Kinetics of Some Outer-Sphere Electron-Transfer Reactions

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Kinetic studies have been made of reactions of $Ru(NH_3)_6^{2+}$ with complex ions of the type $(NH_3)_5Co(III)L$, for a variety of ligands L These reactions are necessarily of the outer-sphere type, and the relative specific rates of reaction are comparable to the relative rates of reduction of the same Co(III) complexes by other agents which require the same type activated complex. A few limited comparisons between some of the results of this study and the Marcus theory of electron-transfer reactions have been possible.

Introduction

Investigations of the rates of outer-sphere electron-transfer reactions in recent years have demonstrated a remarkable consistency in the relative rates of reaction of a number of reducing agents with a series of substituted cobalt(III) ammines.[2-4] Marcus has developed a treatment applicable to outer-sphere reactions which has shown promise of being at least semiquantitative.[4-8]

$Cr(dipy)_3^{2+}$ [9] is important among the reducing agents for which kinetic data have been obtained and which are presumed to react *via* an outer-sphere activated complex. However, there is cause for serious doubt that it does, in fact, react by this type of mechanism. The complex is very substitution-labile, so the possibility exists that even when the activated complex contains three dipyridyls for each Cr^{2+} a coordination position is exposed by opening one of the chelate rings. By contrast, the reducing reagent $Ru(NH_3)_6^{2+}$, which is featured in the work reported here, is found to undergo substitution very slowly compared to the rate at which it can be oxidized; and the product of one electron oxidation is $Ru(NH_3)_6^{3+}$. The reagent $Ru(NH_3)_6^{2+}$ thus seems to be of the genuine "outer-sphere" type, and since it is quite reactive to cobalt(III) complexes, we have considered it worthwhile to study the kinetics of a number of such reactions. The results provide a firm experimental basis for comparing the rates of reduction of a variety of cobalt(III) complexes by the outer-sphere mechanism. The comparison of these results with those obtained with other reducing agents, the mechanisms for which can be classified with less certainty, is of interest.

Experiments have also been done on the reactions of Cu^+ with some cobalt(III) complexes.[10] The reactions of $Co(NH_3)_6^{3+}$ with Cr^{2+}, V^{2+}, Cu^+, and $Ru(NH_3)_6^{2+}$, and of $Ru(NH_3)_6^{3+}$ with Cr^{2+}, V^{2+}, and Cu^+, are all presumably of the outer-sphere type, since in such reactions one partner at least presents only NH_3 groups in the first coordination sphere, and dissociation of H^+ from the NH_3 (which would provide

an electron pair to constitute NH_2^- as a bridging group) prior to electron transfer does not occur. The rates measured for the various reactions mentioned are considered in the light of Marcus' theory[4] which suggests a means of correlating rates for reactions of the outer-sphere type.

Experimental

General Procedures and Treatment of Data.—The reductants used in this study were air sensitive, and all solutions were deaerated with nitrogen which had been scrubbed by passing it through a series of solutions containing $Cr^{2+}(aq)$. All reactions were run in nitrogen atmospheres.

In most of these studies, the reductant was added as the last reagent by means of a syringe to the deoxygenated solution of oxidant, neutral salt, and acid. In some of the early studies, the reductant was added from a buret to a glass mixing device attached to a spectrophotometer cell. This mixing device was so designed that oxidant and reductant could be kept separate until mixing was achieved by tilting. In some experiments the reductant was generated in one compartment of the mixing device, then mixed with oxidant. Solutions were thermostated in a water bath at 25° before mixing. Kinetic determinations were made by observing the change of optical density at a given wave length as a function of time. In some studies the rate of change of optical density at two or more wave lengths was followed during a single run or in successive runs. In a few instances we have been able to follow both the disappearance of $Ru(NH_3)_6^{2+}$ at 275 mμ ($\epsilon \sim 700$)[11] and the decay of the cobalt(III) species. Reasonable agreement between determinations of specific rates at different wave lengths was always observed. In determining the rates of reduction of $Ru(NH_3)_6^{3+}$ the change in optical density at 275 mμ (ϵ_{max} for $Ru(NH_3)_6^{3+}$) was followed.

In order to determine the specific rates of the faster reactions, *i.e.*, reactions of halopentaammines and dihalotetraammines of cobalt(III), it was necessary to use very dilute solutions of reactants. In these instances we followed the decay of the various cobalt(III) charge-transfer bands. In no case did we observe either a broadening of the charge-transfer band or a shift of the band maximum in either NaCl or NaClO$_4$ media (up to ionic strength approximately 0.2). Provided care was taken to exclude catalysts, the results of these studies have been excellent models of precise fit to the integrated rate law (to better than 90% of reaction) and leading to extrapolation to the correct zero-time as well as reproducibility of specific rates.

We have used the usual integrated forms of the rate law

$$\frac{d[Co(III)]}{dt} = -k[Ru(II)][Co(III)]$$

in calculating the specific rates of reaction. The integrated form of the rate law which was actually used necessarily depended on whether absorbancies of several species had to be accounted for at the observed wave length. In the event that the observed absorbancy is entirely due to Co(III), and Co(III) is in excess, this integrated expression reduces to

$$2.303 \log \frac{D_t}{D_t - D_\infty} = -[Co]_\infty kt + \text{const.}$$

(1) Department of Chemistry, Boston University, Boston 15, Mass.

