new spectrum has its maximum intensity at pH 9.5. It consists of nine lines (Figure 2g) whose spacing and intensity relationship speak for a complex formed by two equivalent N^{14} nuclei (the NO groups) and one N^{14} nucleus (NCS group) with almost a double hyperfine constant. Nitrogen-15 experiments confirm these results, exhibiting a nine-line spectrum due to a 1:2:1 triplet from two $N^{15}O$ groups separated into a 1:1:1 triplet by one thiocyanate group. At even higher pH (>11) a quintet spectrum becomes predominant at $g = 2.027$. This corresponds to the one reported by McDonald,[1] *et al.*, in a water solution of $FeSO_4$ in the presence of NO which was attributed to $Fe(NO)_2(OH)_2^-$. It is then evident that at pH 9.5 one thiocyanate group has been replaced by an OH group to form the $Fe(NO)_2NCS(OH)^-$ complex. No such observations are made with the iron–nitrosyl–halide complexes, which give no detectable esr signals above pH 7.

Other spectra can be obtained in ethanol–water solution with a variety of inorganic and organic ligands. Cyanate ion gives results close to the thiocyanate ion. Intense spectra were observed with sulfite, hyposulfite, carbonate, dithionite, and a number of other ligands.

However we wish to emphasize here that these Fe–NO complexes, which give easily detectable esr spectra also in pure water solution in the presence of excess ligand concentration, arise from monomerization of a dimeric structure related to the red Roussin's salt.[1] With the exception of some organic complexes, which show better solubility, no advantages are obtained in the presence of ethanol. Nitrate, nitrite, and sulfate ions seem to give no detectable spectra in water or in alcoholic solutions.

Esr Line Width.—In addition to the above-mentioned variation of the relative intensities of the various species, changes of temperature influence the line width of esr signals significantly. In all cases the best resolution of the hyperfine splitting was obtained at a temperature in the range between −15 and 5° depending on the ligand ion, while an increase of line width was observed above and below this temperature. This means that at least two mechanisms of relaxation are effective with opposite temperature coefficients. At lower temperature, the most probable line-broadening source is motional modulation of the anisotropic g and hyperfine tensors. The increase of line width above the point of maximum resolution may well be attributed to ligand exchange, the lifetime of the radical thus determining the electron spin relaxation time T_2. It is noteworthy that the line width does not depend on ligand concentration and on the number of ions coordinated in the complex (Table I). This would be accounted for only by an SN1 exchange mechanism; that is, a process in which the rate-determining step corresponds to the loss of a ligand ion from the complex which is almost instantly replaced with a new ligand. However, spin rotational relaxation may also account for the observed positive temperature dependence of the line width[14] and more detailed data would be necessary to make an unequivocal attribution. In the present work all spectra were registered at the temperature of maximum resolution.

Acknowledgment.—This research was supported by the Italian National Council for Research.

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[14] W. B. Lewis and L. O. Morgan, *Transition Metal Chem.*, **4**, 77 (1968.)

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation and Kinetics of Hydrolysis of Trifluoroacetatopentaamminechromium(III)

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Although the kinetics of the hydrolysis in alkaline and acid solutions of carboxylatopentaammine complexes of Co(III), Rh(III), and Ir(III)[1-3] have already been reported, the Cr(III) analogs have only recently been prepared.[4] The complexes are usually prepared in aqueous solution by heating the aquopentaammine complex with the required carboxylic acid. In the case of chromium(III), however, this procedure is not possible owing to the rapid loss of ammonia from the metal ion and subsequent formation of a complex mixture of products. Recently preparative procedures involving much less vigorous conditions have been developed in the pentaamminecobalt(III) system.[5,6] These methods have now been applied with some success to the preparation of the carboxylatopentaamminechromium(III) complexes.

