethyl chloride in diethyl ether[32] and of diphenylmethyl chloride in 70% dioxan[27].

No detailed study has been made of the reaction products formed from t-butyl halides and metal ions. The yield of isobutene in the hydrolysis of t-butyl fluoride falls[27] in parallel with increase in the contribution of $k_1[M^+]$ to the total rate $k_0 + k_1[M^+]$. Reaction with strong electrophiles M^+, in contrast to reaction with the solvent, is evidently not accompanied by elimination. The proportion of elimination decreases in the reactions of other alkyl halides with the silver ion[33,34].

III. MODELS OF M^+–S_N1 REACTIONS

According to Ingold[1] t-butyl halides (fluoride, chloride, bromide, and iodide) are hydrolysed by an S_N1 mechanism owing to the enhanced stability of $(CH_3)_3C^+$, in comparison with e.g. CH_3^+, $C_2H_5^+$, iso-$C_3H_7^+$, and steric hindrance to nucleophilic attack at the carbonium centre. The above results show that an S_N1 mechanism is maintained even with induced reactions. The M^+–S_N1 and S_N1 mechanisms differ in the replacement of a solvent molecule in the solvate sheath of the transition state by an M^+ ion having a higher affinity for X^-, and in the quantitative characterisation of the participation of the electrophile in the M^+–S_N1 reaction by the order and the rate constant of the reaction with M^+.

The fundamental model of an M^+–S_N1 reaction[20] is represented by the scheme

$$\begin{array}{lccccccc} & (a) & & (b) & & & (c) & \\ A & RX & \xrightarrow{K_0^{\neq}} & R^{\delta+} \ldots X^{\delta-} & \ldots & S \xrightarrow{kT/h} & R^+ + X^- & \\ & {\scriptstyle M^+}\downarrow\uparrow{\scriptstyle K_{gr.}} & & \downarrow\uparrow K_{tr.} & & & & \\ B & RX \ldots M^+ & \xrightarrow{K^{\neq}} & R^{\delta+} \ldots X^{\delta-} & \ldots M^+ & \xrightarrow{kT/h} & R^+ + XM. & (5) \\ & (d) & & (e) & & & (f) & \end{array}$$

Route A comprises a slow stage of S_N1 solvolysis of RX by the solvent S, involving an activation equilibrium $(a \rightarrow b)$ and breakdown of the transition state $(b \rightarrow c)$ at a rate kT/h.[35] Formation of the complex (d) gives rise to an induced reaction (route B). The activation equilibrium constants are denoted by $K_0^{\neq}$ and $K^{\neq}$, and the equilibrium constant of formation of the complex in the ground state is

$$K_{gr.} = [RX \ldots M^+]/[RX][M^+] \quad . \qquad (6)$$

This mechanism leads to the equation

$$k = \frac{k_0 + k_1[M^+]}{1 + K_{gr.}[M^+]} \quad , \qquad (7)$$

which is well known for such reactions[19,20]; it simplifies to (2) when $K_{gr}[M^+] \ll 1$.

Formulation of the principle of equilibrium solvation of the transition state in S_N1 reactions[36] led to the concept of the equilibrium constant of transition states for M^+–S_N1 and S_N1 reactions. From the chain of equilibria $(b) \rightleftharpoons (a) \rightleftharpoons (d) \rightleftharpoons (e)$ (Eqn. 5) it may be concluded that the transition states (b) and (e) are in equilibrium in the sense that they appear simultaneously and in proportions corresponding to the equilibrium constant (8a)

$$K_{tr.} = \frac{[R^{\delta+}X^{\delta-}M^+]}{[R^{\delta+}X^{\delta-}][M^+]} \quad (8a), \qquad K_{MX} = \frac{[MX]}{[M^+][X^-]} \quad . \qquad (8b)$$

The species $R^{\delta+} \ldots X^{\delta-} \ldots M^+$ can be regarded as the equilibrium solvate (complex) $R^{\delta+} \ldots X^{\delta-}$ together with M^+, where the latter is regarded as a constituent of the medium. The numerical value of K_{tr} is determined directly from kinetic data[19,20].

$$K_{tr.} = K_{gr.}K^{\neq}/K_0^{\neq} = k_1/k_0 \quad . \qquad (9)$$

A quantity similar to K_{tr} has been discussed by other authors[37]. Several consequences follow from a comparison[20] of formulae (8a) and (8b): (i) since the parameters K_{tr} and K_{MX} have the same dimensions (M^{-1}) and are described by similar expressions, the relation between them should be more general than the correlation (3) between k_1 and K_{MX}; furthermore, (ii) K_{tr} and K_{MX} depend differently on the ionic strength, so that values of $K_{tr} = k_1/k_0$ and of K_{MX}, all extrapolated to zero ionic strength, should be used for the correlation. As shown above (Fig. 1) these conclusions agree with experiment. For all the systems studied the numerical values of

$$k_1/k_0 \leq K_{MX} \quad , \qquad (10)$$

which is understandable, since the energy of interaction of M^+ is smaller with the transition state $R^{\delta+} \ldots X^{\delta-}$ than with X^-.

The slope of the Brønsted correlation $\lg k = A + \beta \lg K$ usually indicates[38–41] the position of the transition state on the reaction coordinate: the structure of the transition state resembles either the final or the initial state according as $\beta = 1$ or 0. It is implied that $0 \leq \beta \leq 1$, but there are exceptions[42–47]. Charge separation is nearly complete in S_N1 reactions, so that it is reasonable that the slope of line (4) is close to unity. However, the numerical coincidence[23] of $\beta = 0.84$ and $\delta = 0.8$ [16,48,49] for the transition state in the hydrolysis of t-butyl chloride is probably fortuitous.

A quantitative model has recently been suggested[8] for an M^+–S_N1 reaction. Complete separation of charges ($\delta = 1$, Eqn. 5) is assumed for the transition states—the intimate ion-pair $R^+ \ldots X^-$ for reactions with the solvent, and the trio $R^+ \ldots X^- \ldots M^+$ for those with M^+. Solvation is discussed in terms of a simple coordination model on the assumption that the coordination number of the ion and the energy of local interaction between the ion and a molecule of the medium are the same whether the ion is isolated or present in a pair or in a trio. This applies also to the $M^+ \ldots X^-$ bond energy in the trio and in the complex MX. On these hypotheses the equilibrium constant of disproportionation of the ion-pairs

$$\begin{array}{ccccccc} {\scriptstyle (b)} & & {\scriptstyle (f)} & & {\scriptstyle (e)} & & {\scriptstyle (c)} \\ R^+ \ldots X^- & + & X^- \ldots M^+ & \overset{K}{\rightleftarrows} & R^+ \ldots X^- \ldots M^+ & + & X^- \end{array} \quad , \qquad (11)$$

which from Eqns. (8a), (8b), and (9) is given by $K = k_1/k_0k_{MX}$, is independent of solvation interactions and is determined solely by intramolecular Coulombic interactions. The complete equation

$$\lg k_1 = \lg k_0 + \lg K_{MX} - \frac{Ne^2Z_RZ_M}{2.303RTDl_{R-M}} \qquad (12)$$

includes a Coulombic term allowing for destabilisation of the transition state[8] due to repulsion of the outer groups R^+ and M^+ in the trio $(e$, Eqn. 5). The symbol N in Eqn. (12) denotes Avogadro's number, e is the charge on the electron, Z_R and Z_M are the charges on R and M, and

$$l_{R-M} = r_M + 2r_X + r_R -$$

is the distance between R and M defined in terms of the crystallographic radii of the ions r_i. With the complex structure of R and M taken into account the Coulombic term becomes

$$\left(-\frac{Ne^2}{2.303RTD}\sum_{i \neq j}\frac{Z_iZ_j}{l_{ij}}\right) \quad ,$$

where i and j denotes the local charges in R and M respectively.

Several important consequences follow from the theory. According to (12) the parameter k_1 is strictly proportional to k_0 and K_{MX}, and depends also on the parameters of the transition states Z_R, Z_M, and l_{R-M}. This opens up a path for studying the structure of transition states from kinetic and thermodynamic data. It is significant that the effects of reactants and reaction conditions are transmitted to k_1 along many channels: thus change in M^+ influences k_1 through K_{MX}, Z_M, and l_{R-M}; variation in X through k_0, K_{MX}, and l_{R-M}; and changes in the medium through k_0, K_{MX}, and D. It follows from (12) that

$$E_1 = E_0 + \Delta H_{MX} + \frac{Ne^2 Z_R Z_M}{l_{R-M} D}\left(1 + \frac{T}{D}\frac{dD}{dT}\right) \quad , \quad (13)$$

where E_1 and E_0 are the activation energies of the reactions of RX with M^+ and with the solvent, and

$$\Delta H_{MX} = 2.303RT^2 \frac{d \lg K_{MX}}{dT}$$

is the enthalpy of formation of the complex MX. For reactions of uncharged and cationic halides, when $Z_R Z_M \geqslant 0$, Eqn. (12) leads to the rule (10). With anionic substrates, however, cases are possible in which $K_{tr} > K_{MX}$. Values of $\lg k_1$ found experimentally and calculated by means of Eqn. (12) for several systems are compared in Table 1.[8] The radius of $t\text{-}C_4H_9^+$ was taken[8] to be r_R = 1.8 Å.