(2) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(3) A. A. Vlcek in "Sixth International Conference on Coordination Chemistry," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 590.

(4) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(5) R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960); for other pertinent references see ref. 3.

(6) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(7) D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 78.

(8) D. G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(9) A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).

(10) The details of these studies will be reported separately.

(11) Details of the spectra of ruthenium(II) species will be given elsewhere. Ruthenium(III) spectra are in the literature.[12]

(12) H. Hartmann and C. Buschbeck, *Z. physik. Chem.*, **11**, 120 (1957).

where D_t and D_∞ are the observed optical densities at time t and at "infinite time," respectively, and $[Co]_\infty$ is the final Co(III) concentration.

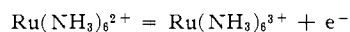The specific rates herein recorded for the $Ru(NH_3)_6^{3+}$ oxidation of $Cu^+(aq)$ have been calculated from the equilibrium constant of

$$Ru(NH_3)_6^{2+} + Cu^{2+}(aq) = Cu^+(aq) + Ru(NH_3)_6^{3+}$$
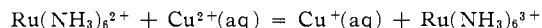
and the observed rate of the reduction of $Cu^{2+}(aq)$ by $Ru(NH_3)_6^{2+}$. We have also used this equilibrium and the known equilibrium constant[13]

$$K = [Cu^+]^2/[Cu^{2+}]$$

to determine the E^0 for

$$Ru(NH_3)_6^{2+} = Ru(NH_3)_6^{3+} + e^-$$

as -0.21 v. The details of the Cu^+–Cu^{2+} system will be discussed elsewhere.

The stoichiometries of $Ru(NH_3)_6^{2+}$–Co(III) reactions have, except for the case of $Co(NH_3)_5N_3^{2+}$, discussed below, been established to be 1:1.

Materials.—Solutions of $NaClO_4$ were prepared from primary standard Na_2CO_3 and $HClO_4$. These solutions were always slightly acidic; the acid titer was determined by titration with standard NaOH. Solutions of NaCl were prepared by weight from recrystallized reagent grade NaCl. All solutions were made with doubly distilled water. In some of the more rapid reactions (with the halopentaammines and dihalotetraammines of cobalt(III)), in which the reactants are of necessity in very dilute solution, we observed catalytic effects. Much of this catalysis was caused by traces of copper ($ca.$ 10^{-7} M), and some was caused by traces of mercurous ion introduced when zinc amalgam-reduced $Ru(NH_3)_6^{2+}$ was used. We have isolated the sources of contamination and can generally guarantee that results reported in this paper are free from catalytic influences. The exception to this is that specific rates reported for some reactions run in NaCl media may be somewhat too large, probably due to small amounts of catalytic material which we have not been able to remove from NaCl by recrystallization. The specific rates determined in NaCl media for those cases in which reactants were necessarily very dilute run from 10% to about 30% higher, depending on the ionic strength, than specific rates for the corresponding reactions determined in $NaClO_4$ media.

Solutions of $Cr^{2+}(aq)$ were generated from $Cr^{3+}(aq)$ electrolytically or by zinc amalgam reduction. $Ru(NH_3)_6^{2+}$ was prepared from $Ru(NH_3)_6^{3+}$ by zinc amalgam reduction, or by reduction with $Cr^{2+}(aq)$. $V^{2+}(aq)$ was prepared by reducing $NaVO_3$ with zinc amalgam. $Cu^+(aq)$ was prepared from $Cu(ClO_4)_2$ by reduction with clean copper metal.

The $trans$-$Co(NH_3)_4(OAc)_2^+$ was prepared essentially according to the literature procedure.[14] We obtained somewhat higher yields when anhydrous acetone was used as solvent. The product was identified spectrophotometrically.[15] We experienced difficulty in the preparation of the cis-$Co(NH_3)_4(OAc)_2^+$ complex and obtained such poor yields of the material that we are not confident in our data for this material.

$Ru(NH_3)_6Cl_3$ was supplied by Johnson-Matthey and Co., London.

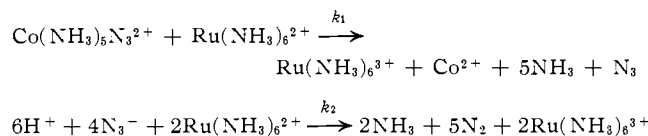## Results

Table I summarizes the kinetic data we have obtained for the $Ru(NH_3)_6^{2+}$ reductions of cobalt(III) ammines. Except in very dilute solutions of reactants, little difference has been noted in behavior in perchlorate and chloride media. Those differences which we have observed may best be attributed to trace impurities or to the usual experimental inaccuracies. The most consistently difficult rates to measure have been the very slowest ones. The finite solubility of the complexes coupled with the very slow spontaneous

(13) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.

(14) M. Linhard and M. Weigel, Z. anorg. Chem., **260**, 65 (1949).

(15) M. Linhard and M. Weigel, ibid., **264**, 321 (1951).

decay of $Ru(NH_3)_6^{2+}$ in solution[16] has generally forced us to use initial slopes in estimating specific rates for these reactions. It has been particularly difficult to obtain accurate data for reactions with specific rates less than about 0.5 M^{-1} sec.$^{-1}$.

