Mechanism of Octahedral Substitutions. Part IX.[1] Grunwald–Winstein Treatment of Spontaneous Aquation of *trans*-Chloronitro- and *trans*-Dichlorobisethylenediaminecobalt(III) Ions in Mixed Aqueous Solvents

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The first-order rate constants of spontaneous aquation of *trans*-chloronitro- and *trans*-dichlorobis(ethylenediamine)cobalt(III) ions were measured in a range of binary mixed solvents, including methanol–, ethanol–, dioxan–, and acetone–water solutions extended to 10% (v/v) water content. Both complexes aquated completely in water-rich mixtures and incompletely in solutions containing higher percentages of organic component.

The logarithms of rate constants correlated linearly with Grunwald–Winstein solvent *Y* values, with slopes of $m = 0{\cdot}32$ for the dichloro- and $m = 0{\cdot}09$ for the chloronitro-complex. The lower susceptibility of the chloronitro-complex to solvent ionizing power indicates that the remaining bonding to the leaving chloride in the transition state is larger in the chloronitro- than in the dichloro-complex. Mechanistic implications are discussed.

THE influence of the mixed solvent composition upon the rate of equation of cobalt–ammine complexes has been a subject of recent interest.[2] The solvent composition has been characterized in terms of the Grunwald–Winstein *Y* parameter representing solvent ionizing power.[3] Correlation of rate constants with *Y* values has been of assistance in diagnosing the reaction mechanism. In the first reported correlation[4] of log *k* and *Y* for the aquation of *trans*-$[Co(en)_2Cl_2]^+$ at 35 °C in water–methanol mixtures no linearity was obtained in the methanol-rich mixtures [above 50% (v/v) methanol]. The *trans*-dichloro-complex has been studied[2b] at 35 °C in a variety of aqueous mixed solvents, but was restricted to 30% (v/v) of organic components. The Grunwald–Winstein treatment of the aquation of *trans*-$[Co(en)_2NO_2Cl]^+$ at 20 °C has been applied to aqueous formic acid mixtures only by Burgess *et al.*[2b] using published data.[5]

We now report our results on the rate of aquation of *trans*-$[Co(en)_2Cl_2]^+$ and of *trans*-$[Co(en)_2NO_2Cl]^+$ at 25 °C in a range of binary mixed solvents, including methanol–, ethanol–, dioxan–, and acetone–water solutions extended to 10% (v/v) water content.

RESULTS AND DISCUSSION

The steric course of reaction (1) in mixed solvents was found to be in agreement with that for aqueous solutions where a mixture of *cis*- and *trans*-products was observed[6] for L = Cl and retention of configuration[7] for $L = NO_2$. Rate constants are in the Table and

$$trans\text{-}[Co(en)_2LCl]^+ + H_2O \underset{k}{\overset{k}{\rightleftharpoons}} [Co(en)_2L(H_2O)]^{2+} + Cl^- \qquad (1)$$

correlations of the logarithms of the rate constants for aquation with the solvent *Y* values are shown in Figures 1 and 2. The reactions went to completion only in purely aqueous solutions. The contribution of the reverse reaction increased in importance as the organic component of the solvent increased. The equilibrium of the aquation is shifted far to the left in mixtures rich in organic solvent, as is seen from the Table, where the equilibrium ratio *Q* is defined as $Q = [Co(en)_2L(H_2O)]^{2+}/[Co(en)_2LCl]^+$. The establishment of the equilibrium has not been pointed out in the previous reports on the aquations of cobalt–ethylenediamine complexes even in as much as 70% (v/v) methanol.[4]

The slope of the straight line for the aquation of *trans*-$[Co(en)_2Cl_2]^+$ ion was found to be $m = 0{\cdot}32$ (Figure 1). The previously reported *m* values are: 0·25 at 25 °C for water-rich methanol–water mixtures;[4] and 0·35 at 35 °C for water–non-aqueous solvents containing up to 30% (v/v) non-aqueous component.[2b] Both these *m* values were determined in water-rich mixed solvents only where the range of *Y* values was small and the determination of the slope was less precise. This is probably the reason that the difference

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[1] Part VIII, Z. Bradić, M. Biruš, D. Pavlović, M. Pribanić, and S. Ašperger, preceding paper.

[2] (*a*) J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2703; (*b*) J. Burgess and M. G. Price, *ibid.*, 1971, 3108.