The good agreement between calculation and experiment (Tables 1 and 2) throughout the range of variation in conditions—M^+, X, and medium—indicates that the initial model was correct. The use of crystallographic radii instead of actual distances in the calculation is explained by the slight effect of the system of radii adopted on the Coulombic correction: thus an error of ±0.5 Å in the determination of l_{R-M} leads to an error of only ±0.1 in $\lg k_1$. It was found also[8] that formula (4) reproduces the experimental data well (Fig. 1) because of the existence of a secondary correlation between the Coulombic term and $\lg K_{MX}$, the slope of which is −0.16, corresponding to the difference between the theoretical slope of unity and the empirical slope of 0.84.

Few of the activation-energy data required for further testing of the theory are yet available. The reactions of t-butyl fluoride with water and with the ions Be^{2+}, Fe^{3+}, Al^{3+} and Sc^{3+} have the same activation energy: $E_0 = E_1 = 25 \pm 1$ kcal mole^{-1}.[26] These values satisfy Eqn. (13), since $\Delta H_{MX} = -1 \pm 1$ for the fluoride complexes of these ions, while the third term in (13) has the value −0.1 when $(T/D)dD/dT = -1.37$.

The S_N1 and M^+–S_N1 mechanisms of the reactions of t-butyl halides are regarded in the above theory as limiting in the sense that complete separation of charges along the R–X bond is achieved in the transition state. On this view there can be no reaction of greater S_N1 character, and Eqns. (12) and (13) should be satisfied for the S_N1 reactions of other substrates. Discrepancies may indicate that a different mechanism is actually operating[9] (Section V).

Results obtained by Anantaraman and his coworkers[14] illustrate the proportionality between k_0 and k_1 with variation in R for typical S_N1 reactions of aralkyl chlorides with mercury(II) chloride (Table 3). They show that changes in k_0 and k_1 by factors of 10^4 correspond to only a fourfold variation in the quantity $(k - k_0)/k_0 = k_1[M^+]/k_0$. The residual effect can be explained by a decrease in the Coulombic term due to an increase in the effective radius of R^+. The electrophile in this system may be either $HgCl_2$ or $HgCl^+$; the latter is present at a lower concentration, but is more active. To obtain an estimate we make the crude assumption that $HgCl^+$ acts as electrophile. The transition state will then have the form $R^+ \ldots Cl^- \ldots Hg^{2+} \ldots Cl^-$, from which we have

$$\lg \frac{k - k_0}{k_0} = \lg K_{MX} + \lg [HgCl^+] - 8.1\left(\frac{2}{l_{R-Hg}} - \frac{1}{l_{R-Cl}}\right) \quad \cdot (14)$$

The terms in brackets allow for the interactions of R^+ with Hg^{2+} and with the terminal Cl^-: $l_{R-Hg} = r_R + 2r_{Cl} + r_{Hg}$ and $l_{R-Cl} = r_R + 3r_{Cl} + 2r_{Hg}$. Application of Eqn. (14) to data for t-butyl chloride yields

$$\lg K_{MX} + \lg [HgCl^+] = 3.39$$

and the radii on other cations R^+ (last column of Table 3). The r_R values obtained increase with the size of the cation, with increasing transfer of positive charge to the periphery of the cation; their order of magnitude appears to be reasonable.

Table 3. Solvolysis (S_N1) of RCl in 0.075 M $HgCl_2$ in 80% aqueous acetone at 20°C.[14]

RCl	$10^7 k^*$, s^{-1}	$\frac{k-k_0}{k_0}$	r_R, Å calc.
t-BuCl	10.4	57	(1.8)
t-AmCl	14.7	70	2.1
Ph(Me)CHCl	4.0	100	2.5
Ph(Et)CHCl	0.93	100	2.4
Ph(*i*-Pr)CHCl	0.24	120	2.7
Ph(*t*-Bu)CHCl	0.02	150	2.9
(*p*-MePh)(Me)CHCl	180	200	3.4
		2500**	

*Values rounded off.
**Maximum value at $r_R = \infty$, calculation based on Eqn. (14).

Winstein and his coworkers[50–53] investigated the "regeneration" of ion-pairs in the M^+–S_N1 reactions of optically active *l*-chlorophenylphenylmethyl and *exo*-norbornyl chlorides with mercury(II) chloride and acetate in 80% aqueous acetone and in formic and acetic acids. The racemisation and solvolysis rate constants k^{rac} and k^t vary linearly with the concentration of mercury(II) chloride over the range 0.001–0.01 M: $k = k_0 + k_1[HgCl_2]$, which corresponds to Eqn. (2). It is assumed that every act of ionisation (k^α) leads to racemisation[53]:

$$d\text{—RCl} + HgCl_2 \xrightarrow{k^\alpha} R^+ \ldots ClHgCl_2^- \begin{cases} \xrightarrow{dl\text{-RCl} + HgCl_2\,(k^{rac})} \\ \xrightarrow[HOS]{dl\text{-ROS} + HCl + HgCl_2\,(k^t)} \end{cases} \quad (15)$$

We then have $k^\alpha = k^{rac} + k^t$, and we can estimate the proportions of the intimate ion-pairs which dissociate and which revert k^t/k^α and k^{rac}/k^α‡. Table 4 lists the proportions of dissociating ion-pairs in the reactions of the organic chlorides with the solvent and with mercury(II) chloride and acetate[51–53]. Although the electrophilic effect for mercury(II) chloride reaches $k_1^t/k_0^t = 10^2$–10^3 M^{-1}, the

‡If configuration is partly maintained during the reversion of ion-pairs to the initial substrate, k^α will give a lower limit to the rate of ionisation of RX. Comparison of the rates of racemisation and of the isotopic exchange of chlorine between RCl and $Hg^{36}Cl_2$ shows[51] that *p*-chlorophenylphenylmethyl chloride is regenerated from the ion-pair $R^+[HgCl_3]^-$, in which the three chlorine atoms are equivalent.

proportion of dissociating ion-pairs amounts to 10–50% for various media, and changes little on passing from reaction with the solvent to reaction with the mercury chloride. This shows that the acceleration of S_N1 reactions on the addition of an electrophile is due mainly to increase in the rate of ionisation k^{α}, not to retardation of the reversion of ion-pairs, as is sometimes assumed [54]. A larger fraction of dissociating ion-pairs are present in the reaction of *exo*-norbornyl chloride with mercury(II) acetate in acetic acid. Mercury acetate accelerates the reaction not only as a stronger electrophile than the chloride but also by supplying acetate ions to R^+.

Table 4. Fraction of dissociating ion-pairs k_1^t/k_1^{α} and electrophilic effect of mercury salts k_1^t/k_0^t in the solvolysis of *p*-chlorophenylphenylmethyl and *exo*-norbornyl chlorides.

Chloride	Solvent	Hg salt	k_1^t/k_0^t, M^{-1}	k_1^t/k_1^{α}
exo-Norbornyl	formic acid	—	—	0.25[a]
		$HgCl_2$	$0.93 \cdot 10^2$	0.51
exo-Norbornyl	acetic acid	—	—	0.09[a]
		$HgCl_2$	$0.89 \cdot 10^2$	0.10
		$Hg(OAc)_2$	$1.6 \cdot 10^5$	0.83
p-Chlorophenyl-phenylmethyl	80% aqueous acetone	—	—	0.43[a]
		$HgCl_2$	$2.4 \cdot 10^3$	0.55

[a]Values of k_0^t/k_0^{α}.

IV. M^+–S_N1 HYDROLYSIS OF INORGANIC HALIDES

The hydration of octahedral cobalt(III), chromium(III), etc. complexes is of the greatest interest, and is assumed to take place, in the absence of metal ions, by an S_N1 (or a dissociative) mechanism [28,41]. The hydration of $CrCl_2(H_2O)_4^+$ and $CrCl(H_2O)_5^{2+}$ is accelerated by Ag^+ and Hg^{2+} ions [55,56]. The complex $CrCl_2(H_2O)_4^+$ interacts with Hg^{2+} and $HgCl^+$ considerably more rapidly than with $HgCl_2$ and $HgCl_3^-$. Similarly, the rate of reaction between $FeCl(H_2O)_5^{2+}$ and $TlCl_n^{(3-n)}$ decreases as n increases from 0 to 3. [57] The stability of the resulting halide complexes falls in the same sequences. Variation of X^- and M^+ in $CrX(H_2O)_5^{2+}$ (X = Cl, Br, I) does not affect the distribution of the products of solvolysis in aqueous methanol $[Cr(H_2O)_6^{3+}]/[Cr(H_2O)_5CH_3OH^{3+}]$ catalysed by Tl^{3+}, Hg^{2+}, and Ag^+ ions, which is regarded as proof of an S_N1 mechanism with the slow stage

$$Cr(H_2O)_5X^{2+} + M^+ \rightarrow Cr(H_2O)_6^{3+} + MX \qquad (16)$$

followed by competing rapid reactions of $Cr(H_2O)_5^{3+}$ with water and with methanol [58]. The fractionation of oxygen-18 in the products of the hydrolysis of $CoX(NH_3)_5^{2+}$ (X = Cl, Br, I) has been studied [59] in the presence of Ag^+, Hg^{2+}, and Tl^{3+}. The reaction with Hg^{2+} yields $CoH_2O(NH_3)_5^{3+}$ enriched with the isotope by a factor of 1.012 relative to the oxygen-18 content of the solvent. An S_N1 mechanism was deduced from the fact that the effect was independent of X^-. In the reactions with Ag^+ and Tl^{3+} the fractionation coefficients are smaller and dependent on X, which indicates a possible contribution by an S_N2 mechanism. In the reaction with Tl^{3+} it is assumed that the attacking water molecule arrives from the inner sphere of the thallium ion [59].