The complex $((NH_3)_5CrO_2C_2F_3)(ClO_4)_2$ has been obtained by two different preparative routes. In the first method $((NH_3)_5CrCl)(ClO_4)_2$ was mixed with an equivalent amount of $AgO_2C_2F_3$ dissolved in N,N-dimethylformamide (DMF). The second method[6] also carried out in DMF used the reaction of $((NH_3)_5CrOH_2)(ClO_4)_3$ with trifluoroacetic anhydride in the presence of a base, N,N-dimethylbenzylamine. A third method,[5] not reported in detail, involves the reaction of $((NH_3)_5CrN_3)(ClO_4)_2$ with isoamyl nitrite and trifluoroacetic acid, also in DMF. The main disadvantage of the latter method is the difficulty in preparing pure $((NH_3)_5CrN_3)(ClO_4)_2$.

The kinetics of the hydrolysis of $(NH_3)_5CrO_2C_2F_3^{2+}$ have been studied in acid and alkaline solution, and the

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

[2] (a) R. B. Jordan and H. Taube, *J. Am. Chem. Soc.*, **88**, 4406 (1966); (b) F. Monacelli, *J. Inorg. Nucl. Chem.*, **29**, 1079 (1967).

[3] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **6**, 379, 1376 (1967).

[4] E. Zinato, R. Lindholm, and A. W. Adamson, *J. Inorg. Nucl. Chem.*, **31**, 449 (1969), have reported the preparation of $((NH_3)_5CrO_2C_2F_3)(ClO_4)_2$ by heating the aquo complex with trifluoroacetic acid in N,N-dimethylacetamide. The reported λ_{max} and extinction coefficients (483 mμ, 50.3; 359 mμ, 34.5) agree reasonably with those reported here.

[5] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

[6] L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968).

results are compared to previous work on analogous complexes.

Experimental Section

General Data.—Silver trifluoroacetate was prepared by mixing freshly prepared silver oxide with a concentrated aqueous solution of trifluoroacetic acid. Water and excess acid were removed by vacuum distillation. The product was dried under vacuum at 65–70° in the absence of light. $((\mathrm{NH_3})_5\mathrm{CrCl})(\mathrm{ClO_4})_2$ was prepared by dissolving $((\mathrm{NH_3})_5\mathrm{CrCl})\mathrm{Cl_2}$ (5 g) in ice-cold 3 *M* $\mathrm{H_2SO_4}$ (500 ml) and adding cold 70% $\mathrm{HClO_4}$ (100 ml), the solution being stirred during the latter addition. The product (~2.5 g) was collected, washed with methanol and ether, and dried under vacuum. $((\mathrm{NH_3})_5\mathrm{CrOH_2})(\mathrm{ClO_4})_3$ was prepared by dissolving $((\mathrm{NH_3})_5\mathrm{CrOH_2})(\mathrm{NO_3})_3$[7] (5 g) in water (60 ml) followed by the addition of ice-cold 70% perchloric acid (30 ml). The solution was cooled thoroughly and 95% ethanol (40 ml) was slowly added, the solution being stirred during the addition. The product was washed with ice-cold 95% ethanol (15 ml) and acetone (15 ml) and dried under vacuum.

$((\mathrm{NH_3})_5\mathrm{CrO_2C_2F_3})(\mathrm{ClO_4})_2$.—Two methods of preparation are described.

(a) $((\mathrm{NH_3})_5\mathrm{CrCl})(\mathrm{ClO_4})_2$ (7.6 g, 20 mmol) was dissolved in a minimum amount of N,N-dimethylformamide (DMF) at room temperature and an excess of silver trifluoroacetate (7 g, 32 mmol) was added. The solvent was allowed to stand over molecular sieves for at least 24 hr prior to use, the preparation being carried out in the presence of molecular sieves. The reaction mixture was tightly stoppered and stored in the absence of light for 12 hr. The AgCl formed was removed by filtration using Celite filter aid. The solvent was removed from the filtrate by vacuum distillation at room temperature until a thick syrup remained. A saturated aqueous solution of sodium perchlorate was added to the syrup and the crude product was collected as the perchlorate salt. As an alternative it has been found that addition of *sec*-butyl alcohol precipitates the crude product from the filtered reaction solution. The complex was recrystallized by dissolving in the minimum amount of water at room temperature followed by the addition of sufficient 70% perchloric acid to make the final solution 1 *M* in perchloric acid. The mixture was cooled for 30 min in a refrigerator and the product was collected, washed with ethanol and ether, and dried under vacuum. All solutions and precipitates of the product complex were protected from light as much as possible during the above operations. *Anal.* Calcd for $((\mathrm{NH_3})_5\mathrm{CrO_2C_2F_3})(\mathrm{ClO_4})_2$: Cr, 11.6; C, 5.43; H, 3.34; N, 15.60. Found: Cr, 11.5; C, 5.60; H, 3.80; N, 15.49.