[3] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; P. R. Wells, ' Linear Free Energy Relationship,' Academic Press, New York, 1968, p. 59.

[4] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.

[5] S. Ašperger, M. Orhanović, and I. Murati, *J. Chem. Soc.*, 1964, 2969.

[6] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637.

[7] S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862.

between the two m values (0·25 and 0·35) was considered insignificant.[2b] The slope of the straight line for the aquation of *trans*-$[\mathrm{Co(en)_2NO_2Cl}]^+$ ion gave $m = 0{\cdot}09$ (Figure 2). For the aquation of *trans*-$[\mathrm{Co(en)_2NO_2Br}]^+$ the reported value [4] of m is *ca.* 0·18 and for aquation of *trans*-$[\mathrm{Co(en)_2NO_2Cl}]^+$ ion in water–formic acid mixtures m was calculated from literature data to be 0·32.[2b] It appears that the precision of the reported m values for the *trans*-dichloro- and *trans*-chloronitro-complex ions was not adequate to consider their differences as significant. The statistical treatment (see Experimental section) of the plots in Figures 1 and 2 allow us to conclude that the m value for *trans*-$[\mathrm{Co(en)_2NO_2Cl}]^+$ ion (0·09) is significantly lower than that for the dichloro-complex ion (0·32). The observed m values reveal that the dichloro-complex is more sensitive than the chloronitro-complex to the solvent ionizing power, suggesting a smaller extent of charge separation in the transition state in the chloronitro- than in the dichloro-complex ion. Since the charge separation parallels the bond weakening this result indicates that the remaining bonding to the leaving chloride in the transition state is larger in the chloronitro- than in the dichloro-complex.

First-order rate constants for aquation of 0·001—0·0001M-*trans*-$[\mathrm{Co(en)_2LCl}]^+$ in mixed aqueous solvent at 25 °C

Non-aqueous component (% v/v)	Y	Methanol				Y	Ethanol			
		L = NO$_2$		L = Cl			L = NO$_2$		L = Cl	
		$10^5k/\mathrm{s^{-1}}$	Q	$10^5k/\mathrm{s^{-1}}$	Q		$10^5k/\mathrm{s^{-1}}$	Q	$10^5k/\mathrm{s^{-1}}$	Q
0	3·49	115·4 [a]	∞	4·000 [b]	∞	3·49	115·4 [a]	∞	4·000 [b]	∞
10	3·28	113·2	—	3·086	12·33	3·31	111·8	31·26	3·100	124·00
20	3·03	98·0	—	2·230	9·86	3·05	103·7	16·54	2·365	39·00
25	—	—	—	—	—	2·91	100·0	14·38	2·010	11·82
30	2·75	85·6	9·00	1·751	6·87	2·72	93·1	12·70	1·630	7·55
50	1·97	71·3	4·00	0·718	2·92	1·66	85·1	5·85	—	—
60	1·49	62·4	2·57	0·575	1·75	1·12	74·3	3·27	0·685	1·65
80	0·38	60·8	0·61	0·399	0·45	0·00	55·1	0·78	0·241	0·32
90	−0·30	—	—	0·179	0·10	−0·75	—	—	0·148	0·17
		Dioxan					Acetone			
0	3·49	115·4 [a]	∞	4·000 [b]	∞	3·49	115·4 [a]	∞	4·000 [b]	∞
10	3·22	86·1	5·10	2·629	29·30	3·23	107·0	—	3·106	—
20	2·88	—	—	2·006	21·22	2·91	98·3	75·92	2·501	—
25	—	—	—	—	—	2·69	98·9	19·00	2·210	44·45
30	2·46	75·1	3·39	1·462	8·26	2·48	95·5	12·70	1·875	9·53
50	1·36	62·7	1·19	0·702	1·47	1·40	82·6	4·05	1·115	4·68
60	0·72	52·7	0·53	0·419	0·45	0·80	72·4	2·10	0·927	3·85
80	−0·83	—	—	—	—	−0·67	42·8	0·39	0·128	0·13

a and *b* values correspond fairly closely to reported data from ref. 6 and from ref. 5.

