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Substitution Reaction of $\left[Rh(NH_3)_5OCOCCl_3\right]^{2+}$ with the Methoxide Ion(*) (**)

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The reaction of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ *and* CH_3O^- *ions was studied kinetically. The rates were found to fit the equation* $k_{obs} = \dfrac{k_1 + k_2K[CH_3ONa]}{1+K[CH_3ONa]}$. *The formation of ion-pairs between the reactants, supported by spectral evidence, is considered to be responsible for the observations.*

Introduction

In recent investigations[1-4] the reaction of acetato- and haloacetatopentamminemetal(III) complexes (metal = Co, Rh, Ir) with OH^- has been studied kinetically and, for some of these systems, with tracer techniques.

Under certain conditions, it appears that the carboxylic carbon atom behaves like an electrophilic center, leading to the OH^- addition to the carbonyl group, which has been held responsible for some of the observed results.

The present research was undertaken in order to extend this study to the reaction between CH_3O^- and $[Rh(NH_3)_5OCOCCl_3]^{2+}$. The latter compound was chosen because of its solubility in absolute methanol, and because of the high electron withdrawing power of the CCl_3 group which is supposed to provide favourable conditions for the carbonyl-addition path.

However, as it will be shown further on, the system was found to react by a different pattern with no evidence for a carbonyl adduct formation.

Experimental Section

Materials. Trichloroacetatopentamminerhodium(III) ion was prepared according to the procedure already described,[3] and isolated as the perchlorate.

Super-dry methanol was prepared by refluxing pure grade anhydrous alcohol over magnesium methoxide,[5] and was purified by fractional distillation.

Sodium methoxide stock solutions were prepared by direct reaction of the alcohol with metallic sodium, carefully cleaned with anhydrous methanol.

The alcohol and the CH_3ONa solutions were kept in tightly stoppered bottles and withdrawn under a stream of dry nitrogen. The stock solutions of CH_3ONa were titrated with standard H_2SO_4 solutions.

Reaction Products. In order to verify the stoichiometry of the reaction, the isolation of the Rh(III) complex which was formed, was attempted as follows: an amount (0.2 g) of $[Rh(NH_3)_5OCOCCl_3](ClO_4)_2$ was treated, at 65°C, with 5 ml of 1 *M* CH_3ONa solution. After 15 minutes and with frequent stirring, the complex dissolved giving a yellow solution, which was filtered on a fritted glass and cooled in a melting-ice bath. Small yellowish crystals separated. They were collected on a filter, washed several times with methanol and acetone, and air dried.

The elemental analysis gave the results reported in Table I, which agree very well with the formula $[Rh(NH_3)_5OCH_3](ClO_4)_2 . \frac{1}{2}CH_3OH$. The presence of two non-equivalent methyl groups is confirmed by the NMR spectrum (D_2O as the solvent), which shows two resonance peaks, the integrals of which are nearly in the ratio 2:1, the lower being due to free methanol. The presence of the non-coordinated alcohol is also confirmed by the gas-chromatographic analysis of a fresh water solution of the complex.

Table I. Reaction Product. Elemental Analysis

	C	H	N	Cl
Found (%)	4.15	4.43	16.16	16.51
Calcd (%) for $[Rh(NH_3)_5OCH_3](ClO_4)_2.\frac{1}{2}CH_3OH$	4.15	4.61	16.13	16.35

On the basis of the given formula the spectrum of the methoxide complex (Figure 1) and those obtained under kinetic conditions from the reacting mixtures were the same within the experimental accuracy.

Further, since no chloride ion was found at the end of the kinetic runs, the possible decomposition of the CCl_3COO^- ion is ruled out.

In conclusion, the above-mentioned results indicate the following overall stoichiometry for reaction (1):

$$[Rh(NH_3)_5OCOCCl_3]^{2+} + CH_3O^- \rightarrow [Rh(NH_3)_5OCH_3]^{2+} + CCl_3COO^- \qquad (1)$$

(*) Structure and Reactivity in Octahedral Complexes - XI.