This method has also been applied to the preparation of the analogous difluoroacetato and trichloroacetato complexes. It is limited however to carboxylic acids which form at least moderately soluble silver salts.

(b) These complexes may be prepared more conveniently by the addition of a slight excess of trifluoroacetic anhydride (0.5 g, 2.4 mmol) to a solution of $((\mathrm{NH_3})_5\mathrm{CrOH_2})(\mathrm{ClO_4})_3$ (1.0 g, 2.2 mmol) in DMF (15 ml) in the presence of excess N,N-dimethylbenzylamine (0.6 g, 4.45 mmol). The product was precipitated 1 min after mixing by the addition of *sec*-butyl alcohol (200 ml) to the reaction mixture. The crude product was recrystallized from water as described previously. *Anal.* Calcd for $((\mathrm{NH_3})_5\mathrm{CrO_2C_2F_3})(\mathrm{ClO_4})_2$: C, 5.43; H, 3.34; N, 15.60. Found: C, 5.57; H, 3.15; N, 15.66.

This seems to be the best general method of preparation although in some cases a significant amount of insoluble dark red material is also produced.

Spectra.—The trifluoroacetato complex is orange-yellow and shows maxima in the visible absorption spectrum at 363 and 482 mμ, with molar extinction coefficients of 30.9 and 49.4, respectively, in 1.0 *M* NaCl solutions.

The infrared spectrum of the complex shows the expected features, with a characteristic C–O stretch at 1795 $\mathrm{cm^{-1}}$, and is very similar to that of $((\mathrm{NH_3})_5\mathrm{CoO_2C_2F_3})(\mathrm{ClO_4})_2$.[8]

Kinetic Procedure.—The rate of hydrolysis in acid solution was determined by following the decrease in absorbance at 238 mμ. To start the reaction a solution of the chromium(III) complex in water was added to a solution of $\mathrm{HClO_4}$–$\mathrm{LiClO_4}$ in the concentrations necessary to give a final ionic strength of 0.10 *M*. All solutions were thermostated prior to mixing and during the reaction. The absorbance decrease was measured using a 1-cm path length cell on a solution approximately 0.015 *M* in chromium(III) complex. Rate constants were obtained from the usual plots of log $(A_t - A_\infty)$ *vs.* time. These plots were generally linear to greater than 80% reaction. The results are summarized in Table I. The reaction product was identified as $(\mathrm{NH_3})_5\mathrm{CrOH_2}^{3+}$ by comparison of the visible spectrum with that of a sample of $((\mathrm{NH_3})_5\mathrm{CrOH_2})(\mathrm{ClO_4})_3$.