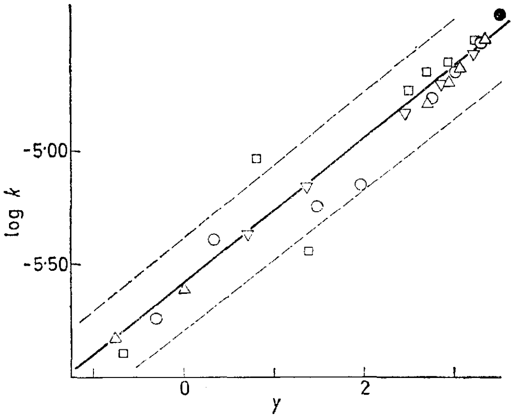

FIGURE 1 Correlation of the logarithms of first-order rate contant (k) for aquation of *trans*-$[\mathrm{Co(en)_2Cl_2}]^+$ in mixed aqueous solvents with solvent Y values. Organic component: ○, methanol; △, ethanol; ▽, dioxan; □, acetone; and ●, water. Broken lines are 95% confidence limits.

It is generally agreed that substitutions of octahedral complexes occur by essentially bond-breaking mechanisms, but the ' details ' can vary. It is suggested that in the aquation of the chloronitro-complex ion the leaving chloride does not completely dissociate before the entering water molecule starts to associate. The term ' solvent assisted dissociation ' has been coined to describe this situation.[8,9] Alternatively it could be claimed that the aquations of both dichloro- and chloronitro-complexes are I_d (interchange dissociation) processes,[10] where ' accidental bimolecularity ' resulted

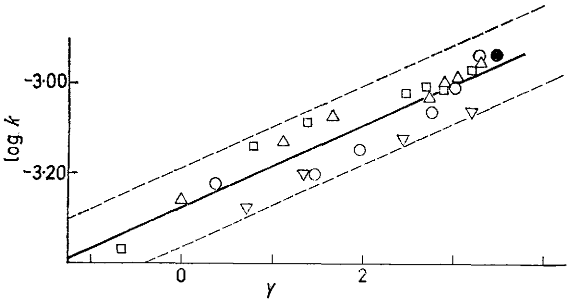

FIGURE 2 Correlation of the logarithms of first-order rate constant (k) for aquation of *trans*-$[\mathrm{Co(en)_2NO_2Cl}]^+$ in mixed aqueous solvents with solvent Y values. Marks are the same as in Figure 1

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[8] T. P. Jones, W. E. Harris, and W. J. Wallace, *Canad. J. Chem.*, 1951, **39**, 2371.

[9] F. Basolo and R. G. Pearson, ' Mechanism of Inorganic Reactions,' Wiley, New York, 1967, p. 239.

[10] The symbolism employed in C. H. Langford and H. B. Gray, Ligand Substitution Processes,' Benjamin, New York, 1965.

in different bond strengths of the incoming water molecule to the central metal atom of the complexes in the transition state.

EXPERIMENTAL

Materials.—*trans*-$[Co(en)_2NO_2Cl]NO_3$ and *trans*-$[Co(en)_2Cl_2]Cl$ were prepared according to described procedures.[11] The absorption spectra of these complexes agreed well with literature data. All other chemicals were Fluka analytical grade.

Kinetics.—Aqueous mixtures of solvents were brought to the appropriate temperature and the weighed amount of the complex was added and quickly dissolved. The complex concentration ranged from 0·001M to 0·0001M. Absorbance change was followed spectrophotometrically on a Cary 16K spectrophotometer at 340 nm for the chloronitro- and at 500 nm for the dichloro-complex. The first-order rate constants were obtained from the slope of the logarithm of the absorbance change against the reaction time. When the reaction did not go to completion the first-order aquation rate constant k was calculated from $k = k_{obs}\ (x_e/a)$, where k_{obs} is the observed first-order rate constant, a is the initial concentration of *trans*-$[Co(en)_2LCl]^+$, and x_e is the equilibrium concentration of the aquo-complex. The kinetic studies showed that the aquation rate constant, in the region of chloride concentration studied, was not significantly affected by the change in chloride concentration. The rate constant, k', of the reverse reaction appears to be a first-order rate constant and hence the extent of ion-pairing in these water-poor mixtures is large. It is well known that in aqueous solution, where the ion-pairing constants are small, the rates of anations of cobalt–amine complexes are of the first order with respect to the nucleophilic reagent [12a] but of zeroth order in methanol solution,[12b] and of nearly zeroth order in 8% aqueous tetramethylene sulphone.[12c]