Most of the data in Table I require little explanation. In many cases we have averaged several determinations and recorded in the table only representative concentrations of the reactants.

The reaction of $Ru(NH_3)_6^{2+}$ with $Co(NH_3)_5N_3^{2+}$ is quite complex. From three determinations of stoichiometry at several concentrations (in a NaCl medium) we have found that 1.5 ± 0.1 mole of $Ru(NH_3)_6^{2+}$ is consumed for every mole of $Co(NH_3)_5N_3^{2+}$. Furthermore, an independent determination has shown that in 0.20 M NaCl ($[H^+] \sim 10^{-3}$), $Ru(NH_3)_6^{2+}$ reacts with NaN_3 at a specific rate of 30 M^{-1} sec.$^{-1}$. Since the observed specific rate of disappearance of $Co(NH_3)_5N_3^{2+}$ is $ca.$ 1 M^{-1} sec.$^{-1}$, we have assumed that the reaction proceeds according to the scheme

$$Co(NH_3)_5N_3^{2+} + Ru(NH_3)_6^{2+} \xrightarrow{k_1}$$
$$Ru(NH_3)_6^{3+} + Co^{2+} + 5NH_3 + N_3$$

$$6H^+ + 4N_3^- + 2Ru(NH_3)_6^{2+} \xrightarrow{k_2} 2NH_3 + 5N_2 + 2Ru(NH_3)_6^{3+}$$

We have assumed the first step is rate determining so we may use the integrated rate expression

$$2.303 \log \frac{[Co(III)]_t}{[Co(III)]_t - [Co(III)]_\infty} =$$
$$-k_1 {}^3/_2 [Co(III)]_\infty t + \text{const.}$$

where $[Co(III)]_t$ is concentration of $Co(NH_3)_5N_3^{2+}$ at time t. The data seem to fit this rate expression well to about 90% of reaction. The specific rate recorded in Table I is k_1 of the above expression.

In most of the studies reported here we have not systematically investigated acid dependencies. Exceptions are the cases of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_4(O_2CCH_3)_2^+$. For the aquo–hydroxy comparison we obtain a result similar to that obtained for $Cr(dipy)_3^{2+}$ as reducing agent,[9] namely that $Co(NH_3)_5OH_2^{3+}$ is reduced faster than is $Co(NH_3)_5OH^{2+}$. In the case of the $trans$-$Co(NH_3)_4(OAc)_2^+$ complex we observe an increase in rate with acidity similar to those reported for the electrolytic reduction of this substance[3] and for the $Cr^{2+}(aq)$ reductions.[17,18] Our data can be represented by the equation $k_{obsd} = k_1 + k_2[H^+]$ with $k_1 = 0.5$ M^{-1} sec.$^{-1}$ and $k_2 = 13$ M^{-2} sec.$^{-1}$.

Table II summarizes our information about rates of reduction of $Ru(NH_3)_6^{3+}$.

Discussion

Qualitative Comparison of Relative Rates.—In Table III are compiled some relative rates of reduction of Co(III) complexes. We have chosen to refer all data to the specific rates of $Co(NH_3)_5OH_2^{3+}$ reductions because the data for the reduction of this complex are the most consistently accurate. There does seem to be a rough correlation between reductions of the oxidizing agents listed in Table III.

(16) J. F. Endicott and H. Taube, unpublished results.

(17) K. D. Kopple and R. R. Miller, Proc. Chem. Soc., 306 (1962).

(18) R. T. M. Fraser, J. Am. Chem. Soc., **85**, 1747 (1963).

