in water are shown. It seems a reasonable conclusion from these data that the methoxide ion reaction in methanol follows the same mechanism as the hydroxide ion reaction in water. If this is an SN1CB mechanism in the latter case, then there is no evidence for an SN2 displacement mechanism involving methoxide ion in methanol.

It also seems reasonable from the effect of structure on reactivity in each case, to assign a common mechanism to the acid hydrolysis reaction in water and to the reaction with various anions in methanol. Because steric acceleration is produced by bulky substituents, an SN1 dissociation mechanism seems most likely. The chief difference between the over-all observed results in the two solvents is that an aqua complex is stable whereas a methanol complex is not. The slower rate of reaction in methanol (by about a factor of 10) is adequately explained in terms of the lower dielectric constant since a separation of charge in the transition state occurs. It may be noted that the reaction with OCH_3^- is actually slower than the reaction with OH^- even though a neutralization of charge occurs in the transition state.

It is perhaps worth mentioning that the data obtained by Brown and Ingold[3] on the reactions of *cis*-$Co(en)_2Cl_2^+$ with weakly basic anions is not necessarily proof of an SN1 mechanism. Thus all of the observations (independence of rate on the nature and concentration of the entering anion, mass law retardation and rate of racemization equal to rate of chloride ion release) are equally in agreement with an SN2 mechanism involving the solvent methanol as a nucleophilic reagent. This is because of the demonstrated instability of the methanol complexes which would be formed as intermediates. In such a case the SN1 and SN2 mechanisms become kinetically indistinguishable and the optical results can also be explained on the basis of rapid racemization of the unstable complex.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. XIV. Reactions of *cis*-$Co(en)_2Cl_2^+$ with Basic Anions in Methanol[1,2]

BY RALPH G. PEARSON, PATRICK M. HENRY AND FRED BASOLO

RECEIVED MAY 25, 1957

Rates of reaction of *cis*-$Co(en)_2Cl_2^+$ with acetate ion, azide ion and nitrite ion in methanol are found to be somewhat greater than for non-basic anions. This is true even after buffering to suppress the considerably greater increases in rate due to methoxide ion. The corrected rate constants do not follow a simple first-order law, the rates being almost zero order in the basic anion at higher concentration. This behavior can be explained on the basis of ion-pair formation for which additional spectrophotometric evidence is presented. Possible mechanisms are suggested for the reaction of the basic anions with the complex ion. A simple SN2 displacement mechanism is unlikely.

This paper represents a continuation of the work reported in reference 1 on the rates of reactions of complexes of the type $Co(AA)_2Cl_2^+$ in methanol solutions with various anions. In particular it was desired to restudy the reaction of *cis*-$Co(en)_2Cl_2^+$ with basic anions since in several such cases an SN2 or displacement mechanism seemed to operate. The evidence for this rested on the observation that the complex ion reacted more rapidly with CH_3O^-, N_3^- and NO_2^- than with $^*Cl^-$, Br^-, NO_3^- and SCN^-, and further the rates with the basic anions were roughly proportional to the concentration of the anion.[3]

The reaction with methoxide ion in methanol is expected to be analogous to the reaction with hydroxide ion in water and as such probably involves a special SN1CB mechanism.[1] In view of the very large rate constant for this reaction of methoxide ion, it is necessary to repeat the earlier experiments[3] in buffered media to suppress the reaction arising from equilibria of the type

$$N_3^- + CH_3OH \rightleftharpoons HN_3 + CH_3O^- \qquad (1)$$

In the case of the *trans*-dichloro complexes of cobalt(III) such buffering usually completely removed any increased rate in the presence of basic anions.

Experimental

The general method of operation was as outlined previously.[1] Reactions were followed by potentiometric titration of chloride ion. Removal of both chlorides was followed in the case of acetate solutions and the first chloride only in the case of azide and nitrite solutions. Ion-pair formation constants were determined spectrophotometrically by measuring the ultraviolet absorption of the solution. The data were treated by the method of Newton and Arcand.[4] The racemization of optically active *cis*-$Co(en)_2Cl_2^+$ was followed by using a water-jacketed Bellingham and Stanley polarimeter.

Results

Table I shows some data obtained for the pseudo-first-order rate constants for the release of chloride ion in acetate solutions. These data, calculated on the basis of one chloride ion only removed in the rate step, show as expected that buffering has a considerable effect on the rate. Thus the rate in unbuffered solution of 0.0192 *M* sodium acetate is cut by a factor of four on adding sufficient acid. Unlike the corresponding *trans*-complexes, however, a limiting rate is reached, after which further addition of acid has no effect. Furthermore it

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[1] For previous papers in this series see THIS JOURNAL, **79**, 5379 (1957).