In alkaline solution the rate of hydrolysis was followed by observing the increase in absorbance at 395 mμ, due to formation of $(\mathrm{NH_3})_5\mathrm{CrOH}^{2+}$. The reaction was initiated by mixing a solution of NaOH with a solution of the chromium(III) complex in NaCl, in the concentrations necessary to give a final ionic strength of 1.0 *M*. All solutions were thermostated prior to mixing. Spectra of the reaction product ($\lambda_{\max}$ at 396 and 508 mμ with $\epsilon_{\max}$ 44.0 and 44.9, respectively) indicate it to be $(\mathrm{NH_3})_5\mathrm{CrOH}^{2+}$ ($\lambda_{\max}$ at 395 and 504 mμ with $\epsilon_{\max}$ 43.6 and 45.2, respectively). The latter was prepared by dissolving $((\mathrm{NH_3})_5\mathrm{CrOH_2})(\mathrm{ClO_4})_3$ in 0.05 *M* NaOH and running the spectrum immediately. Blank experiments have shown that $(\mathrm{NH_3})_5\mathrm{CrOH}^{2+}$ decomposes in alkaline solution more slowly than the hydrolysis of $(\mathrm{NH_3})_5\mathrm{CrO_2C_2F_3}^{2+}$ under the conditions of the kinetic runs. However the decomposition of the product places a lower limit on the hydroxide ion concentration that can be used. The results of this study are summarized in Table III. In all cases the usual plots of log $(A_\infty - A_t)$ were linear to greater than 80% and generally to greater than 90% reaction. The problem of decomposition has prevented further studies on the other more slowly hydrolyzing carboxylate complexes.

For both acid and alkaline hydrolysis the activation energies and entropies were determined from plots of log (k/T) *vs.* $1/T$.

Standard chemicals of reagent grade were used. Lithium perchlorate solutions were prepared by neutralization of lithium carbonate with perchloric acid and were standardized by ion exchange. Solutions were prepared from deionized water which had been distilled from alkaline permanganate. The spectrophotometric measurements were made on Bausch and Lomb 505 and Precision spectrophotometers. The temperature of the spectrophotometric cell holder was controlled using a Colora constant-temperature bath and a Thermistemp temperature controller (Model 71) with the thermistor probe in the cell holder.

Results

The kinetic data summarized in Table I show that the hydrolysis of $(\mathrm{NH_3})_5\mathrm{CrO_2C_2F_3}^{2+}$ in acid solution follows the rate law

$$\frac{-\mathrm{d}\ \ln\ [(\mathrm{NH_3})_5\mathrm{CrO_2C_2F_3}^{2+}]}{\mathrm{d}t} = k_\mathrm{A}$$

There is no indication of any acid catalysis over the range of acid concentration studied. Monacelli, Basolo, and Pearson[1] have observed an acid-catalyzed path for the aquation of the acetatopentaammine complexes of cobalt(III), rhodium(III), and iridium(III) but found no or barely detectable acid catalysis for the analogous trifluoroacetate complexes. Protonation of the carboxylate ligand is not as favorable owing to the lower basicity of $\mathrm{CF_3CO_2}^-$. The chromium(III) complex studied here seems to be consistent with the previous observations.

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[7] G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., Inc., New York, N. Y., 1962.

[8] R. J. Balahura, private communication.

TABLE I

HYDROLYSIS OF $(NH_3)_5CrO_2C_2F_3^{2+}$ IN ACIDIC SOLUTION[a,b]

$[H^+]$, M	10^4k_{obsd}, sec^{-1} 57.5°	67.5°	76.5°
0.0943	2.54	6.89	15.4
0.0754	2.96	6.89	15.4
0.0566	2.69	6.42	14.4
0.0377	2.63	6.89	16.0
0.0189	3.04	6.89	15.4

[a] Ionic strength 0.10 M adjusted with $LiClO_4$. [b] By extrapolation, $k_{obsd} = 8.7 \times 10^{-6}$ sec^{-1} at 25°.

The activation enthalpy and entropy for the aquation are given in Table II along with the values for the cobalt(III), rhodium(III), and iridium(III) systems. As usual the $\Delta H^{\ddagger}$ for the reaction of the chromium(III) complex is lower than that for the other metal ions.