At constant ionic strength induced hydrations are usually of the first order with respect both to the substrate and to M^+. [59,60] Detachment of the first chlorine atom from *cis*-$CoCl_2en_2^+$ (but not from the *trans*-isomer) involves a stage of formation of a stable intermediate:

$$cis\text{-}Co(en)_2Cl_2^+ + Hg^{2+} \underset{}{\overset{K}{\rightleftharpoons}} \left[(en)_2Co\begin{matrix}Cl\\ \diagdown\\ \diagup\\ Cl\end{matrix}Hg\right]^{3+} \qquad (17)$$

with $K = 650\ M^{-1}$. [60] Under the same conditions Tl^{3+}, in contrast to Hg^{2+}, does not give such a complex [61]. Replacement of chlorine in $CoClEDTA^{2-}$ by a carboxyl of ethylenediaminetetra-acetic acid is catalysed by metal ions that form stable complexes with the chloride ion [62–64]. A correlation has been noted between the reaction velocity and K_{MX}, [64] and equilibrium constants of formation of the intermediate have been found from kinetic data. However, the reaction is complicated by a protolytic equilibrium involving a complexone carboxyl uncombined with Co^{3+} and by coordination of this ligand with M^+.

Table 5. Aquation of halogeno-complexes induced by metal ions (in aqueous solution of ionic strength μ at 25 °C).

Complex	M^+	μ	k_1, $M^{-1}\,s^{-1}$	k_0, s^{-1}	$\lg k_1/k_0$	Refs.[a]
1	2	3	4	5	6	7
$Co(NH_3)_5F^{2+}$	Th^{4+}	2	0.031	$4.7 \cdot 10^{-8}$[b]	5.82	71/28
$Co(NH_3)_5F^{2+}$	H^+	0.11	$1.1 \cdot 10^{-4}$	$8.6 \cdot 10^{-8}$	3.10	65/28
cis-$Co(en)_2F^{2+}$	H^+	0.01	$3.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-6}$	3.00	66/66
trans-$Co(en)_2F_2^+$	H^+	0.1	$8.2 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	1.9	66/66
$Co(H_2O)_5F^{2+}$	H^+	1.0	$1.4 \cdot 10^{-3}$	$6.2 \cdot 10^{-10}$	1.34	68/28
$Cr(tren)Fe_2^+$	H^+	0.5	$3.5 \cdot 10^{-3}$	$9.0 \cdot 10^{-6}$	2.58	69/69
$Co(NH_3)_5Cl^{2+}$	Hg^{2+}	2.0	0.55[c]	$6.0 \cdot 10^{-6c}$	4.96	61/28
$Co(NH_3)_5Cl^{2+}$	$HgCl^+$	2.0	0.59[c]	$6.0 \cdot 10^{-6c}$	4.99	61/28
$Co(NH_3)_5Cl^{2+}$	Tl^{3+}	2.0	0.034[c]	$6.0 \cdot 10^{-6c}$	3.75	61/28
$Co(NH_3)_5Cl^{2+}$	$TlCl^{2+}$	2.0	0.012[c]	$6.0 \cdot 10^{-6c}$	3.30	61/28
cis-$Co(en)_2(NH_3)Cl^{2+}$	Hg^{2+}	1.0	$1.5 \cdot 10^{-2}$	$5 \cdot 10^{-7}$	4.5	60/28
trans-$Co(en)_2(NH_3)Cl^{2+}$	Hg^{2+}	1.0	$4.6 \cdot 10^{-3}$	$3.4 \cdot 10^{-7}$	4.13	60/28
cis-$Co(en)_2(H_2O)Cl^{2+}$	Hg^{2+}	1.0	$4.2 \cdot 10^{-2}$	$1.6 \cdot 10^{-6}$	4.41	60/28
trans-$Co(en)_2(H_2O)Cl^{2+}$	Hg^{2+}	1.0	$1.3 \cdot 10^{-2}$	$2.5 \cdot 10^{-6}$	3.74	60/28
cis-$Co(en)_2Cl_2^+$	Hg^{2+}	1.0	200	$2.4 \cdot 10^{-4}$	5.92	60/28
trans-$Co(en)_2Cl_2^+$	Hg^{2+}	1.0	3.8	$3.5 \cdot 10^{-5}$	5.04	60/28
cis-$Co(en)_2Cl_2^+$	$HgCl^+$	1.0	240	$2.4 \cdot 10^{-4}$	6.00	60/28
cis-$Co(en)_2Cl_2^+$	Tl^{3+}	1.0	17	$2.4 \cdot 10^{-4}$	4.84	61/28
trans-$Co(en)_2Cl_2^+$	Tl^{3+}	1.0	0.45	$3.5 \cdot 10^{-5}$	4.11	61/28
cis-$Co(en)_2(Py)Cl^{2+}$	Hg^{2+}	1.0	$1.5 \cdot 10^{-2}$	$5 \cdot 10^{-7}$	4.5	60/60
trans-$Co(en)_2(N_3)Cl^+$	Hg^{2+}	1.0	19	$2.2 \cdot 10^{-4}$	4.93	60/28
cis-$Co(en)_2(NO_2)Cl^+$	Hg^{2+}	1.0	78	$1.1 \cdot 10^{-4}$	5.85	60/28
trans-$Co(en)_2(NO_2)Cl^+$	Hg^{2+}	1.0	77	$9.8 \cdot 10^{-4}$	4.90	60/28
cis-$Cr(H_2O)_4Cl_2^+$	$HgCl^+$	0.50	50	$4.3 \cdot 10^{-5}$	6.06	80/28
trans-$Cr(H_2O)_4Cl_2^+$	$HgCl^+$	0.50	67	$8.3 \cdot 10^{-5}$	5.91	80/28
trans-$Cr(H_2O)_4Cl_2^+$	Hg^{2+}	0.50	31	$8.3 \cdot 10^{-5}$	5.57	81/28
$Cr(NH_3)_5Cl^{2+}$	Hg^{2+}	2.0	$8.7 \cdot 10^{-2}$	$7.3 \cdot 10^{-6}$	4.08	82/28
$Cr(NH_3)_5Cl^{2+}$	$HgCl^+$	2.0	0.10	$7.3 \cdot 10^{-6}$	4.14	82/28
cis-$Co(en)_2(NH_3)Cl^{2+}$	Hg^{2+}	0.2	$5.7 \cdot 10^{-3}$	$5.5 \cdot 10^{-7}$	4.01	84/83
cis-$Co(en)_2(MeNH_2)Cl^{2+}$	Hg^{2+}	0.2	$1.5 \cdot 10^{-2}$	$4.0 \cdot 10^{-7}$	4.57	84/83
cis-$Co(en)_2(EtNH_2)Cl^{2+}$	Hg^{2+}	0.2	$8.8 \cdot 10^{-3}$	$1.5 \cdot 10^{-7}$	4.77	84/83
cis-$Co(en)_2(n\text{-}PrNH_2)Cl^{2+}$	Hg^{2+}	0.2	$1.0 \cdot 10^{-2}$	$3.2 \cdot 10^{-7}$	4.49	84/83
cis-$Co(en)_2(i\text{-}PrNH_2)Cl^{2+}$	Hg^{2+}	0.2	$5.4 \cdot 10^{-2}$	$1.2 \cdot 10^{-6}$	4.65	84/83
$Fe(H_2O)_5Cl^{2+}$	$HgCl^+$	0.5	$1.7 \cdot 10^7$	12	6.15	85/85
$Fe(H_2O)_5Cl^{2+}$	$HgCl_2$	0.5	$8.5 \cdot 10^2$	12	1.85	85/85
$Cr(H_2O)_4Cl_2^+$	Ag^+	6	$3.7 \cdot 10^{-2}$	$6 \cdot 10^{-5}$	2.8	55/28
$Cr(H_2O)_5Cl^{2+}$	Ag^+	6	$1.1 \cdot 10^{-4}$	$2.8 \cdot 10^{-7}$	2.61	55/28
$Cr(H_2O)_5Cl^{2+}$	Hg^{2+}	1.0	$4.8 \cdot 10^{-2}$	$2.8 \cdot 10^{-7}$	5.23	56/28
$Cr(H_2O)_5Cl^{2+}$	$HgCl^+$	1.0	0.11	$2.8 \cdot 10^{-7}$	5.57	56/28
$Ru(NH_3)_5Cl^{2+}$	Hg^{2+}	0.17	$9.0 \cdot 10^{-4}$	$3.8 \cdot 10^{-8}$	4.37	86/86
$Co(NH_3)_5Br^{2+}$	Hg^{2+}	0.03	12	$6.3 \cdot 10^{-6}$	6.28	87/28

[a]The first reference relates to k_1, and the second to k_0.
[b]At 20.5 °C.
[c]At 35 °C.