TABLE I

SUMMARY OF KINETIC DATA FOR REACTIONS OF $Ru(NH_3)_6^{2+}$ WITH Co(III) SPECIES

Oxidant[a]	Medium	Ionic strength	[H+], M	[Co(III)] × 10^5, M	[Ru(II)] × 10^5, M	k,[k] M^{-1} sec.$^{-1}$
RNH_3^{3+}	NaCl	0.20	0.015	197	100	0.011 ± 0.002[c]
RNH_3^{3+}	NH_4Cl, NH_3	0.20	9.2[b]	190	117	≤0.03
ROH_2^{3+}	NaCl	0.22	~10^{-3}	~10^2	...	3.0 ± 0.3[d]
ROH^{2+}	NH_4Cl, NH_3	0.22	9.0[b]	...	...	0.040 ± 0.006[e]
RNO_3^{2+}	NaCl	0.20	~3 × 10^{-3}	~30	~10	34 ± 1[f]
RN_3^{2+}	NaCl	0.22	10^{-3}	~10^2	30	1.2 ± 0.1[f,g]
RCl^{2+}	NaCl	0.18	2 × 10^{-4}	3.41	0.83	2.6 × 10^2
RBr^{2+}	NaCl	0.18	2 × 10^{-4}	1.75	0.98	1.6 × 10^3
RI^{2+}	$NaClO_4$	0.18	2 × 10^{-4}	2.3	1.0	6.7 × 10^3
$R(crotonate)^{2+}$	NaCl	0.19	4 × 10^{-3}	104	16	<0.2
$R(C_2O_4)H^{2+}$	NaCl	0.31	4 × 10^{-3}	201	20	0.6 ± 0.1
$R(fumarate)H^{2+}$ [i]	NaCl	0.21	10^{-2}–10^{-3}	~10^2	~10	0.45 ± 0.05[f]
$R(fumarate)H^{2+}$ [i]	$HClO_4$	0.19	0.18	20	7	0.6 ± 0.07
$R(maleate)H^{2+}$ [i]	$NaClO_4$	0.20	10^{-2}–10^{-3}	~20	~5	~2 × 10^{2h}
$trans$-$Co(NH_3)_4(OAc)_2^+$	NaCl, HCl	0.23	0.14	56	41	2.3 ± 0.3[g]
$trans$-$Co(NH_3)_4(OAc)_2^+$	NaCl, HCl	0.27	0.08	60	23	1.3 ± 0.3[g]
$trans$-$Co(NH_3)_4(OAc)_2^+$	NaCl, HCl	0.30	0.02	60	18	0.7 ± 0.2[g]
cis-$Co(NH_3)_4(OH_2)_2^{3+}$	HCl	9.1 × 10^{-3}	5.1 × 10^{-3}	26	5	56 ± 7
cis-$Co(NH_3)_4(OH_2)_2^{3+}$	NaCl	0.18	~10^{-3}	60	15	~2.7 × 10^2
cis-$Co(en)_2Cl_2^-$	$NaClO_4$	0.15	~10^{-4}	3.17	1.0	8.8 × 10^2
$trans$-$Co(en)_2Cl_2^+$	$NaClO_4$	0.17	~10^{-4}	2.0	0.8	(9 ± 1) × 10^{3f}
$R(butyrate)^{2+}$	NaCl	0.16	<10^{-2}	4.5 × 10^2	3 × 10	0.35 ± 0.06[f]
$RO_2C\langle\overline{}\rangle NCH_3^{3+}$	NaCl	0.25	10^{-2}–10^{-3}	6 × 10	2 × 10	0.2 ± 0.1[f]
$Co(NH_3)_4CO_3^+$	$NaClO_4$	0.19	~10^{-3}	1.8 × 10^2	4.4 × 10	9[i]

[a] Where R = $Co(NH_3)_5$. [b] pH measured after the reaction was complete. [c] Determined at 475 mμ and at about 280 mμ. Precision here is the average deviation of the rate constants determined at different wave lengths from the mean value recorded. In the several other studies of this system we have only obtained the limit ≤0.05. [d] Average of three determinations; $Ru(NH_3)_6^{2+}$ varied from 10^{-4} to 7 × 10^{-4} M. Two other determinations using electrolytically generated $Ru(NH_3)_5^{2+}$ are about 10–15% higher. [e] Average of three determinations. CoA_5OH^{2+} varied from 4.4 × 10^{-4} to 2.5 × 10^{-3} M, $Ru(NH_3)_6^{2+}$ varied from 4.8 × 10^{-4} to 2.0 × 10^{-3} M. The specific rates were determined from initial slopes. [f] Average of two or more determinations. [g] See text. [h] In most attempted determinations $t_{1/2}$ < 10 sec. [i] Initial rate. [j] Elsewhere in this paper we have used the abbreviations: "Fum" for fumarate, "FumH" for bifumarate, "FumCH₃" for methyl fumarate "Mal" for maleate, and "MalH" for bimaleate. [k] In most of the studies cited here the net change in absorbancy in the course of a reaction was greater than 0.100. Absorbancies were reproducible to ±0.003. Only in the cases of some of the carboxylatopentaammines and of the diaquotetraammine of cobalt(III) has this error in measurement seriously limited the precision of the experimental determination of the specific rate—as is indicated in the error limits which are cited.

TABLE II

SUMMARY OF KINETIC DATA FOR REDUCTIONS OF $Ru(NH_3)_6^{3+}$

Reductant	Medium	Ionic strength	[H+], M	[Ru(III)] × 10^5, M	[Red] × 10^5, M	k, M^{-1} sec.$^{-1}$
V^{2+}(aq)	$NaClO_4$	0.176	2 × 10^{-3}	6.75	33.4	80
V^{2+}(aq)	$HClO_4$	5.3 × 10^{-3}	1.5 × 10^{-3}	13.9	77.5	42
Cu^+(aq)	$NaClO_4$	0.20	...	...	...	2.2 × 10^{4a}
Cr^{2+}(aq)	$NaClO_4$	0.20	...	...	...	2 × 10^{2a}

[a] To be described in detail elsewhere.

Of the oxidizing agents listed in Table III, the only one which by its own nature determines that the mechanism is to be of the outer-sphere type is Co-$(NH_3)_6^{3+}$. All of the others contain groups in the first coordination sphere which, because they have electron pairs exposed, could interact with the reducing cation. For the latter agents the mechanism of reduction is in many cases in question. Of the reducing agents listed, the mechanisms of reaction are most definitely established for $Ru(NH_3)_6^{2+}$ and Cr^{2+}-(aq). For the former reagent, one's confidence that the reactions proceed by way of outer-sphere activated complexes rests on the substitution behavior which has already been described. For Cr^{2+}(aq)

one's confidence that the reactions generally proceed by way of inner-sphere activated complexes rests on the evidence that for all the oxidizing agents listed, except $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5NO_3^{2+}$, a ligand derived from the oxidizing agent is found in the first coordination sphere of the Cr(III) products. Comparison of the relative rates for $Ru(NH_3)_6^{2+}$ and Cr-(bipy)$_3^{2+}$ shows that they run parallel and that they agree in the interesting detail that $Co(NH_3)_5OH^{2+}$ is reduced less rapidly than $Co(NH_3)_5OH_2^{3+}$. The similarity of reactivities shown by the two complexes, in the context of the results obtained for Cr^{2+}(aq), which is known in most instances to involve an activated complex different from that which $Ru(NH_3)_6^{2+}$

