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The Effects of Pressure, Temperature and Solvent Composition on Solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in Water-*t*-butyl Alcohol Mixture

Yu Chul Park^{*1} and Young Je Cho

Department of Chemistry, College of Natural Sciences, Kyungpook National University,
Taegu 635. Received May 26, 1987

Rates of solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ have been investigated using spectrophotometric method at various pressures and temperatures in the mixtures of water with the *t*-butyl alcohol which possesses a high structure inducing capacity in water. The values of ΔV^\ddagger obtained from pressure effect on the rate constants were 2.55–5.83 cm³ mol⁻¹. These values were discussed in terms of dissociative mechanism. Extrema found in the variation of ΔH^\ddagger and ΔS^\ddagger with solvent composition correlated with extrema in the variation of the physical properties of the mixtures. The logarithms of rate constants correlated linearly with both Grunwald-Winstein parameter and the reciprocal of dielectric constant (D_s^{-1}). The gradient, m , of Grunwald-Winstein plot for the $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ was 0.09, which is significantly lower than those for the other cobalt (III)-dichloro complexes. It was suggested that the reaction is an I_d mechanism with long extension of Co-Cl bond in the transition state, as found for the C-Cl bond in the transition state for the solvolysis of *t*-butyl chloride.

Introduction

The solvolysis reactions of cobalt(III)-ammine complexes have been extensively investigated using a wide variety of approaches to establish the underlying mechanism.²⁻⁴ The application of activation volume to mechanistic elucidation for aquation of these type complexes has been established and reported.⁵⁻¹⁵

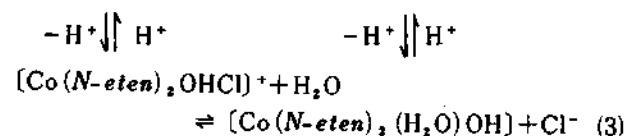
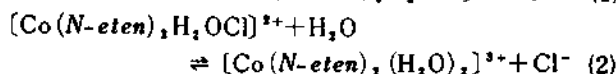
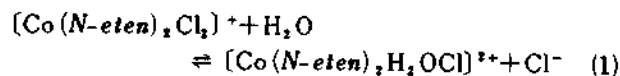
In investigation of the effect of solvent variation on reactivity, the dependences of rate constants on such properties of the mixed solvents as their dielectric constants or their Grunwald-Winstein Y values are often used in the diagnosis of mechanism.^{16,17} The mechanisms for reactions of cobalt (III) have generally been accepted to be dominated by bond-breaking dissociative processes.²⁻¹⁵ Interpretation of such I_d reactions involving the spread of a central charge through the extension of Co-Cl bond based on point charges in a dielectric continuum all require $\log k$ at constant temperature to vary linearly with the reciprocal of the dielectric constant (D_s^{-1}).³

We here report the result of a kinetic investigation of solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ (N-eten: N-ethylethylenediamine) at various pressures in water with added *t*-butyl alcohol which causes great changes in solvent structure. The

rate constants in the mixed solvent are analyzed in terms of Grunwald-Winstein Y parameter representing solvent ionizing power and dielectric constant. The activation volumes obtained from the pressure effect on rate constants are reported and the effects of charge separation on the mechanism of solvolysis are discussed.

Experimental

The complex, $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]\text{Cl}$ was prepared by using previously described method¹⁸ and the spectra data were consistent with literature values.¹⁸ The aquation of dichloro compounds of this type has been shown to occur in steps.¹⁹



The rate of aquation of the second chlorine from the aquo complex as in(2) is very slow. However, the hydroxo complex(3) aquates fairly rapidly. Therefore to determine the kinetics of step (1) without interference from step(3) it is necessary to run the aquation in highly acidic solutions (pH<3.0) which serves to repress reaction(2) and (3) but does not affect reaction (1).

Solvolysis reactions were followed spectrophotometrically at common pressure by means of a Shimadzu-Digital UV-210A. The temperature was maintained by Haake F 4391 circulator. All kinetic experiments were performed at 532 nm in 0.01M aqueous hydrochloric acid(pH2), ionic strength 0.5M (adjusted with NaCl), and binary aqueous mixtures. Rate constants were calculated from gradients of plots of log $(A_0 - A_\infty)/(A_t - A_\infty)$ against time, where A_t =absorbance at time t , etc. Activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) were calculated by least square analysis of $(\ln k_{obs}/T)$ against $1/T$ in the usual way.