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(1) H. Taube and R. B. Jordan, *J. Am. Chem. Soc.*, *86*, 3890 (1964).
(2) R. B. Jordan and H. Taube, *J. Am. Chem. Soc.*, *88*, 4406 (1967).
(3) F. Monacelli, *J. Inorg. Nucl. Chem.*, *29*, 1079 (1967).
(4) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, *6*, 379 (1967).
(5) A. I. Vogel, «Practical Organic Chemistry», Longmans London, p. 169 (1956).

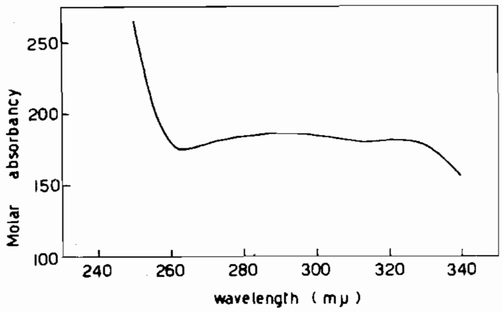

Figure 1. The absorption spectrum of $[Rh(NH_3)_5OCH_3]^{2+}$ ion in the presence of methoxide ion. Solvent methanol, temperature 26°C.

The use of this reaction for the preparation of a series of alkoxide complexes is now under study.

Kinetics. The reaction of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ with the methoxide ion was followed spectrophotometrically by measuring the absorption of the reacting mixture at a suitable wavelength, in the u.v. range.

A small amount (1-2 mg) of the complex was weighed out in a 5-ml volumetric flask and dissolved in a standard sodium methoxide solution, which was obtained by mixing known volumes of the pure alcohol and concentrated methoxide stock solution.

A 1-cm quartz cell was then filled with the reacting mixture and placed into the cell compartment of a Beckman DU spectrophotometer, kept at 26.0±0.1°C by circulating water from a thermostatic bath. The reference solvent was the same sodium methoxide solution used for the reaction.

Alternatively, the kinetic runs were followed by recording the light absorption, at a fixed wavelength, by a Beckman DB recording spectrophotometer. Owing to the operating feature of this instrument, the temperature of the cell compartment (26.0°C) could be controlled only to ±0.25°.

All runs were carried out with a large excess of CH_3O^-, so that its concentration was constant througout the reaction.

The kinetics were followed until a constant reading was obtained and the plots of log $(D_\infty\text{-}D)$ vs time were found to be linear over two or three half-lives. The dependence of the observed pseudo first-order kinetic constants, k_{obs}, on the sodium methoxide concentration is shown in Table II and Figure 2.

Table II. Rates of Reaction of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ with CH_3O^- Ion

$[CH_3ONa]$ (*M*)	$k_{obs} \times 10^4$ (sec^{-1})
0.015	0.79
0.027	0.98
0.027	0.83
0.053	0.96
0.075	1.18
0.076	1.04
0.108	1.22
0.108	1.20
0.162	1.25
0.270	1.38
0.540	1.46
0.540	1.43
0.720	1.51

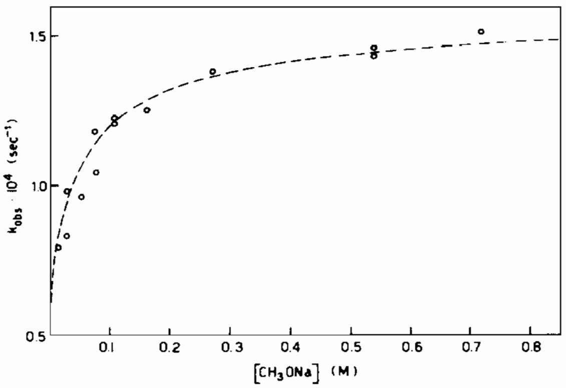

Figure 2. Observed rate constants as function of the CH_3ONa concentration. The line is calculated according to equation (5).