[2] Presented in part at the Dallas Meeting of the A.C.S. April, 1956. This investigation supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

[3] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

[4] T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).

TABLE I

EFFECT OF BUFFERING ON THE RATE OF RELEASE OF CHLORIDE ION FROM *cis*-$Co(en)_2Cl_2^+$ IN SODIUM ACETATE SOLUTIONS IN METHANOL AT 25°

$[OAc^-] = 0.0192\ M$

[HOAc]	$k^a \times 10^2$, min.$^{-1}$
None	45.5
0.0022	13.2
.0048	11.7
.0096	11.5

[a] Calculated on the basis of one chloride only removed in rate step.

was found by following these reactions for longer times that linear first-order plots could be obtained only if it is assumed that two chloride ions are released in the slow step. This is reasonable since by analogy to $Co(en)_2OHCl^+$, $Co(en)_2OAcCl^+$ would be expected to be very reactive.[5]

Accordingly in the data presented in Table II, first-order rate constants were calculated on the basis of two chlorides removed in one step, and all solutions were sufficiently buffered to obtain a rate independent of methoxide ion concentration. The rate of reaction of *cis*-$Co(en)_2Cl_2^+$ with non-basic anions from ref. 3 is also included for comparison. Figure 1 shows these data graphically including the results of runs where the ionic strength was held constant at 0.0192 by the addition of $LiClO_4$.

TABLE II

RATE CONSTANTS FOR THE RELEASE OF TWO CHLORIDE IONS FROM *cis*-$Co(en)_2Cl_2^+$ IN BUFFERED ACETATE SOLUTIONS IN METHANOL AT 25°

Concentration of complex = 6.0×10^{-4} *M*. Acetic acid concentration was always one-half of that of the acetate ion.

$[OAc^-]$	$[LiClO_4]$	$k \times 10^2$, min.$^{-1}$
0.0192	None	4.7
.0144	None	4.5
.0096	None	4.2
.0048	None	3.6
.0024	None	3.3
.0012	None	3.0
.0006	None	2.3
None	None	2.0[a]
0.0144	0.0048	4.0
.0096	.0096	3.4
.048	.0144	2.8
.0012	.0180	2.0
.0006	.0186	1.8

[a] Rate of radiochloride ion exchange from ref. 3.

Table III shows the data obtained for the rate of chloride ion release from *cis*-$Co(en)_2Cl_2^+$ in sodium azide solutions. In this case the first-order plots were linear if plotted on the basis of one chloride only removed in the rate step. After one half-life positive deviations occurred which showed that the second chloride ion was coming off at a sufficient rate to interfere. Table IV shows some fragmentary data obtained with sodium nitrite solutions. Table V has the rates of racemization observed using *d*-$Co(en)_2Cl_2^+$ in the presence of acetate ion and azide ion.

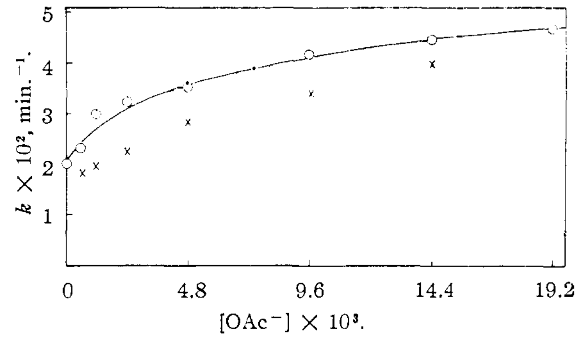

Fig. 1.—Variation of rate of chloride ion release of *cis*-$Co(en)_2Cl_2^+$ with increasing concentration of acetate ion at 25°; ×, ionic strength adjusted to 0.0192 with $NaClO_4$.

Discussion

The data in Table I and III show that failure to buffer solutions of basic anions, in methanol as in water, gives rates of reaction with *cis*-$Co(en)_2Cl_2^+$ that are too high. The effect is smaller, however, than with the *trans*-isomer. This is reasonable since the rate of the reaction with non-basic anions is about seven times greater for the *cis*-isomer than for the *trans*. The same is true in water where the rate of acid hydrolysis is sevenfold greater for the *cis* than for the *trans*-isomer. The rate of reaction of the *cis*-isomer with hydroxide ion, on the other hand, is less than for the *trans*-isomer by a factor of three.[6] In the same way as was done in ref. 1, a value for the rate constant for the reaction with methoxide ion may be estimated from the data of Table I. The result is about 2×10^1 mole^{-1} sec.$^{-1}$, which is about half that of the *trans*-isomer.