Reactions at elevated pressures (up to 1500 bar) were conducted in a high-pressure spectrophotometric cell with sapphire windows in incorporated Shimadzu 210A spectrophotometer. Rate constants were determined by standard least squares using the Guggenheim method. Activation volumes (ΔV^\ddagger_{exp}) were determined by least-square analysis of rate and pressure data using the expression $\ln k_p = \ln k_0 + bp + cp^2$, where $\Delta V^\ddagger_{exp} = -bRT$.

Results and Discussion

The temperature dependence of solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl alcohol was collected in Table 1, in which ΔH^\ddagger and ΔS^\ddagger were calculated and included. The pressure dependence of solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl alcohol was recorded in Table 2. The values of ΔV^\ddagger obtained from pressure effect on the rate constants were included. These values were 5.83-2.55 $\text{cm}^3 \text{mol}^{-1}$. Rate of solvolysis of this complex decreased upon the applications of pressure.

Reaction Mechanism and Activation Volumes.

ΔV^\ddagger values have been employed successfully in the elucidation of reaction mechanism.

It has been recognized that the experimentally determined activation volume (ΔV^\ddagger_{exp}) can be considered as a composite of contributions originating from the displacement of

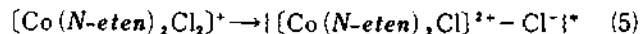
Table 2. Rate Constants and Activation volumes for Solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl Alcohol at 25°C under Various Pressures

W/W % <i>t</i> -BuOH	pressure (bar) $k \times 10^4, \text{sec}^{-1}$				ΔV^\ddagger $\text{cm}^3 \text{mol}^{-1}$
	1	500	1000	1500	
0	2.67	2.40	2.35	2.33	5.83
5	2.51	2.24	2.20	2.17	5.61
10	2.48	2.23	2.19	2.15	5.61
20	2.30	2.10	2.05	2.01	5.00
30	2.15	1.98	1.91	1.88	3.95
40	1.80	1.72	1.70	1.68	2.55

atoms at the activation site (the intrinsic of component, ΔV^\ddagger_{int}) and from changes in electrostriction in forming the activated state (ΔV^\ddagger_{el}). The latter term is principally related to changes in solvation of the precursor and activated states.

$$\Delta V^\ddagger_{exp} = \Delta V^\ddagger_{int} + \Delta V^\ddagger_{el} \quad (4)$$

In coordination chemistry, reactions often involve displacement of charged groups; hence, ΔV^\ddagger_{exp} involves a substantial contribution from ΔV^\ddagger_{el} , which may mask the mechanistically important ΔV^\ddagger_{int} component. ΔV^\ddagger_{exp} for the solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ may be dominated by ΔV^\ddagger_{el} term because the reactant is ionic compound and there is a substantial difference of charge contribution between initial and transition state. Thus ΔV^\ddagger_{exp} obtained from solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ should be explained by the Co-Cl charge separation of the following process.



$$\Delta V^\ddagger = \bar{V}(\text{CoN-eten}_2\text{Cl}^{2+}) - \bar{V}(\text{CoN-eten}_2\text{Cl}_2^+) + \bar{V}(\text{Cl}^-)$$



$$\Delta V^\ddagger = \bar{V}(\text{ClN-eten}_2\text{Co}^{\sigma+} - \text{Cl}^{\sigma-}) - \bar{V}(\text{CoN-eten}_2\text{Cl}_2^+)$$

In view of charge separation, the intermediate form in eq(5) in which Cl^- ion belongs to the complex cobalt differs from that in eq(6) in which Cl^- ion still belongs to cobalt ion. The positive charge of transition state is delocalized at complex cation in eq(5) but that is localized at cobalt cation in eq(6). The extension of Co-Cl bond in eq(5) certainly involves the solvent rearrangement during the activation process associated with significant charge separation. In this case, ΔV^\ddagger_{exp} will be dominated by ΔV^\ddagger_{el} , thus activation volumes will be negative values. According to eq(6), however, the charge separation does not effectively contribute to transition state. Thus the increase of positive charge at transition state is less than that in eq(5). On the contrary, the intrinsic component of activation volume(ΔV^\ddagger_{int}) is increased by Co-Cl bond extension and solvent molecular solvated in complex cation are desolvated by bond extension, hence a positive ΔV^\ddagger_{exp} is possible in eq(6).

