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HERCULES INCORPORATED, WILMINGTON, DELAWARE 19899

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. V. The Exchange of Allylic Trifluoroacetates with Lithium Chloride Catalyzed by Palladium(II) Chloride in Acetic Acid[1]

BY PATRICK M. HENRY[2]

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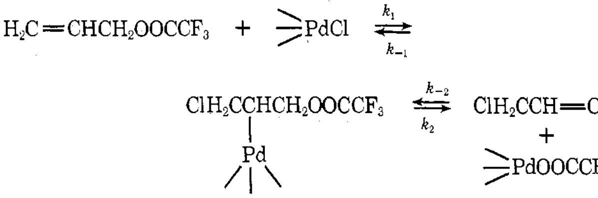
In its simplest form the rate expression for this exchange is rate = $k[Li_2Pd_2Cl_6]$[allyl trifluoroacetate]. By analogy with the kinetics of other Pd(II)-catalyzed exchanges, a more meaningful form of the rate expression is believed to be rate = $k[Li_2Pd_2Cl_6]$[allyl trifluoroacetate][LiCl]/[LiCl]. The form of this rate expression is identical with that found previously for vinylic chloride exchange with radioactive lithium chloride, and it is believed that both proceed by a rapid preequilibrium step to form a π complex which is attacked by chloride to give a chloropalladation adduct in the rate-determining step. Detrifluoroacetoxypalladation then completes the exchange. Evidence for this mechanism is provided by the exchange of crotyl and 3-buten-2-ol trifluoroacetates. Thus crotyl trifluoroacetate gives only 3-chloro-1-butene while 3-buten-2-ol trifluoroacetate gives only crotyl chloride by exchange, a result consistent only with the chloropalladation–detrifluoroacetoxypalladation mechanism. As with previous exchanges, methyl substitution on the double bond causes a marked decrease in rate of exchange.

The previous papers in this series considered vinylic[3a] and allylic[3b] ester exchange and allylic[3c] isomerization as well as vinylic chloride exchange.[1] A logical extension of this work is to allylic chloride exchange. By analogy with ester exchange, allylic chloride exchange would be expected to have the same rate expression as vinylic chloride exchange. Therefore, the special case of the exchange of allylic trifluoroacetate for chloride was chosen for study next. It was previously reported[3b] that, in the absence of acetate, allylic trifluoroacetate exchanged with chloride to give almost exclusively allylic chlorides. This is the first exchange studied in which one type of functional group is exchanged for another. If the exchange is proceeding by the addition–elimination type mechanism postulated for other exchanges, then, in this unsymmetrical type of exchange



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there is the possibility that $k_{-1} \gg k_2$ and the kinetics may reflect the factors involved in the deacetoxypalladation step. In symmetrical exchanges, of course, $k_{-1} = k_2$ and thus exchange occurs half the time addition occurs.

Previously it was shown that vinylic and allylic ester exchange has the rate expression

$$\text{rate} = \frac{[Li_2Pd_2Cl_6][\text{olefin}]}{[LiCl]}(k' + k''[LiOAc]) \qquad (2)$$

while that for vinylic chloride exchange is given by

$$\text{rate} = \frac{[Li_2Pd_2Cl_6][\text{olefin}][LiCl]}{[LiCl]} \qquad (3)$$

Results

All runs were carried out at 25° in dry acetic acid containing varying amounts of $PdCl_2$ and LiCl. The rate expression was defined using allyl trifluoroacetate as substrate. The concentrations of the various species were calculated for any given total Pd(II) ($[Pd(II)]_t$) and chloride ($[Cl]_t$) concentrations using the previously determined values[4] of K_1 and K_D for the equilibria represented by eq 4 and 5. The value of

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftarrows} 2Li_2PdCl_4 \qquad (4)$$

$$2LiCl \overset{K_2}{\rightleftarrows} Li_2Cl_2 \qquad (5)$$

K_1 is 0.1 M^{-1} and the value of K_D is 2.56 M^{-1} at 25°.

If no LiOAc is added, the reaction is, for practical purposes, that represented by eq 1. Only at very long reaction times are traces of allylic acetates observed.

Previous work with allylic ester exchange indicated that the following equilibrium must be considered when determining order in allylic ester[3b]

$$Li_2Pd_2Cl_6 + 2(\text{olefin}) \overset{K_D}{\rightleftarrows} 2LiPdCl_3(\text{olefin}) \qquad (6)$$

The monomeric π complex in eq 6 is unreactive so this equilibrium merely inhibits the rate of reaction. The value of K_2 for allyl trifluoroacetate was found to be 0.13 M^{-1}. For this value of K_2 the inhibition is less than 10% at allyl ester concentrations of 0.02 M. For this reason the rate expression was defined using allyl ester concentrations of 0.02 M or less. At this concentration the data give good first-order plots in allyl ester concentration over at least 4 half-lives. Addition of $LiOOCCF_3$ up to a concentration of 1 M did not affect the rate.