The hydrolysis of inorganic fluorides, like that of organic fluorides, is catalysed by acids ($M^+ = H^+$). Studies have been made of the acid hydrolysis of $CoF(NH_3)_5^{2+}$, [65] *cis*- and *trans*-$CoF_2en_2^+$, [66] *cis*-$CrF_2en_2^+$, [67]

$CrF(H_2O)_5^{2+}$,[68] $CoF_2tren_2^+$,[69] etc. (tren = $N(C_2H_4NH_2)_3$). The reactions are assumed to involve protonation of the fluorine. In the case of $CoF_2tren_2^+$ formation of an intermediate has been detected from kinetic data. A linear dependence of $\lg k$ on H_0 with slope −0.97 has been found[70] for the acid hydrolysis of PF_6^- over the range 2–10 M hydrochloric acid. The hydration of $CoF(NH_3)_5^{2+}$ is accelerated by Th^{4+},[71] and the hydrolysis of XeF_2 by Th^{4+}, Al^{3+}, Be^{2+} and La^{3+} ions[72] in qualitative agreement with the stability sequence of their fluoride complexes. Clark and Jones have found that Zr^{4+}, Th^{4+}, Al^{3+}, Be^{2+}, and Ti^{4+} induce the hydrolysis of BF_4^-, PF_6^-, $AsOHF_5^-$, and AsF_6^- in strongly acid media[73]. Iron(III) complexes induce the hydrolysis of $AsOHF_5^-$.[74] All these reactions are assumed to involve the direct interaction of M^+ with the fluoride ligand[71,73], and they are regarded as similar to the splitting of the Co–Cl bond by the Hg^{2+} ion[74]. Chelate complexes of Cu^{2+}, Th^{4+}, and Zr^{4+} catalyse the hydrolysis of $(iso\text{-}C_3H_7O)_2POF$ and $iso\text{-}C_3H_7P(CH_3)OF$ (Sarin)[75–77]. The mechanism of these reactions is complicated.

The inadequacy of a simple S_N1–S_N2 classification for inorganic complexes has already been stressed[41,78]. Nevertheless, the above results indicate a certain analogy in the kinetics, mechanism, and driving force of the M^+–S_N1 hydrolysis of organic and of inorganic halides. Values of k_1 and k_0 for the hydration of cationic complexes (Table 5) show that the relation between them is close to Eqn. (4) for t-butyl halides[79]. The agreement is improved by introducing an additional term containing the product of the charges Z_1Z_2 to allow for the Coulombic repulsion of the reactants. Sykes et al.[61] had already used Coulombic repulsion to explain the greater activity of Hg^{2+} than of Tl^{3+} contrary to the sequence of KMX for $HgCl^+$ and $TlCl^{2+}$ in the hydrolysis of $CoCl(NH_3)_5^{2+}$ and of *cis*- and *trans*-$CoCl_2en_2^+$. The data compiled in Table 5 satisfy the inequality (10), as would be expected. It is noteworthy that the ratio k_1/k_0 is in all cases larger for *cis*-complexes than for the *trans*-isomers[79].

Table 6. Calculation of rates of M^+–S_N1 hydrolysis of BF_4^- and PF_6^- (aqueous solutions at 25°C; k_1 in M^{-1} s^{-1} and k_0 in s^{-1}).

Ion	BF_4^- $\lg k_0 = -7.0$[68]		PF_6^- $\lg k_0 = -10.9$[68]	
	$\lg k_1$ expt.	$\lg k_1$ calc. from Eqn.(12)	$\lg k_1$ expt.	$\lg k_1$ calc. from Eqn.(12)
H^+	−3.9	−3.7	−6.8	−7.6
Be^{2+}	−1.0	−1.4	−4.3	−5.3
Al^{3+}	−0.8	0.0	−4.0	−3.9
Th^{4+}	+0.2	+1.8	−3.2	−2.1

Equation (12) cannot in general be used to process the results in Table 5: with reactants of like charge the effects of the ionic strength, which differ with different systems, may lead to overestimates of 1–2 units in $\lg k_1$. Nevertheless, several examples have shown[8] that theoretical approaches are applicable to M^+–S_N1 reactions of inorganic halides. The induced hydrolysis of BF_4^- and PF_6^- has been studied[73] in hydrochloric acid (1–2 M) without extrapolation to zero ionic strength. It is difficult to assess the accuracy of the results. An S_N1 mechanism is probable in both cases, since the central atoms in BF_4^- and PF_6^- are shielded from S_N2 attack. Covalent models of the transition states—$F_3B\ldots F^-\ldots M^+$ and $F_5P\ldots F^-\ldots M^+$—were adopted for the calculations. The theoretical equation is $k_1 = k_0KMX$. The results are given in Table 6. Ionic models of the transition states of these reactions—$(F^-)_3B^+\ldots F^-\ldots M^+$ and $(F^-)_5P^{5+}\ldots F^-\ldots M^+$ with $r_F = 1.33$, $r_B = 0.20$, and $r_P = 0.35$ Å—lead to underestimates of k_1 by factors of $10–10^2$. Agreement between calculated and experimental values of k_1 has been shown[8] also for the reactions of $CoBr(NH_3)_5^{2+}$ and $RhCl(NH_3)_5^{2+}$ with Hg^{2+}, which have been studied at a low ionic strength (Table 5). The theoretical equation for the ionic model of the transition state $(NH_3)_5M^{3+}\ldots X^-\ldots Hg^{2+}$ is $(\lg k_1/k_0KMX)_{theor} = -27.9/l_{M-Hg}$.

Data extrapolated to zero ionic strength, as well as information on the actual geometry of the complexes and the delocalisation of charges on the ligands, are required in order to make an extensive test of the theory. It is quite possible that, with accurate values of k_0, k_1, and KMX, the above approach may give valuable information on the structure of transition states.

The above regularities in the detachment of halogens by metal ions can probably be extended to the detachment of other groups. As with halides, the driving force of such reactions is the formation of a stable bond between the metal and the detached group. The hydration of $Fe(CN)_6^{4-}$ is accelerated by mercury(II) and silver(I) salts[90], that of $CrCN^{2+}$,[91] $CrSCN^{2+}$, and $CrNCS^{2+}$[92,93] by mercury(II) salts, and the hydration of $CoCO_3(NH_3)_5^+$ by bivalent mercury, lead, and barium salts[94]. As a consequence of high affinity for the sulphur atom, Ag^+ and Hg^{2+} ions accelerate reactions involving cleavage of phosphorus–sulphur[95] and carbon–sulphur[96–99] bonds. The kinetics and the mechanism of these reactions have not yet been adequately studied.

V. M^+–S_N2 REACTIONS OF PRIMARY AND SECONDARY ALKYL HALIDES

The acceleration of the reactions of primary and secondary alkyl halides by the ions Ag^+[100–108] and Hg^{2+}[4,109–112] (see also Refs. 2 and 3) was originally discussed in terms of Ingold's hypothesis[1] that the mechanism changes from S_N2 to Ag^+–S_N1 (or Hg^{2+}–S_N1) under the influence of M^+. For example, the reaction of benzyl chloride with mercury(II) nitrate in aqueous dioxan was represented by the scheme[4]

$$C_6H_5CH_2Cl + Hg^{2+} \xrightarrow[\text{slow}]{} HgCl^+ + C_6H_5CH_2^+ \longrightarrow \begin{cases} \xrightarrow{NO_3^-} C_6H_5CH_2ONO_2 \\ \xrightarrow{H_2O} C_6H_5CH_2OH + H^+ \end{cases} \quad (18)$$

An M^+–S_N1 mechanism was suggested also for the reactions of primary alkyl bromides with Hg^{2+},[111,112] but the sequence of rates—$C_2H_5Br > n\text{-}C_3H_7Br > iso\text{-}C_4H_9Br$[111]—indicates nucleophilic attack. On the other hand, cases of the rearrangement and racemisation of the alkyl group[1,3,113], indicating intermediate formation of an ion-pair, may be a consequence of a slow reaction with the solvent under the same conditions, but without M^+, also by an S_N1 mechanism. Several later attempts were made[114–121] to prove that a nucleophile was involved in the reactions of primary and secondary alkyl halides with Ag^+, but it was difficult to distinguish the roles of the anion (nitrite, nitrate, perchlorate) as a nucleophile and as a ligand changing the activity of M^+. Furthermore, the reactions were usually studied in anhydrous or nearly anhydrous media, where the effects of ionic association were significant.

The results of detailed kinetic investigations of the hydrolysis of methyl, ethyl, and isopropyl halides in the presence of metal ions in aqueous solution [9,122-130] are summarised in Table 7. These reactions outwardly resemble M^+–S_N1 reactions of t-butyl halides: the kinetics are in most cases represented by Eqn. (2), metal ions that form stable complexes MX—in particular Ag^+, Pb^{2+}, Cd^{2+}, Hg^{2+}, and Tl^{3+}—are active, and the dependence of $\lg(k_1/k_0)$ on $\lg K_{MX}$ is nearly linear for a given alkyl group with electrophiles having the same charge [125,126]. However, significant differences were revealed. Experimental values of $\lg(k_1/k_0)$ are lower than those calculated by means of Eqn. (4) (Fig. 2). The differences increase with enhancement of the S_N2 character of the reactions, i.e. in the sequence isopropyl < ethyl < methyl, and with increase in the charge on the metal ion. The Tl^{3+} ion is less active than Hg^{2+}, although the Lewis acidity of the former is greater (Table 1). Correction for the Coulombic destabilisation of the transition state (Section III) is insufficient to explain the discrepancies, which reach $\Delta \lg(k_1/k_0) = 4$–6 for Hg^{2+} and Tl^{3+}.