ΔV^\ddagger_{exp} reported for the solvolysis of cobalt(III)-ammine complexes with chloride as leaving group are as follows:

Case 1 ($\Delta V^\ddagger_{exp} < 0$); $-9.9 \text{cm}^3 \text{mol}^{-1}$ for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, $-4.6 \text{cm}^3 \text{mol}^{-1}$ for $trans\text{-}[\text{Co}(\text{NH}_3)_4(\text{NH}_2\text{CH}_3)\text{Cl}]^{2+}$ and $-2.3 \text{cm}^3 \text{mol}^{-1}$ for $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}]^{2+}$.¹⁵

Case 2 ($\Delta V^\ddagger_{exp} > 0$); $11 \text{cm}^3 \text{mol}^{-1}$ for $trans\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^{\ddagger}$, $7.5 \text{cm}^3 \text{mol}^{-1}$ for $[\text{Co}(\text{tren})\text{Cl}_2]^+$ (tren; tris (2-aminoethyl)-amine)¹² and $8.7 \text{cm}^3 \text{mol}^{-1}$ for $trans\text{-}[\text{Co}(\text{dtcd})(\text{N}_3)\text{Cl}]^+$ (dtcd; 5.12-dimethyl 1,4,8,11-tetraazacyclotetradeca-4,11

Table 1. Rate Constants and Activation Parameters for Solvolysis of $trans\text{-}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl Alcohol at Several Temperature

W/W % <i>t</i> -BuOH	$k \times 10^4, \text{sec}^{-1}$				ΔH^\ddagger kJmol^{-1}	ΔS^\ddagger $\text{JK}^{-1} \text{mol}^{-1}$
	25°C	30°C	35°C	40°C		
0	2.65	4.23	7.45	14.31	85	-28
5	2.55	3.95	6.86	14.11	86	-27
10	2.50	3.84	6.28	13.46	83	-38
15	2.50	3.73	6.01	12.35	79	-49
20	2.45	3.70	5.94	12.28	80	-47
25	2.31	3.95	5.78	12.19	82	-40
30	2.10	3.45	5.74	10.64	81	-45
35	1.94	3.25	4.91	10.35	82	-43
40	1.83	3.04	4.82	9.85	83	-39

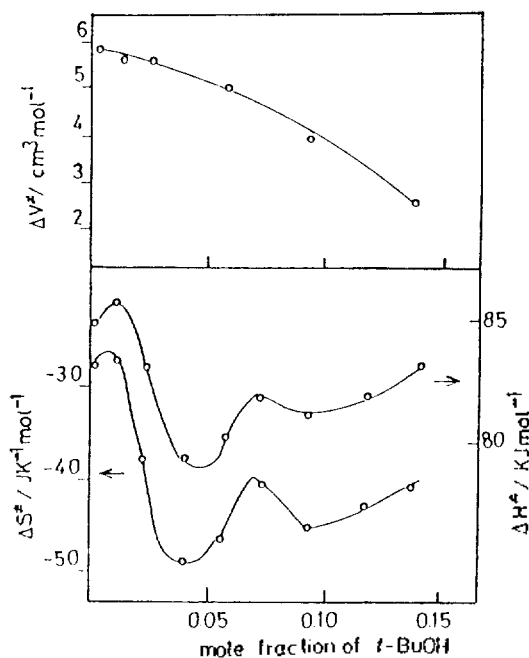


Figure 1. Plots of ΔV^\ddagger , ΔS^\ddagger and ΔH^\ddagger against mole fraction of *t*-butyl alcohol for solvolysis of $\text{trans}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl alcohol.

diene).¹³ Although there is no apparent mechanistic change occurring, there is a trend toward positive $\Delta V^\ddagger_{\text{exp}}$ in the complex ion with large cation and multidentate ligand. The activation volumes of solvolysis of $\text{trans}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl alcohol are 5.83-2.55 $\text{cm}^3 \text{mol}^{-1}$ in Table 2. The solvolysis of $\text{trans}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ is likely the bond break dominant dissociative mechanism which the charge separation proceeds to eq(6). Because of the large size of $\text{trans}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ and N-ethylethylenediamine as non-leaving group, the five coordinated intermediate in eq(6) might be stabilized.