TABLE II

ACTIVATION PARAMETERS FOR HYDROLYSIS IN ACID SOLUTION OF TRIFLUOROACETATOPENTAAMMINE COMPLEXES

Complex	$\Delta H_A^{\ddagger}$, kcal mol^{-1}	$\Delta S_A^{\ddagger}$, eu	Ref
$(NH_3)_5CrO_2C_2F_3^{2+}$	20.2	−25	This work
$(NH_3)_5CoO_2C_2F_3^{2+}$	26	−2	1
$(NH_3)_5RhO_2C_2F_3^{2+}$	25	−6	1
$(NH_3)_5IrO_2C_2F_3^{2+}$	24	−14	1

Monacelli, Basolo, and Pearson[1] have interpreted the similarity of the rates for the cobalt(III), rhodium(III), and iridium(III) complexes as evidence for carbon–oxygen bond breaking in the aquation reaction. It should be noted however that the similarity in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the cobalt and rhodium complexes is not particularly unusual; the aquations of $(NH_3)_5CoBr^{2+}$ [9] and $(NH_3)_5RhBr^{2+}$ [10] have $\Delta H^{\ddagger}$ values of 24.0 and 25.0 kcal mol^{-1} and $\Delta S^{\ddagger}$ of −4 and −5 eu, respectively. In addition, for the alkaline hydrolysis path, which is known to proceed with C–O bond breaking, the values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are much less sensitive to a change in the metal ion (Table IV). These considerations show that it is very dangerous to draw any conclusions about the detailed mechanism of the aquation from the relative rate constants.

The kinetic results for the hydrolysis of $(NH_3)_5CrO_2C_2F_3^{2+}$ in alkaline solution are summarized in Table III. It is apparent from the data in this table that the hydrolysis rate is not first order in hydroxide ion concentration. The results may be adequately described by a rate law of the form

$$\frac{-\mathrm{d}\ln[(NH_3)_5CrO_2C_2F_3^{2+}]}{\mathrm{d}t} = k_1[OH^-] + k_2[OH^-]^2$$

Under conditions pseudo first order in hydroxide ion $k_{obsd} = k_1[OH^-] + k_2[OH^-]^2$ and plots of $k_{obsd}/[OH^-]$ *vs.* $[OH^-]$ should be linear. This type of plot for each temperature studied is shown in Figure 1. A least-squares analysis of the data yields the values for k_2 shown in Table III. The least-squares analysis gave values for k_1 which were either slightly negative or zero within the limits of error. At 20° an upper limit (of

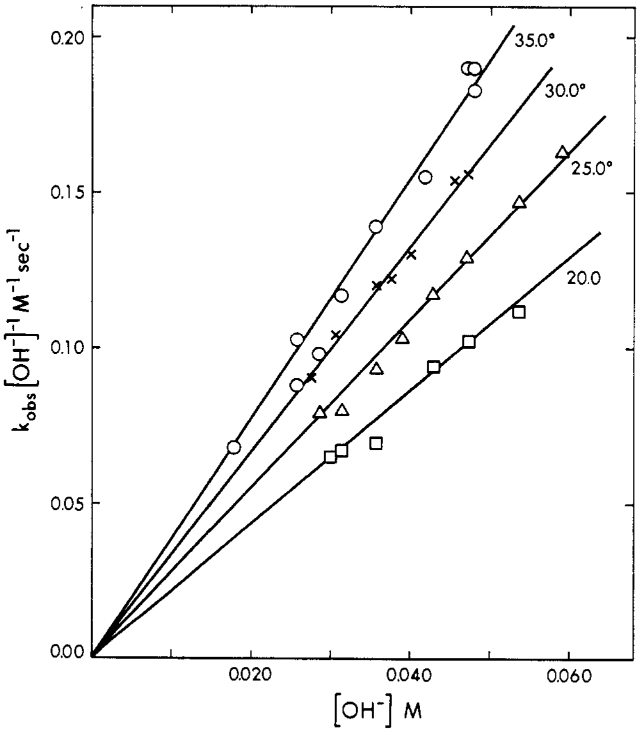

Figure 1.—Alkaline hydrolysis of $(NH_3)_5CrO_2C_2F_3^{2+}$. Variation of $k_{obsd}/[OH^-]$, M^{-1} sec^{-1}, with $[OH^-]$.