Statistical Treatment of Results.—The assessment of correlation of the logarithms of the rate constants with the Y values in both the dichloro- and nitrochloro-complex was obtained in terms of correlation coefficients r and the test of significance. The correlation coefficients were calculated from standard equations [13] ($r_{Cl} = 0{\cdot}98$ and $r_N = 0{\cdot}94$) and Kendall's t variables from the formula $t = r(n-2)^{\frac{1}{2}}/(1-r^2)^{\frac{1}{2}}$, where n is the number of measurements ($n_{Cl} = 27$ and $n_N = 25$) (subscripts Cl and N mean dichloro- and nitrochloro-system, respectively).

The calculated t variables ($t_{Cl} = 24{\cdot}6$ and $t_N = 13{\cdot}4$) are higher than the tabulated values [13] according to the student distribution with the level of significance of 0·01 [$t_{Cl} = 2{\cdot}79$ and $t_N(\text{lit}) = 2{\cdot}81$] showing a correlation in general.

The best least-squares lines in Figures 1 and 2 are represented by the equations: $\log k_{Cl} = 0{\cdot}32Y - 5{\cdot}59$ and $\log k_N = 0{\cdot}09Y - 3{\cdot}28$.

The standard deviation σ of log k and Y was calculated according to the literature [13] ($\sigma_{Cl\,\log k} = 0{\cdot}430$, $\sigma_{Cl\,Y} = 1{\cdot}31$; $\sigma_{N\,\log k} = 0{\cdot}108$, $\sigma_{N\,Y} = 1{\cdot}15$).

The standard error of the slope from equation (2) is $s_{mCl} = 0{\cdot}0946$ and $s_{mN} = 0{\cdot}0616$.

$$s_m = \left(\frac{1}{n-2}\,\frac{\sigma_{\log k}}{\sigma_Y} - m^2\right)^{\frac{1}{2}} \tag{2}$$

A significant difference between the slopes for the dichloro- ($m_{Cl} = 0{\cdot}32$) and that for the nitrochloro-complex ($m_N = 0{\cdot}09$) has been shown by F- and t-tests. The F-value ($F = 2{\cdot}33$) follows from $F = (s_{mCl})^2/(s_{mN})^2$. The tabulated F-value [13] according to the Fisher distribution with the level of significance of 0·01 ($F_{lit} = 2{\cdot}64$) is higher than that calculated ($2{\cdot}64 > 2{\cdot}33$) showing no significant difference between the variances of the slopes for the dichloro- and the nitrochloro-complex.

From $t_{ClN} = (m_{Cl} - m_N)/s_{ClN}$, $t_{ClN} = 10{\cdot}33$, where s_{ClN} is 0·022 as calculated from equation (3).

$$s_{ClN} = \left(\frac{[(n_{Cl}-1)s_{mCl}{}^2 + (n_N-1)s_{mN}{}^2](n_{Cl}+n_N)}{(n_{Cl}+n_N-2)\cdot n_{Cl}\cdot n_N}\right)^{\frac{1}{2}} \tag{3}$$

The tabulated t-value [13] according to the Student distribution with the level of significance of 0·01 ($t_{lit} = 2{\cdot}58$) is lower than that calculated ($2{\cdot}58 < 10{\cdot}33$) showing a significant difference between the values of the slopes for the dichloro- ($m_{Cl} = 0{\cdot}32$) and the nitrochloro- ($m_N = 0{\cdot}09$) systems. This difference merits chemical explanation.

The 95% confidence limits * were calculated as previously described.[14]

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* The 95% confidence limits in Figures 1 and 2 appear as straight lines with the same gradients as the best least-squares lines. Actually they are curves but the deviation from the linearity in the region studied is too small to be observed.

[11] A. Werner, *Annalen*, 1912, **386**, 1.

[12] (*a*) Ref. 9, p. 203; (*b*) S. Ašperger, M. Flögel, and M. Papić, *J. Chem. Soc.* (*A*), 1967, 110; (*c*) C. H. Langford and M. P. Johnson, *J. Amer. Chem. Soc.*, 1964, **86**, 229.

[13] M. R. Spiegel, ' Theory and Problems of Statistics,' McGraw-Hill, New York, 1961.

[14] S. Ašperger and I. Murati, *Analyt. Chem.*, 1954, **26**, 543.