Thermodynamic Activation Parameters. A plot of ΔH^\ddagger against ΔS^\ddagger , from which the determined isokinetic temperature was 283°K was linear despite the irregular variation of ΔH^\ddagger and ΔS^\ddagger with solvent composition as shown in Figure 1. Both ΔH^\ddagger and ΔS^\ddagger showed minima in the region of mole fraction of *t*-butyl alcohol $x_2 \approx 0.04$ and $x_2 \approx 0.01$. These mole fractions roughly correlate with the physical properties of water co-solvent mixtures. The partial molar volume of *t*-butyl alcohol, $V_2 - V_2^0$, and the excess enthalpy of mixing ΔH^\ddagger in water-*t*-butyl alcohol mixture have a deep minimum at $x_2 \approx 0.04$ ^{35,20,21} and a minimum at $x_2 \approx 0.1$ ^{35,21}, respectively. These extrema in physical properties at low x_2 in water-*t*-butyl alcohol are associated with sharp changes in solvent structure and show clearly the specific influence on the transition state parameters. It is suggested that the extrema described for the lower x_2 (0.04) correspond on the exertion of maximum strain by the branched alkyl groups lying in the cavities between the 'flickering clusters' of water on the cluster of structured water and that the extrema at the higher x_2 (0.1) correspond to the beginning of break down of the structure of the "clusters" due to the increasing stress within them.²²

Activation entropies for the solvolysis of $\text{trans}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ were negative values and represented irregular variation with solvent composition. But activation volumes

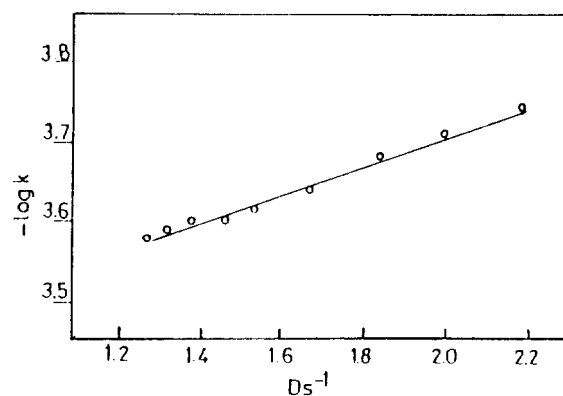


Figure 2. Plot of $-\log k$ against the reciprocal of the dielectric constant for solvolysis of $\text{trans}[\text{Co}(\text{N-eten})_2\text{Cl}_2]^+$ in water-*t*-butyl alcohol at 25°C.

for the solvolysis of the complex were positive values and monotonously decreased with solvent composition in Figure 1. A negative ΔS^\ddagger for equation of cobalt(III)-ammine complexes is paralleled by a negative ΔV^\ddagger ^{23,24} and indeed the expectation of a correlation of ΔS^\ddagger and ΔV^\ddagger has been presented on several occasions.^{11,25} It has been pointed out, however, that an exact correlation need not be expected^{13,24} and it is apparent that no correlation is observed in Figure 1.

It is likely that ΔV^\ddagger will be affected by the initial charge on the complex, the formal charge on the leaving group, and the type and size of the non-leaving group. The steric interaction of the latter with the leaving group and with each other, and their motion during activation will play a role in determining the charge in solvation occurring.

The Effect of Solvent Composition on the Rate.

Solvation is an important factor in determining reactivity; the variation of reaction rates with solvent composition often provides insight into reaction mechanism. The solvent composition has been characterized in terms of the Grunwald-Winstein Y parameter representing solvent ionizing power.¹⁷

Interpretations of I_d reactions involving the spread of a central charge through the extension of Co-Cl bond on point charges in a dielectric continuum mostly require $\log k$ at constant temperature to vary linearly with the reciprocal of the dielectric constant (D_s^{-1}). In Figure 2, $\log k$ at 25°C varied linearly with D_s^{-1} which were obtained by interpolating the data of Brown and Ives²⁶ and of Broadwater and Kay.²⁷