TABLE III

RATE OF RELEASE OF CHLORIDE ION FROM *cis*-$Co(en)_2Cl_2^+$ IN SODIUM AZIDE SOLUTIONS IN METHANOL AT 25°

Complex is 6.0×10^{-4} *M*.

$[N_3^-]$	$[HN_3]$	$k \times 10^2$, min.$^{-1}$
0.0012	None	6.5
.0012	0.0006	3.4
.0024	.0012	3.7
.0048	.0024	4.8
.0096	.0048	5.1
.0192	.0096	5.5
.0192	.0048	5.7
.0192	.0036	5.4
.0192	.0096	2.2[a]
None	None	2.0[b]

[a] Also 0.0192 *M* in chloride ion. Rate followed spectrophotometrically. [b] From ref. 3.

TABLE IV

RATE OF RELEASE OF CHLORIDE ION FROM *cis*-$Co(en)_2Cl_2^+$ IN THE PRESENCE OF NITRITE ION AT 25° IN METHANOL

Complex is 6.0×10^{-4} *M*

$[NO_2^-]$	$[HNO_2]$	$k \times 10^2$, min.$^{-1}$
0.0240	0.0048	5.8
0.0240	0.0016	5.6

The most interesting result is that, after sufficient buffering, a residual rate remains in the case

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[5] R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 2673 (1956).

[6] R. G. Pearson, R. S. Meeker and F. Basolo, *ibid.*, **78**, 709 (1956).

of the *cis*-isomer in the presence of basic anions which is greater than the rate of reaction with non-basic anions. This is contrary to what is found in the case of the *trans*-isomer and its alkyl substituted derivatives generally.[1] As Fig. 1 shows this residual rate is not a simple function of the concentration of the basic anion. The data for azide ion when plotted look very similar. A plausible explanation for the fact that the order with respect to the anion approaches zero at high concentration is that ion-pairs are formed which react more rapidly than the original complex ion.[7] According to the theory of such ion-pairs,[8] the degree of association expected is a function of the sizes and charges of the ions and the dielectric constant of the medium. For the ion $Co(en)_3^{3+}$ in water ion-pair formation constants of 21 and 11 have been reported for Br^- and N_3^-, respectively.[9] Since the dielectric constant of methanol (32) is less than that of water (78) by a factor of 2.5, it is expected that ion-pair formation for $Co(en)_2Cl_2^+$ with N_3^- in methanol will be less than for $Co(en)_3^{3+}$ in water.

In fact it is found by the usual method of examining the shifts in the ultraviolet absorption spectra produced by the formation of ion-pairs,[10] that *trans*-$Co(en)_2Cl_2^+$ does not give such an interaction with Cl^- and Br^- within experimental error. However *cis*-$Co(en)_2Cl_2^+$ does show substantial shifts to longer wave lengths in the ultraviolet upon the addition of Cl^- and Br^-. Table VI shows the zero-time optical density changes obtained with chloride ion added to solutions of *cis*- and *trans*-$Co(en)_2Cl_2^+$. Approximate ion-pair formation constants of 135 for Cl^- and 35 for Br^- have been calculated from such data in the case of *cis*-isomer. Since ionic strength was not held constant, these values are only rough and apply to an ionic strength of the order of 0.02. Ion-pairs could not be detected with certainty in the case of *cis*-$Co(en)_2Cl_2^+$ and N_3^- and OAc^- because of the rapid reaction between the ions.

TABLE V

SPECTRAL SHIFTS INDICATING ION-PAIR FORMATION FOR *cis*-$Co(en)_2Cl_2^+$ AND Cl^-

Concentration of complex is 4.0×10^{-4} *M*

$[Cl^-]$, *M*	Optical density 300 mμ	 310 mμ
None	0.400	0.309
0.0031	.428	.340
.6062	.434	.349
.0125	.444	.354
.0936	.463	.366
None[a]	.490	.500
0.0936[a]	.490	.501

[a] *trans* isomer.