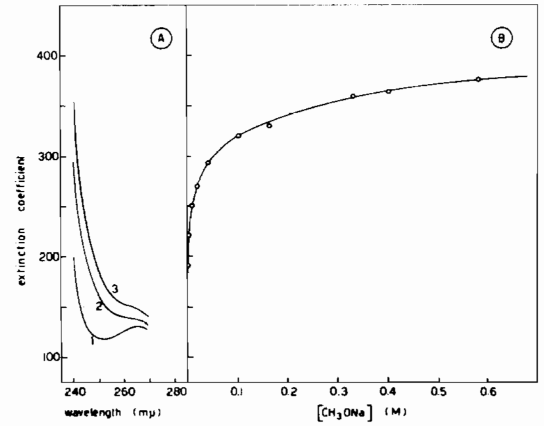

Figure 3. Influence of CH_3ONa on the absorption spectrum of $[Rh(NH_3)_5OCOCCl_3]^{2+}$. (a) Molar concentration of CH_3ONa: 0 (1); 0.042 (2); 0.33 (3). (b) Wavelength 240 mμ.

Influence of the Methoxide Ion Concentration on the Spectrum of $[Rh(NH_3)_5OCOCCl_3]^{2+}$. Figure 3a shows the spectrum, at 26°C, of some methanol solution of trichloroacetatopentamminerhodium(III) perchlorate with different amounts of CH_3ONa. By increasing the methoxide ion concentration the extinction coefficient, ε, of the rhodium complex, below 270 mμ, increased remarkably. Since, at these wavelengths the light absorption changes rapidly as a consequence of the reaction between the complex and the base, the reported spectra are those obtained by extrapolation to zero time.

When the extinction coefficient, for a given wavelength, is plotted against the methoxide concentration, the curve reported in Figure 3b is obtained. Such a curve shows clearly the tendency to a limiting value, ε_{lim}. This behaviour is typical of an equilibrium reaction, which occurs as soon as the reactants are mixed together, yielding a species of higher absorbancy.

A detalied analysis of the curve according to this hypothesis requires the knowledge of the activities of both solutes and, since these last are not available, the equilibrium constant associated with the reaction cannot be exactly calculated. It can be, however, estimated by the following procedure. For dilute solutions, the molar extinctions are related to $[CH_3O^-]$ by the equation:

$$\frac{\varepsilon - \varepsilon_o}{\varepsilon_{lim} - \varepsilon} = K[CH_3O^-] \qquad (2)$$

where ε_o is the value of ε at zero CH_3O^- concentration, ε_{lim} is its asymptotic value, and K is the equilibrium constant. Unfortunately, ε_{lim} cannot be directly measured since it is reached at very high sodium methoxide concentrations, which do not allow satisfactory optical measurements. However, it can be estimated ca. 400 M^{-1}cm^{-1}. When the ratio $\frac{\varepsilon - \varepsilon}{\varepsilon_{lim} - \varepsilon}$ becomes equal to unity (i.e., when the extinction coefficient is half way from ε_o and ε_{lim}), the reciprocal of $[CH_3ONa]$ is equal to K. This occurs for $[CH_3ONa] = 0.05$ *M*, which is a sufficiently dilute solution to consider the eq. (2) at least roughly followed. The value obtained is thus $K = 2 \,.\, 10$ M^{-1}, which applies to an ionic strength of about $5 \,.\, 10^{-2}$ *M*.

Results and Discussion

The ionic strengths of the solutions for both kinetic and spectral measurements was essentially that resulting from the dissolved sodium methoxide. Owing to the high concentrations of the latter, it was not possible to predict, on any theoretical ground, the extent of the general salt effect. Also the degree of association between CH_3O^- and Na^+, which should not be negligible at the highest concentrations, is not known. Indeed, these facts could make difficult a *detailed* interpretation of the reaction profile of Figure 2.

The use of an «inert» salt like $NaClO_4$, in order to keep constant the ionic strength, would not be safe from complications since the reactive substrate is positively charged.[6] Actually, from preliminary experiments, it seems that the addition of large amounts of $NaClO_4$ changes completely the reaction picture to a more complicate one.

However, since the large spectral changes reported in Figure 3 are not likely to be due to general salts effects,[7*] the close parallelism between absorption and reactivity changes with increasing $[CH_3ONa]$ is a strong indication of the salt effect to play a minor role. Instead, the data suggest that, within the considered CH_3ONa concentration range, two reactive species, A and B, in mutual fast equilibrium are present, both undergoing a slow decomposition to the products according to the following reactions:

$$A + CH_3O^- \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} B \qquad (3)$$

$$\begin{tikzcd} A \arrow[dr, "k_1", "(a)"'] & \\ & {[Rh(NH_3)_5OCH_3]^{2+} + CCl_3COO^-} \quad (4) \\ B \arrow[ur, "k_2"', "(b)"] & \end{tikzcd}$$

For reasons which become clear further on, it is now convenient to let unspecified the nature of both compounds A and B. The first, in particular, may not be necessarily the starting $[Rh(NH_3)_5OCOCCl_3]^{2+}$ ion.