TABLE III

RELATIVE RATES OF REDUCTION OF Co(III) COMPLEXES

(Temperature is $+25°$ unless otherwise noted)

Oxidant	d.m.e.[a,b] 1.26 M NaClO4, 0.14 M HClO4	Ru(NH3)6^{2-},[c] $\mu = 0.2$	Cr(bipy)3^{2-},[d] $\mu = 0.05$ at 4°	V^{2+}(aq)	Cr^{2+}(aq)	Cu^+(aq)[r]
RNH_3^{3+}	0.008	0.003	0.011	$0.007^{f,k}$	$0.00016^{e,k}$	$\geq 2 \times 10^{2s}$
ROH_2^{3+}	1.00	1.00^h	1.00^h	$1.00^{i,k}$	$1.00^{j,l}$	$>10^{2s}$
ROH^{2+}		0.01	0.6		3×10^{6l}	
RNO_3^{2+}	6.5	12				
RN_3^{2+}	4.2	0.4				
RCl^{2+}		87	15	12^k	$>10^{6m}$	
RBr^{2+}		5.3×10^2	>40		$>10^{6m}$	$\sim 10^5 - 10^{7t}$
RI^{2+}		2×10^3			$>10^{6m}$	
$ROxH^{2+}$	0.035	0.2		$35 + 36(H^+)^n$	$820 + 180(H^+)^n$	$(1.0 \pm 0.5) \times 10^{4u}$
$RFumH^{2+}$	0.026	0.16			$2.4 + 6.4(H^+)^{o,q}$	
$RMalH^{2+}$	0.05	70		$24 + 19(H^+)^n$	$360 + 180(H^+)^n$	
$cis\text{-}Co(NH_3)_4(OAc)_2^+$	$9.6(H^+)^2$	$1 + [12(H^+)]^q$		$22 + 44(H^+)^n$	$27 + 90(H^+)^p$	
$trans\text{-}Co(NH_3)_4(OAc)_2^+$	$13(H^+)^2$	$0.2 + 4(H^+)$			$54 + 36(H^+)^p$	
$cis\text{-}Co(NH_3)_4(OH_2)_2^{3+}$	108	80			14^p	

[a] Actually, relative values of $k/D^{1/2}$, where D is the diffusion coefficient. [b] Ref. 3. [c] Present work. [d] Ref. 9. [e] $\mu = 1.0$ M. [f] $\mu = 0.4$ M. [g] $k = 3.0 \pm 0.3$ M^{-1} sec.$^{-1}$. [h] $k = 2.1 \times 10^3$ M^{-1} sec.$^{-1}$. [i] $k = 0.5$ M^{-1} sec.$^{-1}$. [j] $k = 0.55$ M^{-1} sec.$^{-1}$. [k] Ref. 1. [l] A. Zwickel and H. Taube, J. Am. Chem. Soc., 81, 1288 (1959). [m] J. Halpern, private communication. [n] Ref. 18. [o] D. K. Sebera and H. Taube, J. Am. Chem. Soc., 83, 1785 (1961). [p] Ref. 17. [q] Value of term in brackets is questionable. [r] The values listed are specific rate constants not relative rates. In the case of this reductant, the rates of reductions are too uncertain to provide a meaningful standard for listing relative rates. [s] $\mu = 0.2$ M; change of cobalt(III) absorbancy too small for precise measurement. [t] Preliminary estimate, details will be presented elsewhere; $\mu \simeq 5 \times 10^{-3}$ M. [u] $\mu \simeq 0.1$ M; four determinations at different reactant concentrations.

requires, suggests that $Ru(NH_3)_6^{2+}$ and $Cr(bipy)_3^{2+}$ do react by similar mechanisms.

Comparison of the entries for the dropping mercury electrode and $Ru(NH_3)_6^{2+}$ reveals that the relative rates for the two reducing agents are very similar. Over a range of more than 10^4 in the rates, only one deviation is noted among the pentaammine complexes: the maleato complex is relatively much more reactive when it is reduced by $Ru(NH_3)_6^{2+}$ than when it is reduced by the electrode. The agreement in the other cases is so striking that despite the exception, it seems certain that the reductive reactions by the two agents have essential features in common. In particular, it supports the conclusion[3] that atom or group transfer to the electrode from the oxidizing agent is not a feature of the reducing action of the electrode. It should be pointed out that exact agreement between the entries in the two columns cannot be expected; salt effects in the two sets of reactions are often different, and in addition, the relative rates for the electrode process are expected to be sensitive to the applied e.m.f.