Assuming that ion-pairs are formed also with the basic anions, it is then possible to account for the detailed shape of the rate constant *vs.* concentration curve shown in Fig. 1. The equation used is

$$k_{\text{obsd.}} = \frac{k_1 + k_2K[X^-]}{1 + K[X^-]} \tag{2}$$

where k_1 is 2.0×10^{-3}, k_2 is the rate constant for reaction of the ion-pair and K is the ion-pair formation constant. If the ionic strength is not held constant, the Debye–Hückel theory is used to correct K.

$$\log K = \log K_0 - \sqrt{3.9} \tag{3}$$

where K_0 is the constant at infinite dilution. The solid curve in Fig. 1 is then calculated using the parameters $k_2 = 6.0 \times 10^{-3}$ min.$^{-1}$ and $K = 2.4$ ($\mu = 0.0192$). Similarly for azide ion, the data can be reproduced by $k_2 = 1.0 \times 10^{-2}$ min.$^{-1}$ and $K = 43$ ($\mu = 0.0192$). All that can be said is that these values are reasonable considering the value of $K = 135$ for Cl^- and the sizes of acetate ion and azide ion. The analysis cannot be complete however because the variations of k_1 and k_2 with ionic strength are not considered. If ionic strength is held constant so that K is invariant (and small in value), a nearly linear relationship between $k_{\text{obsd.}}$ and $[OAc^-]$ is observed as Fig. 1 shows.

Equation 2 is the theoretical equation for mechanisms in which the first step is a rapid, reversible formation of an ion-pair

$$Co(en)_2Cl_2^+ + X^- \rightleftarrows Co(en)_2Cl_2^+, X^- \tag{4}$$

and the slow step may be either of three reactions: a dissociation reaction of the ion-pair (SN1 IP); a displacement reaction of the ion-pair (SN2 IP); or a displacement reaction of the free ions $Co(en)_2Cl_2^+$ and X^-(SN2). These three are kinetically indistinguishable because of the equilibrium in 4. If the facts that *trans*-$Co(en)_2Cl_2^+$ neither forms ion-pairs nor reacts with basic anions are correlated, then it seems likely that it is the ion-pair which is the reactant. The failure of *trans*-$Co(en)_2Cl_2^+$ to show similar behavior to the *cis*-isomer is attributed to the zero dipole moment of this symmetrical species. The *cis*-isomer would have a large dipole moment in addition to its net charge. Presumably the anion is held on the side of the ion opposite to the two chloro groups.

Ion-pair formation is not a sufficient cause for an increased rate of reaction since the *cis*-complex forms ion-pairs with chloride and bromide ion, but the rate of reaction is not accelerated by increasing concentrations of these ions under conditions where ion-pair formation is not complete. Nor is the rate different from that with NO_3^- and CNS^-, and from the rate of racemization.[3] Only basic anions increase the rate.[11] Pyridine, which would not form an associated pair with the complex, does not cause an accelerated rate. Since the nucleophilic character of an anion toward metal complexes is generally expected to parallel basicity toward hydrogen ion, it is certainly possible that the ion-pair reacts by an SN2 displacement process.

This is not the only explanation for the reactivity however. Another possible mechanism would

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[7] A. W. Adamson and R. G. Wilkins, THIS JOURNAL, **76**, 3379 (1953).

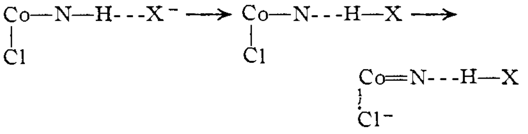
[8] N. Bjerrum, *Kgl. Danske Videnskab Selskab*, **9**, 7 (1926).

[9] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

[10] M. Linhard, *Z. Elektrochem.*, **50**, 244 (1944).

[11] The observation that iodide ion causes an increase in rate similar to basic anions (A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955)) must be re-examined since the reaction is very complex. Oxidation–reduction appears to be involved.

be based on the possibility that there is a strong interaction of a basic anion with the acidic protons of the complex in an ion-pair. Such interaction, which is indeed expected on electrostatic grounds, would permit the electrons of the N–H bond to behave at least somewhat like the electrons of an amido group. That is, they would perhaps be labilized enough to form a partial π-bond to the cobalt atom, and help to release chloride ion.[12]



$$\underset{\displaystyle \mathrm{Cl}}{\mathrm{Co}}\text{—N—H---X}^- \longrightarrow \underset{\displaystyle \mathrm{Cl}}{\mathrm{Co}}\text{—N---H—X} \longrightarrow \underset{\displaystyle \mathrm{Cl}^-}{\mathrm{Co}}\text{=N---H—X} \qquad (5)$$

There are some reasons for preferring this mechanism. One is that the complex *cis*-Co(trien)Cl_2^+ shows a very large rate of reaction with azide ion in buffered media, Table VI, in comparison with *cis*-Co(en)$_2$$Cl_2^+$ although the rates of reaction with neutral ligands is nearly the same. The trien complex also has a rate of reaction with hydroxide ion in water which is about 200 times greater than for the bis-(ethylenediamine) complex.[6] However, it is not the methoxide rate which is involved in the azide ion solutions as shown by changing the buffer ratio. Another reason for preferring an SN1 IP mechanism is that, if optically active *cis*-Co(en)$_2$$Cl_2^+$ is used, an inactive product is formed with azide ion and acetate ion and the rate of racemization is the same as the rate of reaction with the two anions (see Tables II, III and V). It would be expected that a bimolecular displacement process should be more stereospecific.