Another reason for using low allyl trifluoroacetate concentrations is the fact that chloride is being formed during the course of the reaction. However, in no case was the change in chloride concentration more than 2 or 3% during the time the run was followed, so even if the rate has a strong [LiCl] dependence, the rate would not be affected within experimental error. As it turns out, this consideration is not important

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[1] Paper IV: P. M. Henry, *J. Org. Chem.* **37**, 2443 (1972).

[2] Address correspondence to the Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

[3] (a) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971); (b) *ibid.*, **94**, 1527 (1972); (c) *ibid.*, **94**, 4437 (1972).

[4] P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971).

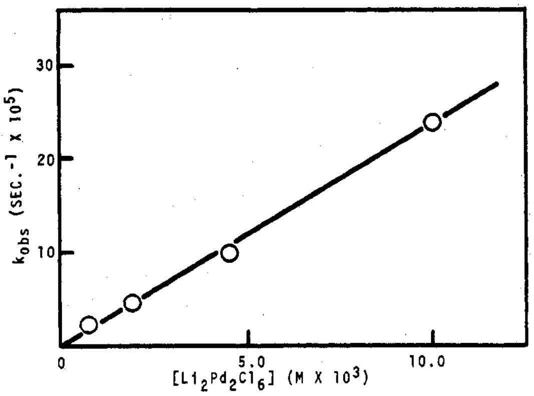


Figure 1.—Plot of k_{obsd} *vs.* [$Li_2Pd_2Cl_6$]; [LiCl] = 0.20 ± 0.002 *M*.

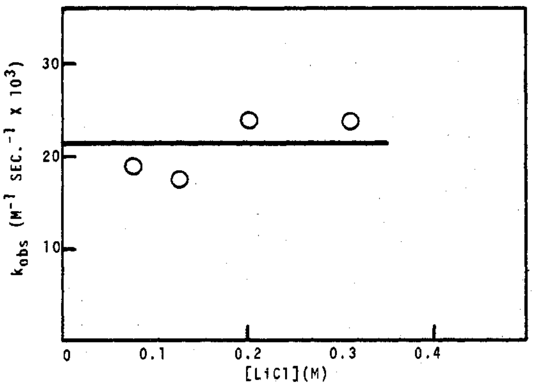


Figure 2.—Plot of k_{obsd}/[$Li_2Pd_2Cl_6$] *vs.* [LiCl].

since, as shall be shown, the rate is not dependent on [LiCl].

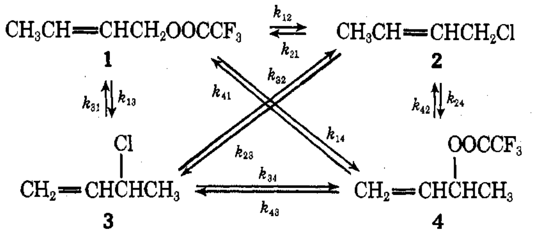
A plot of the first-order rate constant k_{obsd} *vs.* [$Li_2Pd_2Cl_6$], shown in Figure 1, has zero intercept and is linear, indicating a reaction first order in [$Li_2Pd_2Cl_6$]. A plot of k_{obsd}/[Li_2Pd_2Cl] *vs.* [LiCl], shown in Figure 2, indicates a reaction zero order in [LiCl].

The complete rate expression in its simplest form is thus

$$\text{rate} = k[Li_2Pd_2Cl_6][C_3H_5O_2CCF_3] \qquad (7)$$

The value of k at 25° is 2.2×10^{-2} M^{-1} sec^{-1}.

The exchange of 3-buten-2-ol and crotyl trifluoroacetates with chlorides was also studied. The complete reaction sequence is given in eq 8.



(8)

The kinetic data were treated in the same fashion as similar systems in previous papers of this series. Thus, since the reaction goes to completion, k_{31}, k_{42}, k_{21}, and k_{34} are very close to zero while k_{23} and k_{32} can be measured independently. One run was made starting with **1** and another with **4**. The data were treated using a computer program in which the product distribution change with time was calculated for a given set of rate constants.

One problem in treating the present data was the fact that equilibration of the crotyl chloride and 3-chloro-1-butene was much more rapid than exchange so that even at low conversion equilibration of the two isomers was well advanced. Fortunately, the rates of isomerization of the trifluoroacetate esters (k_{14} and k_{41}) were very slow so the system was much less complicated than those previously encountered.[8b] In particular, if one assumes **1** gives only **3** and **4** gives only **2**, the values of k_{13} and k_{42} can be readily calculated. Since k_{23} and k_{32} can be measured independently, the values of these four rate constants can be inserted in the computer program without making any further assumptions as to values of the rate constants. As Table I shows, the product distributions are reproduced within experimental error. This result indicates that exchange only occurs with isomerization.