The fact that $V^{2+}(aq)$ causes ester hydrolysis in the reaction with $(NH_3)_5CoFumCH_3^{2+}$, just as $Cr^{+2}(aq)$ does, while $Cr(bipy)_3^{2+}$ and $V(bipy)_3^{2+}$ do not,[19] suggests that in this reaction $V^{2+}(aq)$ makes a direct bond to the organic group, as $Cr^{2+}(aq)$ is known to do. But it is by no means certain that all reactions of $V^{2+}(aq)$ proceed via inner-sphere activated complexes. In fact, the close correspondence of the first three entries for $V^{2+}(aq)$ in Table III with those in the same row for $Ru(NH_3)_6^{2+}$ and $Cr(bipy)_3^{2+}$ implies that $V^{2+}(aq)$ reacts with the three oxidizing agents in question by way of outer-sphere activated complexes. When $HC_2O_4^-$ and $HMal^-$ are ligands, the reactions of the

(19) R. T. M. Fraser and H. Taube, J. Am. Chem. Soc., 83, 2238 (1961).

complexes with $V^{2+}(aq)$ may again be of the outer-sphere type. Direct replacement of H_2O on $V^{2+}(aq)$ by $C=O$ puts the π-system of the carbonyl group into position for efficient overlap with the d_ϵ electrons of $V^{2+}(aq)$, and this may be part of the reason for the change in mechanism which is indicated for the V^{2+}-(aq) reductions.

The dependable entries for $Cu^+(aq)$ are too few to provide a basis for general conclusions about the mechanisms by which this reducing agent reacts. Since a d_γ electron is lost by $Cu^+(aq)$ as in the case of $Cr^{2+}(aq)$, it might be expected that the mechanisms of reaction for the two reducing agents would be similar. However, the increase in rate when $Co(NH_3)_5C_2O_4H^{2+}$ compared to $Co(NH_3)_6^{3+}$ reacts is small for $Cu^+(aq)$ compared to $Cr^{2+}(aq)$, and is in the same range as it is for $Ru(NH_3)_6^{2+}$. This item of evidence suggests an outer-sphere activated complex for $Cu^+(aq)$. It is possible that details of geometry in the first coordination sphere for $Cu^+(aq)$ and $Cr^{2+}(aq)$ on oxidation are quite different and thus would be expected to affect the mechanism of the reduction process differently.

Finally, in considering the pentaammine series, attention is drawn to the striking differences between the entries for $Cr^{2+}(aq)$ and for the other reducing agents. When $Cr^{2+}(aq)$ reacts, only with $Co(NH_3)_6^{3+}$ is the reaction mechanism certainly of the outer-sphere kind; with $Co(NH_3)_5NO_3^{2+}$, the mechanism is not known but it is probably of the inner-sphere type. In all other cases, there is good evidence that reaction proceeds via inner-sphere activated complexes. In particular, the high rates for $Co(NH_3)_5MalH^{2+}$ and $Co(NH_3)_5C_2O_4H^{2+}$ compared to $Co(NH_3)_5OH_2^{3+}$ are to be noted, and for $Co(NH_3)_5OH^{2+}$ compared to $Co(NH_3)_5OH_2^{3+}$. The aquo–hydroxy comparison may be diagnostic of mechanism, but the factors which

TABLE IV

TESTS OF THE CONSISTENCY OF MARCUS THEORY

No.	Reaction	k_{12}, M^{-1} sec.$^{-1}$	k_{11}, M^{-1} sec.$^{-1}$	K_{12}^d	f_{12}	k_{22} (calcd.), M^{-1} sec.$^{-1}$
1	Ru(NH$_3$)$_6^{3+}$ + V^{2+}(aq)	7.3 × 10^{2a}	1 × 10^{-2b}	9 × 10^7	0.2	3
2	Ru(NH$_3$)$_6^{3+}$ + Cr^{2+}(aq)	2 × 10^{2a}	≤2 × 10^{-5c}	3.2 × 10^{10}	0.11	≥0.6
3	Co(NH$_3$)$_6^{3+}$ + V^{2+}(aq)	3.3 × 10^{-3e}	1 × 10^{-2b}	1.3 × 10^{8f}	0.53	1.3 × 10^{-9}
4	Co(NH$_3$)$_6^{3+}$ + Ru(NH$_3$)$_6^{2+}$	1 × 10^{-2a}	3^g	1.4 × 10^{-2f}	0.9	2.6 × 10^{-3}

[a] This study. [b] K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958). [c] A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954). [d] Standard oxidation potentials from ref. 13 and as reported in this study. [e] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). [f] Bjerrum[h] has determined the Co(NH$_3$)$_6^{2+}$–Co(NH$_3$)$_6^{3+}$ potential at 30° in 1 N NH$_4$NO$_3$ as −0.055 v. and in 2 N NH$_4$NO$_3$ as −0.035 v. The value from ref. 13 is closer to what we would expect at infinite dilution. Since this calculation is so sensitive to the values of E^0 and since the other values of E^0 employed here are referred to infinite dilution, we feel −0.1 v. is a better estimate. If we had chosen −0.15 v., k_{22} would have been 2.5 × 10^{-10} and 3 × 10^{-4} M^{-1} sec.$^{-1}$ in the respective calculations. [g] k_{22} calculated in reaction 1 above. [h] J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions. Theory of Reversible Step Reactions," P. Haase and Son, Copenhagen, 1941.

govern the rates are still too poorly understood to justify confidence on this point. The difference in the pattern of reactivity for Cr^{2+}(aq) compared to the other reducing agents may not be a matter of difference in mechanism *per se*, but the difference both in mechanism and in rates may reflect ways that the electronic structure of the different metal ions can affect their chemical behavior. Particularly for reactions of the inner-sphere type we may expect relative rates to reflect the individualities of the reaction partners.