TABLE III

HYDROLYSIS OF $(NH_3)_5CrO_2C_2F_3^{2+}$ IN ALKALINE SOLUTION, $\mu = 1.0$ M (NaCl)

Temp, °C	$10^2[OH^-]$, M	$10k_{obsd}/[OH^-]$, M^{-1} sec^{-1} Calcd	Exptl	k_2,[a] M^{-2} sec^{-1}
20.0	3.00	0.63	0.65	
	3.14	0.66	0.67	
	3.57	0.75	0.69	2.11 ± 0.11
	4.29	0.91	0.94	
	4.72	1.00	1.03	
	5.35	1.14	1.12	
25.0	2.86	0.75	0.79	
	3.14	0.83	0.80	
	3.57	0.95	0.93	
	3.90	1.05	1.03	2.90 ± 0.06
	4.28	1.16	1.17	
	4.72	1.28	1.29	
	5.35	1.47	1.47	
	5.90	1.63	1.63	
30.0	2.77	0.91	0.90	
	3.08	1.02	1.04	
	3.58	1.18	1.20	
	3.75	1.24	1.22	3.35 ± 0.07
	4.00	1.33	1.30	
	4.55	1.51	1.54	
	4.73	1.57	1.56	
35.0	1.78	0.62	0.68	
	2.58	0.95	1.03	
	2.58	0.95	0.88	
	2.85	1.06	0.98	
	3.14	1.18	1.17	4.10 ± 0.15
	3.57	1.36	1.39	
	4.18	1.61	1.55	
	4.73	1.84	1.90	
	4.80	1.86	1.83	
	4.90	1.86	1.90	

[a] Values determined by least-squares analysis. Errors are approximate 95% confidence limits.

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(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1967, p 164.

(10) S. C. Chan, *Australian J. Chem.*, **20**, 61 (1967).

the 95% confidence limits) was 2.5×10^{-3} M^{-1} sec^{-1}. The actual value of k_1 is too small to determine accurately and could well be several orders of magnitude smaller than the upper limit given. Comparison of other pentaammine systems[11] shows that k_1 for chromium(III) is generally about $^1/_{100}$ times as great as for cobalt(III). Therefore k_1 is estimated to be about 2×10^{-4} M^{-1} sec^{-1} for $(NH_3)_5CrO_2C_2F_3^{2+}$ based on the analogous rate constant for $(NH_3)_5CoO_2C_2F_3^{2+}$.[2a]

A term second order in hydroxide ion has been observed for several carboxylatopentaamminecobalt(III)[2a,3] and -rhodium(III)[2b] complexes. The ^{18}O tracer work of Jordan and Taube[2a] has shown that this hydrolysis path involves carbon-oxygen bond breaking in $(NH_3)_5CoO_2C_2F_3^{2+}$. Subsequent kinetic studies[3] have shown that this reaction is quite sensitive to the carboxylate ligand and insensitive to the metal ion. The activation parameters for the alkaline hydrolysis of $(NH_3)_5CrO_2C_2F_3^{2+}$ confirm this generalization when compared to previous results (see Table IV). The mechanism of this reaction, as discussed previously,[2a] is thought to involve the concerted attack of two hydroxide ions, one making a bond with the acyl carbon atom of the ligand and the second removing a proton from the first. The process is considered to be concerted because formation of likely intermediates seems inconsistent with the low activation energy for the over-all reaction. The great similarity in activation parameters, especially $\Delta S_2^{\ddagger}$, indicates that the same mechanism is operative for all of the trifluoroacetato complexes studied thus far.

TABLE IV

ACTIVATION PARAMETERS FOR ALKALINE HYDROLYSIS OF TRIFLUOROACETATOPENTAAMMINE COMPLEXES[a]

Complex	First order $\Delta H_1^{\ddagger}$, kcal mol^{-1}	First order $\Delta S_1^{\ddagger}$, eu	Second order $\Delta H_2^{\ddagger}$, kcal mol^{-1}	Second order $\Delta S_2^{\ddagger}$, eu	Ref
$(NH_3)_5CrO_2C_2F_3^{2+}$	...	...	6.62[b]	−34.3[b]	This work
$(NH_3)_5CoO_2C_2F_3^{2+}$	22.7	10	6.8	−37	2a
$(NH_3)_5RhO_2C_2F_3^{2+}$	18.0	−13	7.5	−36	2b

[a] All values are for ionic strength 1.0 M adjusted with NaCl. [b] The values of k_2 calculated from these parameters at 20, 25, 30, and 35° are 2.25, 2.77, 3.39, and 4.12, respectively. These may be compared to the experimental values given in Table II.