The Laidler-Landskroener equation¹⁶ for the charge spread of a Co-Cl bond in the initial and transition state in a dielectric continuum has been extended^{3a} to include the differential effect of structure changes in the solvent on the initial and transition states:

$$RT \ln (k_w/k_s) = Ne^2/2 (1/D_s - 1/D_w) \{ Zm^2/rm + Zx^2/rx - Zc^2/rc + 3/2 (Gm/r^3m + Gx/r^3x - Gc/r^3c) \} + Gt(M)n + Gt(X)n - Gt(C)n \quad (7)$$

In equation(7), k is the rate constant in water(w) and in the mixed solvent(s), N , e and r are Avogadro's number, the electronic charge and radius, respectively. G is related to dipole moment, and $Gt(i)$ is the free energy of transfer of i from water into the mixture excluding the contribution from the electrostatic term already present on the right-hand side.

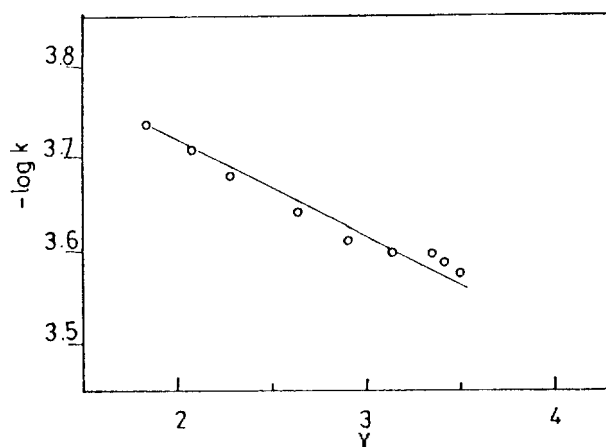


Figure 3. Plot of $-\log k$ against the Grunwald-Winstein Y parameter for solvolysis of $\text{trans-}[\text{Co}(\text{N-eten})_2 \text{Cl}_2]^+$ in water-*t*-butyl alcohol.

The linearity in the plot of $\log k$ against D_s^{-1} for the solvolysis of this complex (Figure 2) shows that

$$G t(\text{C})n = G t(\text{M})n + G t(\text{X})n \quad (8)$$

The linearity of this plot confirms that this solvolysis in the mixed solvent is similar to the S_N1 solvolysis of *t*-butyl chloride in water-ethyl alcohol²⁸ where the extension of C-Cl bond in transition state to form separate ions is virtually complete.²⁹

Correlation of rate constants with Y values have been of assistance in diagnosing the reaction mechanism. The Y values were calculated using the data of Robertson and Sugamori³⁰ in the region 20-50% *v/v* *t*-butyl alcohol. For solvolysis of the $\text{trans-}[\text{Co}(\text{N-eten})_2 \text{Cl}_2]^+$ in water-*t*-butyl alcohol, plots of $\log k$ against the respective solvent Y values showed a reasonable linear correlation in Figure 3. The gradient, m , of this plot was 0.09 for the $\text{trans-}[\text{Co}(\text{N-eten})_2 \text{Cl}_2]^+$, which is significantly lower than that for the cobalt(III) dichloro complex ion (0.32).²⁶ Although there is no mechanistic change, the reported values of m show wide variety; values of m for the cobalt(III)-ammine complexes in mixed solvent are 0.32 for $\text{trans-}[\text{Co}(\text{en})_2 \text{Cl}_2]^+$ ion in water-methanol,²⁶ 0.09 for $\text{trans-}[\text{Co}(\text{en})_2 \text{NO}_2\text{Br}]^+$ in water-methanol²⁶, 0.08 for $\text{trans-}[\text{Co}(\text{Py})_4 \text{Cl}_2]^+$ in water-propan-2-ol³⁰ and 0.14 for $\text{trans-}[\text{Co}(\text{Py})_4 \text{Cl}_2]^+$ in water-*t*-butyl alcohol.²¹

It is thus suggested that the leaving chloride in the solvolysis of the $\text{trans-}[\text{Co}(\text{N-eten})_2 \text{Cl}_2]^+$ complex ion does not completely dissociate before the entering water molecule starts to associate; that means the reaction is an I_d mechanism with long extension of the Co-Cl bond in the transition state, as found for the C-Cl bond in the transition state for the solvolysis of *t*-butyl chloride. This long extension of Co-Cl bond is indicated as being virtually complete in the transition state. This is consistent with the results derived from activation volumes. Also the linearity of this plot confirms that solvolysis of $\text{trans-}[\text{Co}(\text{N-eten})_2 \text{Cl}_2]^+$ in the water-*t*-butyl alcohol is similar to the S_N1 solvolysis of *t*-butyl chloride in water-*t*-butyl alcohol, which is mechanistically agreed with the result of Figure 2.