An interesting point which first was reported by Vlcek[3] is that the reductions of the diacetatotetraammine–cobalt(III) complexes at the dropping mercury electrode involve [H$^+$], and, in fact, in the acid range covered in Vlcek's experiments, two hydrogen ions are called for in making up the activated complex for the reduction of cobalt(III). The observations for Ru(NH$_3$)$_6^{2+}$ and the dropping mercury electrode do differ for the reduction of the diacetato complexes; the former reagent exhibits a two-term rate law, but no term second order in [H$^+$] appears. The reduction by Cr^{2+}(aq) has a rate law similar to that exhibited by Ru(NH$_3$)$_6^{2+}$, although the reaction with Cr^{2+}(aq) is of the inner-sphere type.

The Results in Relation to Marcus' Theory.—Marcus[4] has proposed a correlation of rates of oxidation-reduction reactions proceeding by "outer-sphere" mechanisms with the rates of electron exchange for the component couples and the driving force for the reaction. When the work terms are small[4] as is likely in the case for reactions between ammine and aquo complexes, the correlation takes the form

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (1)$$

where k_{12} is the observed specific rate of the oxidation-reduction reaction, k_{11} and k_{22} are the isotopic exchange specific rates for the component couples, K_{12} is the equilibrium constant for the reaction, and

$$\ln f_{12} = \frac{(\ln K_{12})^2}{4 \ln \dfrac{k_{11}k_{22}}{Z^2}}$$

(Z is the collision frequency for the uncharged species which we, as Marcus did, will take to be 10^{11} M^{-1} sec.$^{-1}$.)

Unfortunately, despite the large number of measurements which have been made, many of the parameters needed for a searching test of Marcus' theory a remissing. However, some tests of consistency can be applied. These consist of calculating some quantity such as a self-exchange specific rate from independent sets of data to learn whether reasonably constant (or, if only limits can be set, consistent) values are obtained. The notation to be used is this: subscript "1" will refer to the reducing agent which reacts and subscript "2" to the oxidizing agent. If k_{22} in eq. 1 is regarded as the unknown, it will be noticed that the unknown appears also in the factor f_{12}. f_{12}, however, is not very sensitive to the value of k_{22}, thus the value of k_{22} can be extracted from a set of known values of k_{12}, K_{12}, and k_{11} by a process of iteration. Two such sets of calculations are reported in Table IV.

For the two reductions of Ru(NH$_3$)$_6^{3+}$, the calculated values of k_{22} are consistent and are in reasonable agreement with the observation that the rate of the reaction Ru(NH$_3$)$_5$Cl^{2+} + Ru(NH$_3$)$_6^{2+}$ is 4 × 10^2 M^{-1} sec.$^{-1}$,[20] since rates of reactions of ruthenium(III) are not very sensitive to the ligands. For the reductions of Co(NH$_3$)$_6^{3+}$ it is necessary to compare the calculated values of k_{22} with the upper limit of 8 × 10^{-10} M^{-1} sec.$^{-1}$ at 65° which Stranks[21] has set for the rate of electron exchange between Co(NH$_3$)$_6^{2+}$ and Co(NH$_3$)$_6^{3+}$. At 25°, the upper limit can reasonably be set as 3.3 × 10^{-12} M^{-1} sec.$^{-1}$. The value of k_{22} estimated from the V^{2+}(aq) reduction of Co(NH$_3$)$_6^{3+}$ is much greater than the upper limit set by experiment; however, this may only reflect on the inaccuracy of the values of the oxidation potentials at infinite dilution (see footnote f, Table I). The value for k_{22} calculated from the Ru(NH$_3$)$_6^{2+}$ reduction of Co(NH$_3$)$_6^{3+}$, however, is inconsistent both with the upper limit set by experiment and with the value of k_{22} calculated from the V^{2+}(aq)–Co(NH$_3$)$_6^{3+}$ reaction. This discrepancy still exists even if k_{11} for the Ru(NH$_3$)$_6^{2+}$–Ru(NH$_3$)$_6^{3+}$ isotopic exchange is taken to be 10^3 greater than the calculated value used in the determination of k_{22} from reaction 4 (Table IV).

The ΔF° term arising in Marcus' theory is the standard free energy of the elementary electron-transfer step[4] and the standard oxidation potentials employed

(20) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).
(21) D. R. Stranks, *Discussions Faraday Soc.*, **29**, 73 (1960); N. S. Biradar and D. R. Stranks, *Trans. Faraday Soc.*, **58**, 2421 (1963).

in the above calculations may reflect the differences of the spin states of cobalt(II) and cobalt(III) as well as the free energy of the elementary electron-transfer step.[22] However, no such variation of oxidation potential seems sufficient to account for the discrepancy observed between values of k_{22} calculated for the V^{2+} and the $Ru(NH_3)_6^{2+}$ reactions. Marcus' theory is not invalidated by failing to account for the rates of reaction in a few particular cases. It does offer promise[24,25] of correlating rates of electron transfer in a large number of "normal" cases, suggesting that some special effects are operating in the reactions of $Co(NH_3)_6^{3+}$ with reducing agents; one will need to go beyond the theory to discover what these special effects are.