Table 7. Rate constants of M^+–S_N2 reactions in aqueous solutions of zero ionic strength at 25°C (k_0 in s^{-1} and k_1 in $M^{-1}\,s^{-1}$).

	Reaction	Ref.	$\lg k_0$ [131,132]	$\lg k_1$ expt.	$\lg k_1$ calc. from Eqn.(19)
1	MeCl+Hg^{2+}	125	−7.62	−5.2	−5.2
2	MeBr+Hg^{2+}	125	−6.39	−2.5	−2.4
3	MeI+Ag^+	127	−7.13	−2.6	−2.6
4	MeI+2Ag^+	127	−7.13	−0.8[a]	−0.8[a]
5	MeI+Hg^{2+}	125	−7.13	+0.1	0.0
6	EtCl+Hg^{2+}	125	−7.70	−4.7	−4.7
7	EtBr+2Ag^+	123	−6.42	−2.7[a]	−3.0[a]
8	EtBr+Pb^{2+}	126	−6.42	−6.6	—
9	EtBr+Cd^{2+}	126	−6.42	−6.5	−6.6
10	EtBr+Hg^{2+}	122,126	−6.42	−1.8	−1.8
11	EtBr+Tl^{3+}	128	−6.42	−3.9	−3.8
12	EtI+Ag^+	129	−6.82	−1.8	−2.0
13	EtI+2Ag^+	129	−6.82	−0.1[a]	0.0[a]
14	EtI+Hg^{2+}	125	−6.82	+1.2	+1.1
15	*i*-PrCl+Hg^{2+}	125	−6.67	−2.2	−2.3
16	*i*-PrCl+Tl^{3+}	128	−6.67	−2.8	−2.7
17	*i*-PrBr+Ag^+	129	−5.42	−2.2	−2.0
18	*i*-PrBr+2Ag^+	129	−5.42	−0.7[a]	−0.8[a]
19	*i*-PrBr+Cd^{2+}	126	−5.42	−5.0	−4.9
20	*i*-PrBr+Hg^{2+}	125	−5.42	+0.9	+0.8
21	*i*-PrBr+Tl^{3+}	128	−5.42	−0.4	−0.5

[a] $\lg(k_2,\ M^{-2}\,s^{-1})$.

The above reactions have therefore been included [9] in the M^+–S_N2 type, their driving force being an electrophilic contribution to heterolysis of the C–X bond with simultaneous attack by the nucleophile on the carbonium centre. Since bonds in the transition state

$$H_2O^{+\delta_B}\cdots\overset{|}{C}{}^{+\delta_C}\cdots X^{-\delta_X}\cdots M^+$$

are partly covalent (it is assumed that $\delta < 1$), the electronic effect may be transmitted by an induction mechanism. Displacement of the electrons towards M^+ lowers the electron density on the $H_2O\ldots C<$ bond in the transition state, which diminishes the S_N2 character of the reaction. This effect, termed [9] "inductive retardation", should be most intense with methyl halides, when overlapping of the orbitals at this bond is greatest, and with multicharged ions, e.g. Tl^{3+}, having a high electron affinity.

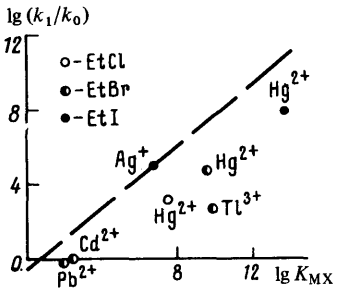


Figure 2. Comparison of values of $\lg(k_1/k_0)$ for the reactions of $C_2H_5X + M^+$ with correlation (4) for t-C_4H_9X (broken lines).

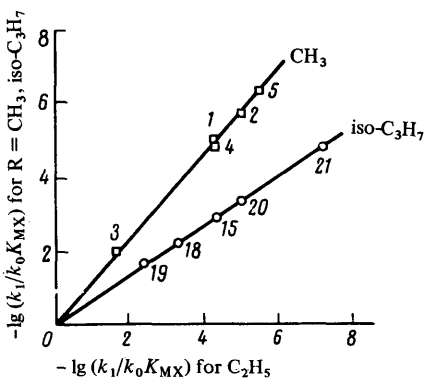


Figure 3. Correlation between values of $\lg(k_1/k_0K_{MX})$ for CH_3X, iso-C_3H_7X, and C_2H_5X with variation in M^+ and X. For the reactions of RX with two silver ions, k_1 and K_{MX} have been replaced by k_2 and K_{Ag_2X}. Numbering as in Table 7.

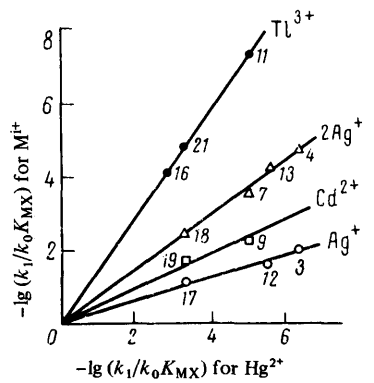


Figure 4. Correlation between values of $\lg(k_1/k_0K_{MX})$ for Tl^{3+}, $2Ag^+$, Cd^{2+}, and Ag^+ and for Hg^{2+}, with variation of R and X.

The effects of R, X, and M^+ in M^+–S_N2 reactions (Table 7) are reproduced by the equation

$$\lg(k_1/k_0) = \lg K_{MX} - P_R \cdot P_X \cdot P_M \quad , \qquad (19)$$

where P_R, P_X, and P_M are positive constants depending on the properties of the respective species. The overall effect of the metal ion is determined by competition between electrophilic bonding of X^-, represented by the term $\lg K_{MX}$, as for t-butyl halides, and inductive retardation ($P_R P_X P_M$). Equation (19) leads to the correlations

$$\left(\lg\frac{k_1}{k_0K_{MX}}\right)_{R_1} = \frac{P_{R_1}}{P_{R_2}}\left(\lg\frac{k_1}{k_0K_{MX}}\right)_{R_2}, \text{ varying X, } M^+ \qquad (20)$$

$$\left(\lg\frac{k_1}{k_0K_{MX}}\right)_{X_1} = \frac{P_{X_1}}{P_{X_2}}\left(\lg\frac{k_1}{k_0K_{MX}}\right)_{X_2}, \text{ varying R, } M^+ \qquad (21)$$

$$\left(\lg\frac{k_1}{k_0K_{MX}}\right)_{M_1} = \frac{P_{M_1}}{P_{M_2}}\left(\lg\frac{k_1}{k_0K_{MX}}\right)_{M_2}, \text{ varying R, X} \qquad (22)$$

which can be verified directly (Figs. 3–5). Table 8 gives values of P_R, P_X, and P_M determined [9] for the standard conditions $P_{Br} \equiv 1$ and $P_{Hg} \equiv 12.8$; Table 7 compares experimental values of k_1 with those calculated by means of Eqn. (19). For M^+–S_N1 reactions of t-butyl halides $P_R = 0$ (if Coulombic repulsion is neglected). The interpretation of P_M as an induction constant of the M^+ ion is confirmed by comparing [9] P_M and the equilibrium constant $K_{MOH} = [MOH][H_2O]/[M^+][OH^-]$, which is determined mainly by charge transfer to the aquo-ion

$$\begin{matrix} H \\ H \end{matrix}\!\!\searrow\!\!\nearrow O \rightarrow M^+ ,$$

and by the correlation of P_M with the electron affinity of the M^+ ions in the gas phase.

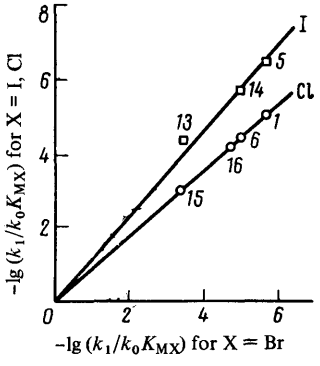


Figure 5. Correlation between values of $\lg(k_1/k_0K_{MX})$ for I, Cl, and Br with variation of R and M^+.

The above results indicate the occurrence of a broad spectrum of S_N2 reactions depending on the overlap of nucleophile and $R^{\delta+}$ orbitals in the transition state. Here S_N1 reactions correspond to the limit at which the action of the solvent nucleophile is restricted by solvation. The overlap of the orbitals is determined by the nucleophilic character of the medium and the nature of the alkyl group; it depends little on the strength of the electrophile, at least in the range from H_2O to Tl^{3+}. The above slight diminution of S_N2 character of the reaction due to the inductive effect of M^+ is consistent with data on the reactions of alkyl halides with sodium and silver nitrites forming the basis of Kornblum's rule [114,133,134]. Since electrophiles accelerate S_N1 reactions more strongly than S_N2 reactions (Fig. 2), the variations in mechanism indicated in Table 9 are possible under the influence of metal ions.