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References

1. Present Address: Visiting Professor, Department of Chemistry, Northern Illinois University, DeKalb, IL, 60115, U.S.A.
2. (a) C. H. Langford, *Inorg. Chem.*, **3**, 228 (1964). (b) M. Pribranic, M. Birus, D. Pavlovic and S. Asperger, *J. Chem. Soc. Dalton*, 2518 (1973); (c) U. Mayer, *Pure Appl. Chem.*, **41**, 291 (1975); (d) B. Perlmutter-Hayman, *Prog. Inorg. Chem.*, **20**, 229 (1975).
3. (a) C. F. Wells, *J. Chem. Soc. Faraday I*, **73**, 1851 (1977); (b) C. N. Elgy and C. F. Wells, *J. Chem. Soc. Dalton*, 2405 (1980); (c) A. E. Eid and C. F. Wells, *J. Chem. Soc. Faraday I*, **77**, 1621 (1981); (d) G. S. Groves and C. F. Wells, *ibid.*, **78**, 619 (1982); (e) A. E. Eid and C. F. Wells, *ibid.*, **79**, 253 (1983); (f) I. M. Sidahmed and C. F. Wells, *J. Chem. Soc. Dalton*, 1969 (1984).
4. Y. Ch Park, Z. U. Bae and S. W. Kim, *J. Korean Chem. Soc.*, **31**, 37 (1987).
5. W. E. Jones, L. R. Carrey and T. W. Swaddle, *Can. J. Chem.*, **50**, 2739 (1972).
6. W. E. Jones and T. W. Swaddle, *ibid.*, **50**, 2757 (1972).
7. D. R. Stranks, *Pure Appl. Chem.*, **38**, 303 (1974).
8. H. Lentz and S. O. Oh, *High Temp-High Pressures*, **7**, 91 (1975).
9. D. A. Palmer and H. Kelm, *Inorg. Chim. Acta*, **19**, 117 (1976).
10. M. V. Twigg, *ibid.*, **24**, 184 (1977).
11. D. A. Palmer and H. Kelm, *Inorg. Chem.*, **16**, 3139 (1977).
12. G. A. Lawrance, *Inorg. Chim. Acta*, **34**, 275 (1980).
13. G. A. Lawrance and S. Suvachittanont, *Aust. J. Chem.*, **22**, 273 (1980).
14. G. A. Lawrance, *Inorg. Chem.*, **21**, 3687 (1982).
15. G. A. Lawrance, K. Schneider and R. V. Eldik, *ibid.*, **23**, 3922 (1984).
16. K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, **52**, 200 (1956).
17. E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).
18. F. Basolo, *ibid.*, **75**, 227 (1953).
19. R. G. Pearson, C. R. Boston and F. Basolo, *ibid.*, **75**, 3089 (1953).
20. K. Nakanish, *Bull. Chem. Soc. Jpn.*, **22**, 793 (1960).
21. C. N. Elgy and C. F. Wells, *J. Chem. Soc. Faraday Trans I.*, **79**, 2367 (1983).
22. C. F. Wells, *ibid.*, 624 (1974).
23. M. V. Twigg, *Inorg. Chim. Acta*, **24**, L84 (1977).
24. G. A. Lawrance and S. Suvachittanont, *ibid.*, **32**, L13 (1979).
25. G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **51**, 821 (1973).
26. A. C. Brown and D. J. G. Ives, *J. Chem. Soc.*, 1608 (1962).
27. T. L. Broadwater and R. L. Kay, *J. Phys. Chem.*, **74**, 3802 (1970).
28. P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).
29. M. H. Abraham, *Prog. Phys. Org. Chem.*, **11**, 1 (1974).
30. R. E. Robertson and S. G. Sugamori, *J. Am. Chem. Soc.*, **91**, 7256 (1969).