On this ground, the general equation (5) is proposed

$$k_{obs} = \frac{k_1 + k_2K[CH_3O^-]}{1 + K[CH_3O^-]} \qquad (5)$$

where k_1 and k_2 are the first-order rate constants for A and B, respectively.

Owing to the above mentioned uncontrolled ionic strength conditions, the fit of eq. (5) with experimental points would be expected not to be as good as it is. Actually, the plot of $k_{obs}(1+K[CH_3ONa])$ vs $K[CH_3ONa]$, assuming for K the value 20 M^{-1}, (see Experimental), is fairly linear with an intercept, k_1, of $6.0 \,.\, 10^{-5}$ sec^{-1} and a slope, k_2, of $1.5 \,.\, 10^{-4}$ sec^{-1}. Now the question arises as to the nature of A and B and of the equilibrium (3).

Infrared evidence of carbonyl adducts between carboxylic derivatives and alkoxide ions had been previously found.[8] Their formation is favoured by the presence of activating groups like CF_3 and CCl_3, bonded to the reactive center, and by solvents of low dielectric constant.

The present research was undertaken with the hope of finding kinetic and spectral evidence for the formation of a carbonyl adduct between a basic anion, such as CH_3O^-, and $[Rh(NH_3)_5OCOCCl_3]^{2+}$. This was, in fact, what would be expected on the basis of the results obtained for the base-hydrolysis of this and related complexes.[1-3]

The reactions (3) and (4b) are formally in agreement with this hpyothesis. However, if (3) were the carbonyl-addition of CH_3O^- on the co-ordinated carboxylic ligand, B should then react by oxygen-carbon fission and $[Rh(NH_3)_5OH]^{2+}$ ion would be expected as the primary reaction product.[*] This appears to be, definitely, not the case, since in all the experiments the only reaction product which could be detected spectrophotometrically was $[Rh(NH_3)_5OCH_3]^{2+}$ and, at 26°C, the spectrum of $[Rh(NH_3)_5OH]^{2+}$ in methoxide solutions changes very slowly (probably as a consequence of the decomposition of the complex by loss of ammonia), so that the alkoxo complex must be generated independently through the metal-ligand bond rupture. Furthermore, also methanolic solutions of $[Rh(NH_3)_5OCH_3]^{2+}$ and $[Rh(NH_3)_5OH]^{2+}$ show slight spectral changes with increasing CH_3ONa concentration, supporting the idea that reaction (3) is not specific for carbonyl-containing compounds.

The reaction with methoxide ion has been studied for several amine complexes of Co(III) and the rates were found to be first-order with respect to the concentration of the base.[9] This behaviour was interpreted as an indication of S_N1 CB mechanism.[10]

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[*] The addition of $NaClO_4$ to a complex solution up to 0.4 *M* concentration does not change the extinction coefficient of the latter.

[6] F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», John Wiley, New York, p. 378 (1958).

[7] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, *78*, 15 (1956).

[*] Also the formation of CCl_3COOCH_3 ester should be expected. However, the blank experiments showed that the water content of the solutions, though small, was sufficient to hydrolyze the amount of ester which might be formed, before any attempt could have been made for its detection.

[8] M. L. Bender, *J. Am. Chem. Soc.*, 75, 5986 (1953).

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

[10] F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», John Wiley, New York, p. 151 (1958).

The same hypothesis would also be consistent with the present findings, providing however, that the acidity of Rh-N-H protons were so high, compared to Co-N-H protons, as to allow a nearly complete conversion of the substrate to the amido form, with CH_3O^- concentrations lower than 1 *M*. This fact is unlikely since, on the contrary, there are indications for the opposite situation to occur.[11,12]

Furthermore, owing to the low value of the ratio k_2/k_1 in this case the reactivity of the conjugate base would not differ significantly from that of the parent acid, which is also unlikely.