Table 8. Values of the parameters P_R, P_X, and P_M for M^+–S_N2 reactions [9].

R	i-Pr		Et		Me	
P_R	0.261±0.004		0.386±0.005		0.440±0.002	
X	Cl		Br		I	
P_X	0.862±0.004		(1)		1.13±0.04	
M^+	Ag^+	Pb^{2+}	Cd^{2+}	$2Ag^+$	Hg^{2+}	Tl^{3+}
P_M	4.2±0.3	5.7	6.3±0.5	9.5±0.3	(12.8)	18.6±0.2

Table 9.

Reaction with solvent		Reaction with M^+ in same medium
S_N1	I →	M^+–S_N1
	III ↗	
S_N2	II →	M^+–S_N2

Transition III, corresponding to S_N2 reactions with slight overlap of the orbitals, has not yet been demonstrated, but may occur in the solvolysis of n-propyl bromide in 90% formic acid in the presence of Hg^{2+}, when the formation of propan-2-ol can be explained [113] only by a 1–2 hydride shift in the n-propyl cation. Another approach [135–139], which describes the kinetics of the reactions of primary and secondary alkyl halides with a nucleophile N^- in terms of the general scheme of S_N1 reactions

$$RX \rightleftharpoons R^+ \ldots X^- \xrightarrow{N^-} RN + X^-$$

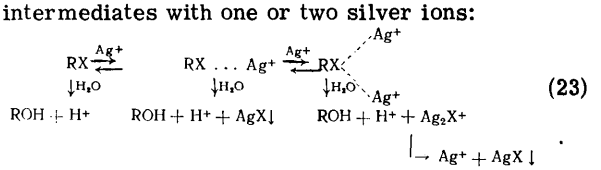
seems less probable, in view of the above differences between M^+–S_N1 and M^+–S_N2 reactions and the fact that the transition state $N^- \ldots R^{\delta+} \ldots X^{\delta-}$ for S_N reactions should be more stable than an intimate ion-pair $R^+ \ldots X^-$. Transition III can be expected also for isopropyl and benzyl halides. Results for the hydrolysis of isopropyl halides in the presence of metal ions (Table 7) are in fact reproduced by Eqns. (4) and (12) for M^+–S_N1 reactions, although less accurately than by Eqn. (19). This can be interpreted as indicating that the mechanism for isopropyl halides is intermediate between M^+–S_N1 and M^+–S_N2. The formation of propene in the hydrolysis of isopropyl bromide in the presence of silver ions [129] is consistent with an M^+–$E2$ mechanism and with elimination from the ion-pair. The electrophilic contribution of metal ions to the hydrolysis of benzyl fluoride [140,141] is conveyed approximately by correlation (4) for M^+–S_N1 reactions [26,27].

The above model of M^+–S_N2 reactions is equivalent to Swain's push–pull mechanism suggested in 1948.[142,143] However, only by the use of aquo-ions of metals has it become possible in principle to study the role of the electrophile with the nucleophile and the medium fixed.

VI. ASPECTS OF THE REACTIONS OF ALKYL HALIDES WITH SILVER IONS

Until recently the mechanism of the reactions of alkyl halides with silver salts[11,54,100–108,114–121,130,144–151] remained obscure owing to the complexity of the kinetics, especially in non-aqueous media, and the unusual reaction orders with respect to silver—from 0 to 2 and higher, including fractional orders. The traditional explanation of these anomalies was based[114,116–121,130,152] on the nucleophilic contribution of anions (nitrate and perchlorate), the influence of the ionic strength, and the effects of ionic association in low-polarity solvents. The hypothesis that these reactions were accelerated significantly by precipitated silver halides[1,3] has not been confirmed[54,123,118–121,130,153].

Detailed kinetic studies of the hydrolysis of t-butyl chloride[25], isopropyl bromide[129], ethyl bromide[123], ethyl iodide[129], and methyl iodide[127] in the presence of silver ions in aqueous media indicate that these complications are due to a special mechanism involving the formation of intermediates with one or two silver ions:

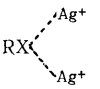


(23)

This mechanism corresponds to the kinetic equation[24,123]

$$k \equiv -\frac{1}{[RX]}\frac{d[RX]}{d\tau} = \frac{k_0 + k_1[Ag^+] + k_2[Ag^+]^2}{1 + K_{gr}[Ag^+]}, \qquad (24)$$

where k_0, k_1, and k_2 are the rate constants of reaction with the solvent and with one and two silver ions, and $K_{gr} = [RX...Ag^+]/[RX][Ag^+]$ is the stability constant of the intermediate $RX...Ag^+$. The concentration of the intermediate



is assumed[123,127,129] to be minute. In M^+–S_N1 reactions ($R = t\text{-}C_4H_9$) intermediates of these types dissociate with the formation of R^+, whereas in M^+–S_N2 reactions ($R = CH_3$, C_2H_5, iso-C_3H_7) they undergo nucleophilic attack by water, but the stepwise scheme (23) is the same in the two cases. Partition kinetic methods have been elaborated[19,24,26] which enable us to determine not only the rate constant but also the solubility of the substrates, which depends on complex formation between the alkyl halide and the silver ion.

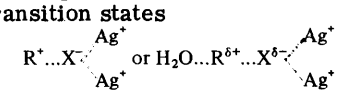
Table 10 gives the values of K_{gr} for the complexes $RX...Ag^+$ together with values, obtained spectrophotometrically in aqueous solution at 25°C, for the kinetically stable $CH_2X_2...Ag^+$ species. The stability of the complexes increases in the sequences Cl < Br < I and $CH_3 < C_2H_5 <$ iso-C_3H_7. Their formation is a consequence of the low hydration energy of the silver ion and its comparatively high affinity for halogen. Complex formation between RX and Hg^{2+} is considerably weaker[122,125], although HgX^+ is more stable than AgX. Mercury(II) chloride forms a complex with benzyl bromide[155]. Many observations have been made in non-aqueous media of complexes of alkyl halides with the silver ion[149,150] and other Lewis acids (see reviews[156,157]).

Values of k_1 and k_2 are given in Table 7. Reactions of the first order with respect to the silver ion do not differ from the reactions of alkyl halides with other metal ions. Reaction paths of the second order ($2Ag^+$, Table 7) occur[9,25,123,127] as a consequence of the great stability of the complexes Ag_2X^+ with the anion as centre of coordination. The composition, stability, and structure of complexes of this type—Ag_2X^+, Ag_3X^{2+}, Hg_2X^{3+}, Cd_2X^{3+}, and several others—have been widely discussed[158–161].

Table 10.

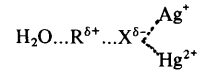
Substrate	MeI[127]	EtI[129]	EtBr[123]	*i*-PrBr[129]	CH_2Cl_2[154]	CH_2Br_2[154]	CH_2I_2[154]
K_{gr}, M^{-1}	15	32	1.6	4.2	0.1	0.5	20.2

Reactions involving two silver ions provide a further example of the generality of the correlation between the rate of the induced detachment of a halide ion and the stability of the complexes formed in the rate-determining stage. The transition states



(for M^+–S_N2 reactions), of which the complex Ag_2X^+ is a fragment in both cases, are advantageous despite the Coulombic repulsion of the two silver ions. The second silver ion acts as a catalyst, promoting detachment of the halide ion and ultimately being regenerated (Eqn. 23). Values of k_2 for the reactions of methyl iodide, ethyl iodide, ethyl bromide, and isopropyl bromide (Table 7) agree with those calculated by means of Eqn. (19), with $P_2Ag \simeq 2PAg$ (Table 8). The additivity of the effects of the two silver ions is consistent with the interpretation of P_M as a measure of the inductive effect of the metal ion. Agreement between k_2 and K_{Ag_2X} has been shown also for t-butyl chloride[25].

Reaction paths of the third order with respect to the silver ion[127] and of the second order with respect to Hg^{2+},[125] corresponding to the complexes Ag_3X^{2+} and Hg_2X^{3+}, have not yet been observed, but the stability constants suggest that such reactions are possible at salt concentrations of 5–10 M. The hydrolysis of ethyl bromide in solutions containing both Ag^+ and Hg^{2+} ions reveals[124] a component rate $k_2[RX][Ag^+][Hg^{2+}]$ of the first order with respect to each ion, which corresponds to the transition state



in which one of the two silver ions has been replaced by an Hg^{2+} ion. A cross route has been found also for silver and cadmium ions[124]. Kinetic data have been used to estimate[124] stability constants of hitherto unknown complexes with an anionic centre of coordination and two different metal ligands—$HgBrAg^{2+}$ ($10^{9.3}$ M^{-2}) and $CdBrAg^{2+}$ (10^7 M^{-2}).

A reaction path involving two silver ions has been found in the hydrolysis of 1-benzoyl-1-methylethyl bromide[162]. Competition between reactions of first and second orders with respect to silver ions has been

observed [95-99] in the cleavage of carbon–sulphur and phosphorus–sulphur bonds. Mechanism (23) can therefore be regarded as general for the reactions of silver ions with substrates having a soft basic centre such as a halogen or sulphur.