In the reaction between $Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ the over-all free energy of activation should reflect some compromise between the standard oxidation potential

of $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ and the standard oxidation potential (-1.8 v.[13]) of $Co(H_2O)_6^{2+}$–$Co(H_2O)_6^{3+}$ since the ultimate cobalt(II) product is $Co^{2+}(aq)$. Evidently the immediate cobalt(II) species, once formed, decays rapidly into the equilibrium cobalt(II) species. The other ruthenium(II)–cobalt(III) reactions reported in this paper seem to be more favorable thermodynamically.[26]

(22) This point has been discussed with regard to the standard oxidation potential of $Co(NH_3)_5OH_2^{2+}$–$Co(NH_3)_5OH_2^{3+}$.[23]

(23) A. Haim and H. Taube, J. Am. Chem. Soc., **85**, 499 (1963).
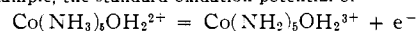
(24) G. Dulz and N. Sutin, Inorg. Chem., **2**, 917 (1963).

(25) R. J. Campion, N. Purdie, and N. Sutin, ibid., in press.

(26) For example, the standard oxidation potential of
$$Co(NH_3)_5OH_2^{2+} = Co(NH_2)_5OH_2^{3+} + e^-$$
has been estimated to be -0.33 v.[27]

(27) R. G. Yalman, Inorg. Chem., **1**, 16 (1962).

The Role of Dissolved Lithium in the Reaction between Triethylsilane and Ethylamine

By Arlen Viste and Henry Taube

The reaction of triethylsilane with ethylamine is not significantly catalyzed by dissolved lithium itself. Instead the reaction appears to be catalyzed by small amounts of a strong base such as lithium ethylamide, presumably present as an impurity in the lithium–ethylamine solution.

Introduction

In 1934 Kraus and Nelson[1] reported that triethylsilane reacts with ethylamine in the following way.

$$(C_2H_5)_3SiH + C_2H_5NH_2 \xrightarrow{Li} (C_2H_5)_3SiNHC_2H_5 + H_2$$
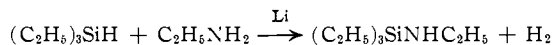
The stoichiometry with respect to Et_3SiH and H_2 was established, and the product $Et_3SiNHEt$ was isolated and identified. By adding the lithium to a solution of Et_3SiH in $EtNH_2$, they found that the reaction begins as soon as the blue color due to lithium develops, and (qualitatively) the rate of reaction increases as the Li concentration is increased. It was shown that an initial mole ratio of Li to Et_3SiH of either 1 or 0.1 results in catalysis. Accordingly, they concluded that "the reaction is a homogeneous one and the lithium evidently serves merely as a catalyst."

Later, in a paper devoted to preparative work utilizing this and similar reactions, Dolgov, et al.,[2] offered the view that the reaction is instead base-catalyzed, the base being the alkali amide formed by the reaction of the alkali metal with the solvent. Presumably the possibility of base catalysis was suggested in part by kinetic studies of the reaction between a trialkylsilane and alcohol or water, beginning with that of Price.[3]

Our main interest was in the possibility of genuine catalysis by lithium; if this were to take place, the reaction would offer a convenient means of studying the kinetics of a reaction involving a metal in solution.

Experimental

Reagents.—Anhydrous ethylamine (Eastman No. 506) was dried with metallic lithium and then distilled on the vacuum line into a storage vessel where it was kept over lithium wire until use. After each use, the ethylamine was distilled back to this storage vessel. For most experiments, triethylsilane (Peninsular ChemResearch No. 436) was sealed off in fragile Pyrex ampoules under vacuum. Triethylfluorosilane (Peninsular ChemResearch No. 2747) was redistilled. When used, it was outgassed on the vacuum line and condensed into the reaction flask. Small pieces of lithium metal (Lithium Corporation of America) were sealed off in fragile Pyrex ampoules under vacuum.

Apparatus and Procedure.—About 95% of the 420-ml. volume available to the reaction system consisted of a glass vessel which could be submerged in a thermostated bath in a dewar. The reaction vessel was connected to a manometer for pressure measurements. The solution and the gas above it were stirred with a multipole magnetic stirrer enclosed in an evacuated glass jacket and driven by a variable speed motor. Two evacuated glass tubes served as ampoule breakers. Each was sealed to a reagent ampoule (Li or Et_3SiH) and contained a small bar magnet allowing it to be manipulated by a horseshoe magnet outside the reaction vessel. The reaction vessel was thermostated in a strip-silvered dewar. The bath liquid (usually methanol) was periodically circulated through a cooling coil in a Dry Ice–methanol slush in a separate dewar by means of a self-priming pump, which was controlled by a thermistor temperature controller (Yellow Springs Instrument Co., Model 63RB). For most of the experiments, temperature stability was about $\pm 0.1°$. Total drift in

(1) C. A. Kraus and W. K. Nelson, J. Am. Chem. Soc., **56**, 195 (1934).

(2) B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, Zh. Obshch. Khim., **24**, 678 (1954).

(3) F. P. Price, J. Am. Chem. Soc., **69**, 2600 (1947).