(11) Reference 9, p 180.

Contribution from the Shell Development Company,
Emeryville, California 94608

Electrochemical Preparation of Rhodium(0) Complexes

By D. C. Olson and W. Keim

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In recent years considerable interest has developed in coordination compounds containing metals in their lower oxidation states. These compounds are generally prepared by the chemical reduction of similar compounds containing the metal in a higher oxidation state. The use of electrochemical reduction for this purpose has not been investigated to any appreciable extent, although it should have certain advantages over chemical reduction in many applications. For example (a) since the redox chemistry of the starting materials can be examined using electrochemical techniques, it is possible to start with a better understanding of the system; (b) since the potential can be precisely controlled, a greater selectivity in reducing conditions is available; and (c) the system is probably cleaner since the reducing agent is an inert electrode. The supporting electrolytes commonly used in electrochemistry can in general be separated from the electrolysis products without undue difficulty. In many cases, where the reactants and products are sufficiently conducting, it is not necessary to add a supporting electrolyte at all.

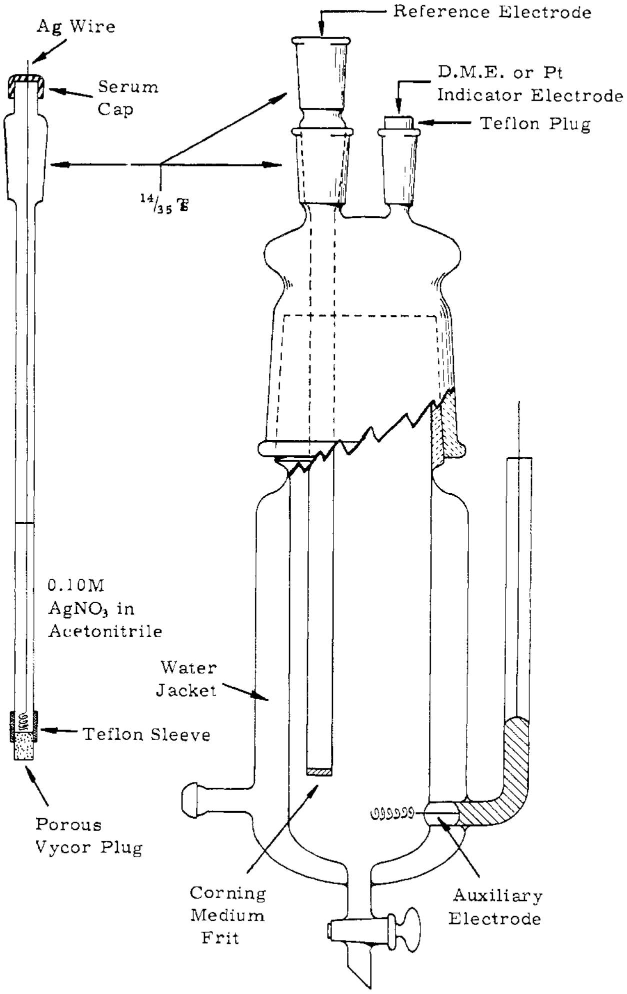

Figure 1.—Construction of the polarographic cell and reference electrode.

The preparation of two new Rh(0) complexes, $Rh((C_6H_5)_3P)_4$ and $Rh((C_6H_5)_2PCH_3)_4$, by electroreduction of Rh(I) compounds in acetonitrile is described in this paper.

Experimental Section

Apparatus.—A controlled-potential polarograph constructed in this laboratory and a Moseley 2D-2A X-Y recorder were used