Thus the Brønsted relation is widely applicable to the effects of the electrophilic contribution to the detachment of halogens and perhaps other groups in the reactions of organic and inorganic substrates. These reactions can be included among the M^+–S_N1 and M^+–S_N2 types. In order to calculate the rate constant of an M^+–S_N1 reaction in terms of a model of the transition state with complete charge separation along the bond undergoing cleavage, it is sufficient to take into account the Lewis acidity of the electrophile. In an M^+–S_N2 reaction the electrophilic contribution is accompanied by retardation due to the inductive effect of the electrophile. Reaction paths of the second order with respect to silver ions conform to the general rules for M^+–S_N1 and M^+–S_N2 reactions.

NOTE ADDED IN PROOF

The theory of M^+–S_N1 reactions outlined in this Review has recently been generalised [163] to the S_N1 solvolysis of t-butyl halides. Interaction of the transition state with the medium is separated into Coulombic interaction in the ion-pair and actual solvation, which is taken into account on the basis of a coordination model and the solvation energies of the ions. Direct theoretical calculation gave quantitative agreement with experimental rates of solvolysis with the medium varied within wide limits, which provides reliable evidence of the generality of the S_N1 and M^+–S_N1 mechanisms.

REFERENCES

1. C. K. Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1959.
2. A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962.
3. C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom", Elsevier, Amsterdam, 1963.
4. J. Roberts and L. P. Hammett, J. Amer. Chem. Soc., 59, 1063 (1937).
5. J. N. Brønsted and K. Pedersen, Z. phys. Chem., 108, 185 (1924).
6. R. P. Bell, "Acid–Base Catalysis", Clarendon Press, Oxford, 1949.
7. E. S. Rudakov and I. V. Kozhevnikov, Tetrahedron Letters, 1333 (1971).
8. E. S. Rudakov and I. V. Kozhevnikov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 9, 165 (1972).
9. E. S. Rudakov and I. V. Zamashchikov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 9, 301 (1972).
10. L. G. Sillén, "Stability Constants of Metal-ion Complexes", Special Publication No. 17, The Chemical Society, London, 1964.
11. C. Prevost and R. Boyer, Bull. Soc. chim. France, 782 (1949).
12. R. Anantaraman and K. Saramma, Naturwiss, 50, 497 (1963).
13. R. Anantaraman and K. Saramma, Canad. J. Chem., 43, 1770 (1965).
14. R. Anantaraman and M. R. Nair, Canad. J. Chem., 44, 2415 (1966).
15. V. N. Setkina, D. N. Kursanov, and E. V. Bykova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 758 (1959).
16. G. A. Clarke and R. W. Taft, J. Amer. Chem. Soc., 84, 2295 (1962).
17. E. S. Rudakov and I. V. Kozhevnikov, Dokl. Akad. Nauk SSSR, 186, 354 (1969).
18. E. S. Rudakov, V. P. Tret'yakov, and V. B. Bystrenko, Kinetika i Kataliz, 10, 935 (1969).
19. V. P. Tret'yakov, E. S. Rudakov, and V. B. Bystrenko, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 6, 542 (1969).
20. E. S. Rudakov and I. V. Kozhevnikov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 6, 560 (1969).
21. E. S. Rudakov, I. V. Kozhevnikov, and V. V. Zamashchikov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 6, 573 (1969).
22. I. V. Kozhevnikov and E. S. Rudakov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 7, 761 (1970).
23. E. S. Rudakov and I. V. Kozhevnikov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 7, 771 (1970).
24. E. S. Rudakov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 7, 779 (1970).
25. I. V. Kozhevnikov and E. S. Rudakov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 8, 517 (1971).
26. I. V. Kozhevnikov, E. S. Rudakov, and N. P. Shkol'naya, Reaktsionn. Sposobnost' Org. Soed. (Tartu), 8, 499 (1971).
27. I. V. Kozhevnikov, Candidate's Thesis, Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, 1972.
28. F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions" (Translated into Russian), Mir, Moscow, 1971.
29. J. Koskikallio, Acta Chem. Scand., 21, 397 (1967).
30. E. F. Caldin, "Fast Reactions in Solution" (Translated into Russian), Mir, Moscow, 1966.
31. Y. Pocker, J. Chem. Soc., 1972 (1960).
32. Y. Pocker and R. F. Buchholz, J. Amer. Chem. Soc., 92, 2075 (1970).
33. R. L. Buckson and S. G. Smith, J. Org. Chem., 32, 634 (1967).
34. S. Winstein and R. E. Buckler, J. Amer. Chem. Soc., 64, 2780 (1942).
35. S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948.
36. E. S. Rudakov, "Termodinamika Mezhmolekulyarnogo Vzaimodeistviya"(Thermodynamics of Intermolecular Interaction), Nauka, Novosibirsk, 1968.
37. L. P. Hammett, "Fundamentals of Physical Organic Chemistry" (Translated into Russian), Mir, Moscow, 1972.
38. J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963.
39. T. C. Bruice and S. J. Benkovic, "Mechanisms of Bio-organic Reactions" (Translated into Russian), Mir, Moscow, 1970.
40. R. A. Marcus, J. Phys. Chem., 72, 891 (1968).
41. C. H. Langford and H. B. Gray, "Processes of Ligand Substitution" (Translated into Russian), Mir, Moscow, 1969.
42. F. G. Bordwell, W. J. Boyle, J. A. Hautala, and K. C. Yee, J. Amer. Chem. Soc., 91, 4002 (1969).
43. R. A. Marcus, J. Amer. Chem. Soc., 91, 7224 (1969).
44. A. J. Kresge, J. Amer. Chem. Soc., 92, 3210 (1970).