TABLE VI

RATES OF REACTION OF *cis*-Co(en)$_2$$Cl_2^+$ AND *cis*-Co(trien)$_2$-Cl_2^+ WITH AZIDE ION AND RADIOACTIVE CHLORIDE ION IN METHANOL AT 25°

Complex	$[N_3^-]$	[HN]	k, min.$^{-1}$
cis-Co(en)$_2$$Cl_2^+$	0.0048	0.0024	4.8×10^{-3}
	Rate with	$^*Cl^-$	2.0×10^{-3}
cis-Co(trien)Cl_2^+	0.0048	0.0024	5.3×10^{-1}
	.0048	.0048	4.8×10^{-1}
	Rate with	$^*Cl^-$	1.3×10^{-3}

One final observation of interest is that a complex containing no acidic protons, *e.g.*, *trans*-Co(py)$_4$-Cl_2^+ reacts quite rapidly with azide ion and acetate ion in methanol, but by decomposition of the entire complex. Pyridine (py) is released as in the reaction with hydroxide ion in water. In these cases it appears that an SN2 reaction occurs but leads to a fundamental change in the structure of the compound.

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[12] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Conversion of Ortho- to Parahydrogen on Iron Oxide–Zinc Oxide Catalysts[1]

BY R. ELDO SVADLENAK AND ALLEN B. SCOTT

RECEIVED MARCH 29, 1957

The conversion of normal hydrogen to the equilibrium form at −195° over γ-Fe_2O_3, α-Fe_2O_3, and a series of iron oxide–zinc oxide mixtures heated at several temperatures to produce varying degrees of reaction to form zinc ferrite, has been studied. γ-Fe_2O_3 is the most efficient of these catalysts, followed by α-Fe_2O_3. The mixed catalysts heated at temperatures not greater than 500° were moderately efficient, the first-order rate constant k being about 1.0 sec.$^{-1}$. k was nearly independent of σ, the catalyst surface per unit volume of reacting gas. The shape of the k *vs.* σ curve was calculated on the basis of simple assumptions. Mixtures heated at temperatures over 500° yielded values of k far below the calculated curve, and also underwent a marked change in magnetic susceptibility. It is concluded that an antiferromagnetic structure is a better catalyst for this conversion than a paramagnetic structure even when the latter is accompanied by some ferrimagnetism, but that the ferromagnetic form is superior to either.

Introduction

The study of ferrite catalysts has for some time been a matter of interest because of the possibility that a distinct relationship may be found between the catalytic activity and the magnetic state of the solid. Hüttig[2] and co-workers studied the oxidation of carbon monoxide and the decomposition of nitrous oxide over a series of catalysts made by heating equimolar mixtures of zinc oxide and iron oxide at several elevated temperatures to produce differing degrees of reaction to form zinc ferrite. Bupp and Scott[3] reported upon the decomposition of nitrous oxide over the same series of catalysts and did not confirm the existence of a catalytically active phase intermediate in structure between the mixture and the compound, as reported by Hüttig.

All of these results were complicated by the fact that the reaction used as a test of catalytic activity had to be carried out at temperatures around 500°, at which temperature the catalyst itself undergoes considerable change in surface area and magnetic properties during the course of a single measurement of catalytic efficiency.

In the present investigation, the conversion of normal hydrogen to the equilibrium form (49.73% parahydrogen)[4] at −195° was used as a test of catalytic activity. This reaction has the advantage of taking place rapidly at low temperature

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[1] Presented at the 128th meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955. From a thesis submitted by R. Eldo Svadlenak in partial fulfillment of the requirements for the Ph.D. degree, Oregon State College. Published with the approval of the Oregon State College Monographs Committee as Research Paper No. 320, Department of Chemistry, School of Science.

[2] G. Hüttig, *Sitzber. Akad. Wiss. Wien, math.-nat. Kl.*, **7**, 648 (1936).

[3] L. P. Bupp and A. B. Scott, THIS JOURNAL, **73**, 4422 (1951).

[4] A. Farkas, "Light and Heavy Hydrogen," Cambridge, London, 1935, p. 14.