A satisfactory interpretation of the nature of reaction (3) can be given, however, in terms of outer-sphere association between the reactants, favoured by the relatively low dielectric constant of the medium. Direct evidence of ion-pair formation between positively charged metal complexes and anions, in both water and methanol, have been found in a number of cases.[7,13-17] Yet, such ionic associations are known to be usually more reactive than the parent ions,[14,18-21] in agreement with the present observed trend.

In line with this interpretation, the simplest case, which could be proposed, is the one where species A is $[Rh(NH_3)_5OCOCCl_3]^{2+}$ and B the 1:1 ion pair $[Rh(NH_3)_5OCOCCl_3]^{2+}, CH_3O^-$. On this ground the reaction (4a) would bccome a solvolytic process, and k_1 the measure of the reactivity of the free complex with methanol.

For the amminecobalt(III) complexes it is currently accepted that methanolysis and aquation are essentially the same reaction,[22] the first one being about ten times slower than the second, probably as a result of the lower solvation properties of the alcohol.

Unfortunately, kinetic data are not available for the aquation of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ but it should not be faster than that of $[Rh(NH_3)_5OCOCF_3]^{2+}$ which has been studied extensively.[23] From the known activation energy and the constants at higher temperatures, the value $3 \,.\, 10^{-7}$ sec $^{-1}$ can be calculated for the pH independent aquation of the latter, at 26°C. Thus, methanolysis of trichloroacetatopentamminerhodium(III) would appear faster than its aquation by a factor of 200 or more, which is unlikely.

A better understanding of the whole experimental evidence can be obtained assuming that even at the lowest $[CH_3ONa]$ considered in the experiments, the starting complex is fully converted into the 1:1 ion-pair and, hence, reaction (3) refers to the further step of the association process ($B = [Rh(NH_3)_5OCOCCl_3]^{2+}$, $2\ CH_3O^-$). According to this, k_1 becomes the rate constant of the 1:1 ion-pair which does not need to be lower than the aquation rate constant of the free complex.

This hypothesis is strongly supported by the fact that the related complex *trans*-$[Coen_2ClCH_3OH]^{2+}$ and Cl^- ion are completely 1:1 associated in methanol for $[Cl^-]/[complex] < 5$ and $[Cl^-] < 1 \,.\, 10^{-2}M$.[24]

The two-step association mechanism implies, however, that the spectrum of the 1:1 ion-pair be nearly the same as that of $[Rh(NH_3)_5OCOCCl_3]^{2+}$ in pure methanol, at least in the region above 240mμ (see Figure 3), while the observed changes are due to the further 1:2 association. This is not a common situation but canont be excluded *a priori*.

Finally, it should be noted that the proposed mechanism does not exclude the formation of a carbonyl adduct, but since the experimental results do not show any evidence of such process it cannot give any detectable contribution to the studied reaction.

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(11) S. A. Johnson, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, *85*, 1741 (1963).

(12) C. H. Langford and H. B. Gray, «Ligand Substitution Processes», W. A. Benjamin, Inc., New York, p. 94 (1966).

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

(14) R. G. Pearson, P. M. Henry and F. Basolo, *J. Am. Chem. Soc.*, *79*, 5382 (1957).

(15) A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, *79*, 2458 (1957).

(16) E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, *63*, 755 (1959).

(17) B. Bosnich, C. K. Ingold and M. L. Tobe, *J. Chem. Soc.*, 4074 (1965).

(18) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, *75*, 1943 (1953).

(19) S. C. Chan, *J. Chem. Soc.*, (A), 1124 (1966).

(20) A. McAuley and V.D. Gomwalk, *J. Chem. Soc.*, (A), 1694 (1966).

(21) For a survey of the argument see also: M. L. Tobe, «Mechanisms of Inorganic Reactions» in «Advances in Chemistry Series» edited by the *American Chemical Society*, No. 49, p. 7 (1965).

(22) F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», John Wiley, New York, p. 147 (1958).

(23) F. Monacelli, F. Basolo and R. G. Pearson, *J. Inorg. Nucl. Chem.*, *24*, 1241 (1962).

(24) B. Bosnich, J. Ferguson and M. L. Tobe, *J. Chem. Soc.*, (A), 1636 (1966).