45. A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, J. Amer. Chem. Soc., 93, 413 (1971).
46. F. G. Bordwell and W. J. Boyle, J. Amer. Chem. Soc., 93, 511 (1971).
47. F. G. Bordwell, W. J. Boyle, and K. C. Yee, J. Amer. Chem. Soc., 92, 5926 (1970).
48. I. A. Koppel', Candidate's Thesis, Tartu University, 1968.
49. M. H. Abraham and G. F. Johnston, J. Chem. Soc. (A), 1610 (1971).
50. A. Ledwith, M. Hojo, and S. Winstein, Proc. Chem. Soc., 241 (1961).
51. A. F. Diaz, I. L. Reich, and S. Winstein, J. Amer. Chem. Soc., 92, 7598 (1970).
52. J. P. Hardy, A. Ceccon, A. F. Diaz, and S. Winstein, J. Amer. Chem. Soc., 94, 1356 (1972).
53. J. P. Hardy, A. F. Diaz, and S. Winstein, J. Amer. Chem. Soc., 94, 2363 (1972).
54. D. J. Pasto and K. Garves, J. Org. Chem., 32, 778 (1967).
55. P. J. Elving and B. Zemel, J. Amer. Chem. Soc., 79, 5855 (1957).
56. J. H. Espenson and J. P. Birk, Inorg. Chem., 4, 527 (1965).
57. T. J. Conochioli, G. H. Nancollas, and N. Sutin, Proc. Chem. Soc., 113 (1964).
58. S. P. Ferraris and E. L. King, J. Amer. Chem. Soc., 92, 1215 (1970).
59. F. A. Rosey and H. Taube, J. Amer. Chem. Soc., 79, 255 (1957).
60. C. Bifano and R. G. Linck, Inorg. Chem., 7, 908 (1968).
61. S. W. Foong, B. Kipling, and A. G. Sykes, J. Chem. Soc. (A), 118 (1971).
62. R. Dyke and W. C. E. Higginson, J. Chem. Soc., 2788 (1963).
63. W. C. E. Higginson and M. P. Hill, J. Chem. Soc., 1620 (1959).
64. S. P. Tanner and W. C. E. Higginson, J. Chem. Soc., 1164 (1969).
65. S. C. Chan, J. Chem. Soc., 2375 (1964).
66. F. Basolo, W. R. Matoush, and R. G. Pearson, J. Amer. Chem. Soc., 78, 4883 (1956).
67. K. R. A. Fehrmann and C. S. Garner, J. Amer. Chem. Soc., 83, 1276 (1961).
68. T. W. Swaddle and E. L. King, Inorg. Chem., 4, 532 (1965).
69. K. Kuo and S. K. Madan, Inorg. Chem., 10, 229 (1971).
70. A. E. Gebala and M. M. Jones, J. Inorg. Nuclear Chem., 31, 771 (1969).
71. A. A. Vlček, Nature, 197, 786 (1963).
72. M. T. Beck and L. Dozca, J. Amer. Chem. Soc., 89, 5713 (1967).
73. H. R. Clark and M. M. Jones, J. Amer. Chem. Soc., 92, 816 (1970).
74. W. L. Johnson and M. M. Jones, Inorg. Chem., 5, 1345 (1966).
75. T. Wagner-Jauregg, B. E. Hackley, T. A. Lies, O. O. Owens, and R. Proper, J. Amer. Chem. Soc., 77, 922 (1955).
76. R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hyytiainen, S. C. Chaberek, and A. E. Martell, J. Amer. Chem. Soc., 79, 3030 (1957).
77. R. L. Gustafson and E. E. Martell, J. Amer. Chem. Soc., 84, 2309 (1962).
78. A. A. Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Khimiya, Leningrad, 4th edition 1971, p. 458.
79. I. V. Kozhevnikov and E. S. Rudakov, Inorg. Nuclear Chem. Letters, 8, 571 (1972).
80. J. P. Birk, Inorg. Chem., 10, 66 (1971).
81. J. P. Birk, Inorg. Chem., 9, 735 (1970).
82. J. H. Espenson and S. R. Hubbard, Inorg. Chem., 5, 686 (1966).
83. S. C. Chan and S. F. Chan, J. Chem. Soc. (A), 202 (1969).
84. S. C. Chan and F. Leh, J. Chem. Soc. (A), 138 (1966).
85. D. Gibson and D. W. Caryle, Inorg. Chem., 10, 2078 (1971).
86. A. B. Venediktov and A. V. Belyaev, Zhur. Neorg. Khim., 17, 2222 (1972) [Russ. J. Inorg. Chem., No. 9 (1972)].
87. J. N. Brønsted and R. Livingston, J. Amer. Chem. Soc., 49, 435 (1927).
88. I. G. Ryss and M. M. Slutskaya, Zhur. Fiz. Khim., 21, 549 (1947).
89. I. G. Ryss and V. B. Tul'chinskii, Zhur. Neorg. Khim., 9, 836 (1964) [Russ. J. Inorg. Chem., No. 4 (1964)].
90. M. E. Baldwin, S. C. Chan, and M. L. Tobe, J. Chem. Soc., 4637 (1961).
91. J. P. Birk and J. H. Espenson, Inorg. Chem., 7, 981 (1968).
92. M. Orhanovic and N. Sutin, J. Amer. Chem. Soc., 90, 4286 (1968).
93. A. Haim and N. Sutin, J. Amer. Chem. Soc., 87, 4210 (1965).
94. R. B. Jordan, A. M. Sargeson, and H. Taube, Inorg. Chem., 5, 486 (1966).
95. B. Saville, J. Chem. Soc., 4624 (1961).
96. B. Saville, J. Chem. Soc., 4062 (1962).
97. D. P. N. Satchell and I. I. Secemski, Chem. and Ind., 1632 (1969).
98. D. P. N. Satchell and I. I. Secemski, Tetrahedron Letters, 1991 (1969).
99. D. P. N. Satchell and I. I. Secemski, J. Chem. Soc. (B), 1306 (1970).
100. K. A. Burke and F. G. Donnan, J. Chem. Soc., 85, 555 (1904).
101. K. A. Burke and F. G. Donnan, Z. phys. Chem., 69, 148 (1909).
102. F. G. Senter, J. Chem. Soc., 97, 346 (1910).
103. F. G. Senter, J. Chem. Soc., 99, 95 (1911).
104. E. D. Hughes, C. K. Ingold, and S. Masterman, J. Chem. Soc., 1236 (1937).
105. W. A. Cowdrey, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 1243 (1937).
106. I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 166 (1946).
107. I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 169 (1946).
108. I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 173 (1946).
109. B. H. Nicolet and D. R. Stevens, J. Amer. Chem. Soc., 50, 135 (1928).
110. B. H. Nicolet and D. R. Stevens, J. Amer. Chem. Soc., 50, 212 (1928).
111. C. T. Benfey, J. Amer. Chem. Soc., 70, 2163 (1948).
112. S. Oae and C. A. Van der Werf, J. Amer. Chem. Soc., 75, 5037 (1953).
113. J. S. Coe and V. Gold, J. Chem. Soc., 4940 (1960).

114. N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. K. Iffland, J. Amer. Chem. Soc., **77**, 6269 (1955).
115. J. A. Vona and J. Steigman, J. Amer. Chem. Soc., **81**, 1095 (1959).
116. G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, J. Amer. Chem. Soc., **82**, 704 (1960).
117. E. Melandez-Andrew, Ann. Chim., **7**, 695 (1962).
118. Y. Pocker and D. N. Kevill, J. Amer. Chem. Soc., **87**, 4760 (1965).
119. Y. Pocker and D. N. Kevill, J. Amer. Chem. Soc., **87**, 4771 (1965).
120. Y. Pocker and D. N. Kevill, J. Amer. Chem. Soc., **87**, 4778 (1965).
121. Y. Pocker and D. N. Kevill, J. Amer. Chem. Soc., **87**, 5060 (1965).
122. E. S. Rudakov, V. V. Zamashchikov, E. G. Gushchina, V. P. Tret'yakov, and V. D. Belyaev, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **7**, 788 (1970).
123. E. S. Rudakov, V. V. Zamashchikov, and R. I. Rudakova, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **7**, 804 (1970).
124. E. S. Rudakov, V. D. Belyaev, and V. V. Zamashchikov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **8**, 207 (1971).
125. E. S. Rudakov, V. V. Zamashchikov, V. D. Belyaev, and E. G. Gushchina, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **8**, 219 (1971).
126. E. S. Rudakov, S. G. Popov, V. V. Zamashchikov, and V. D. Belyaev, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **8**, 881 (1971).
127. E. S. Rudakov, V. V. Zamashchikov, and V. D. Belyaev, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **9**, 31 (1972).
128. V. V. Zamashchikov and E. S. Rudakov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **9**, 281 (1972).
129. V. V. Zamashchikov and E. S. Rudakov, Reaktsionn. Sposobnost' Org. Soed. (Tartu), **9**, 287 (1972).
130. D. W. Colcleugh and E. A. Moelwyn-Hughes, J. Chem. Soc., 2542 (1964).
131. R. E. Robertson, Progr. Phys. Org. Chem., **4**, 213 (1967).
132. R. L. Heppolette and R. E. Robertson, Canad. J. Chem., **44**, 677 (1966).
133. N. Kornblum, Org. Reactions, **12**, 101 (1962).
134. S. A. Shevelev, Uspekhi Khim., **39**, 1773 (1970) [Russ. Chem. Rev., No. 10 (1970)].
135. H. Weiner and R. A. Sneen, J. Amer. Chem. Soc., **87**, 287 (1965).
136. H. Weiner and R. A. Sneen, J. Amer. Chem. Soc., **87**, 292 (1965).
137. J. W. Larsen and R. A. Sneen, J. Amer. Chem. Soc., **91**, 362 (1969).
138. J. W. Larsen and R. A. Sneen, J. Amer. Chem. Soc., **91**, 6031 (1969).
139. J. M. W. Scott, Canad. J. Chem., **48**, 3807 (1970).
140. H. R. Clark and M. M. Jones, J. Amer. Chem. Soc., **91**, 4302 (1969).
141. H. R. Clark and M. M. Jones, J. Catalysis, **24**, 472 (1972).
142. C. G. Swain, J. Amer. Chem. Soc., **70**, 1119 (1948).
143. C. G. Swain and W. P. Langsdore, J. Amer. Chem. Soc., **73**, 2813 (1951).
144. E. Gand, Bull. Soc. chim. France, **13**, 303 (1945).
145. C. Prevost and E. Singer, Bull. Soc. chim. France, 1068 (1950).
146. H. Martin, Compt. rend., **232**, 1762 (1951).
147. C. Prevost, Compt. rend., **236**, 288 (1953).
148. J. Landais, Ann. Chim., **8**, 575 (1963).
149. D. N. Kevill and V. V. Likhite, Chem. Comm., 247 (1967).
150. D. N. Kevill, G. H. Johnson, and V. V. Likhite, Chem. and Ind., 1555 (1969).
151. D. N. Kevill, W. A. Reis, and J. B. Kevill, Tetrahedron Letters, 957 (1972).
152. G. D. Parfitt, A. L. Smith, and A. G. Walton, J. Phys. Chem., **69**, 661 (1965).
153. P. S. Walton and M. Spiro, J. Chem. Soc. (B), 42 (1969).
154. L. J. Andrews and R. M. Keefer, J. Amer. Chem. Soc., **73**, 5733 (1951).
155. S. Koshy and R. Anantaraman, J. Amer. Chem. Soc., **82**, 1574 (1960).
156. N. M. Alpatova, V. V. Gavrilenko, Yu. M. Kessler, O. R. Osipov, and D. N. Maslin, "Kompleksy Metalloorganicheskikh, Gidridnykh i Galoidnykh Soedinenii Alyuminiya" (Complexes of Organometallic, Hydride, and Halide Compounds of Aluminium), Nauka, Moscow, 1970.
157. G. A. Olah and C. U. Pittman, Adv. Phys. Org. Chem. (Translated into Russian), Mir, Moscow, 1969, p. 338.
158. K. B. Yatsimirskii, Dokl. Akad. Nauk SSSR, **77**, 819 (1951).
159. K. H. Lieser, Z. anorg. Chem., **304**, 296 (1960).
160. K. H. Lieser, J. Inorg. Chem., **26**, 1575 (1964).
161. M. T. Beck, "Chemistry of Complex Equilibria", Akadémia Kiadó, Budapest, 1970.
162. D. J. Pasto and J. P. Sevenair, J. Amer. Chem. Soc., **93**, 711 (1971).
163. E. S. Rudakov, Dokl. Akad. Nauk SSSR, **212**, 417 (1973).

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