Table I

Calculated and Observed Product Distribution Change with Time for Exchange of Crotyl and 3-Buten-2-ol Trifluoroacetates with Lithium Chloride[a,b]

Time, min	Concn × 10^2, *M*							
	[1]		[2]		[3]		[4]	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
	Crotyl Trifluoroacetate Run (1)							
3	1.92	1.89	0.0	<0.02	0.0	<0.02	0.079	0.080
84	1.73	1.72	0.11	0.08	0.10	0.12	0.065	0.070
168	1.55	1.53	0.21	0.21	0.18	0.18	0.055	0.061
336	1.34	1.23	0.39	0.44	0.22	0.26	0.043	0.046
	3-Buten-2-ol Trifluoroacetate Run (4)							
3	0.042	0.042	0.0	<0.02	0.0	<0.02	1.90	1.89
37	0.033	0.039	0.14	0.11	0.0	<0.02	1.80	1.78
120	0.027	0.038	0.29	0.27	0.10	0.07	1.54	1.57
206	0.032	0.034	0.41	0.42	0.18	0.14	1.37	1.35
390	0.019	0.027	0.60	0.66	0.27	0.25	1.10	1.01

[a] Values of the rate constants used in calculating product distributions are (sec^{-1}) $k_{42} = 2.7 \times 10^{-5}$, $k_{13} = 2.14 \times 10^{-5}$, $k_{23} = 1.07 \times 10^{-4}$, and $k_{32} = 2.53 \times 10^{-4}$; all other rate constants are zero. [b] [Pd(II)]$_t$ = 0.0224 *M;* [Cl]$_t$ = 0.4868 *M*.

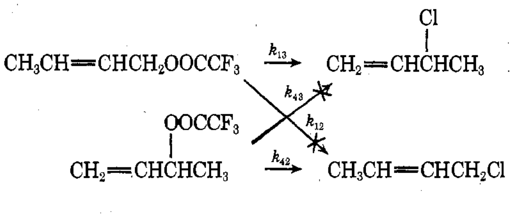


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Table II gives the rate constants for several allylic esters.

TABLE II
RATE CONSTANTS FOR EXCHANGE OF VARIOUS ALLYLIC TRIFLUOROACETATES WITH LITHIUM CHLORIDE

Allylic trifluoroacetate	10^2k, M^{-1} sec^{-1}
$CH_2{=}CHCH_2OOCCF_3$	2.2
$CH_3CH{=}CHCH_2OOCCF_3$	0.26
$CH_2{=}CHCH(OOCCF_3)CH_3$	0.33
$CH_2{=}C(CH_3)CH_2OOCCF_3$	0.0028

Discussion

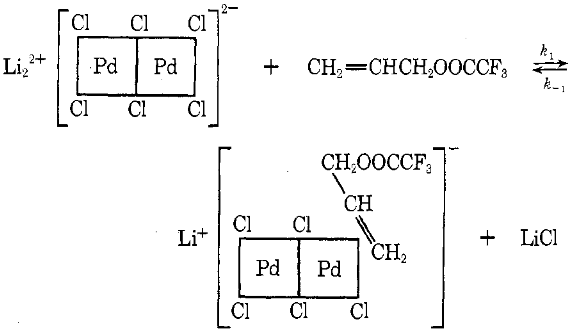
The rate expression shown in eq 7 is identical with that previously found for vinylic chloride exchange. However, the olefin is almost certainly complexed before reacting as shown in eq 10. This equilibrium re-

$$Li_2Pd_2Cl_6 + C_3H_5O_2CCF_3 \rightleftharpoons LiPd_2Cl_5(C_3H_5O_2CCF_3) + LiCl \quad (10)$$

quires a [LiCl] term in the denominator of the rate expression which must be canceled out by a [LiCl] term in the numerator. Thus, as with vinylic chloride exchange, we prefer the rate expression to be written as

$$\text{rate} = \frac{k[Li_2Pd_2Cl_6][C_3H_5O_2CCF_3][LiCl]}{[LiCl]} \quad (11)$$

The complete reaction scheme would be that shown in eq 12–14.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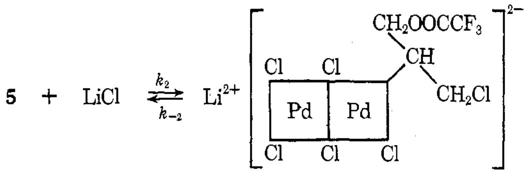
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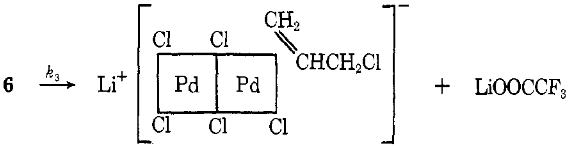
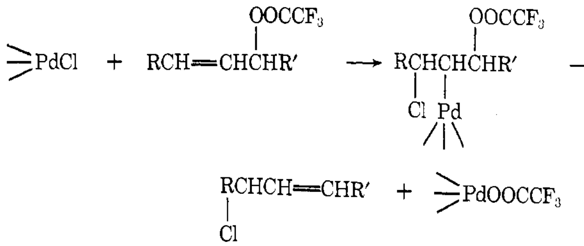
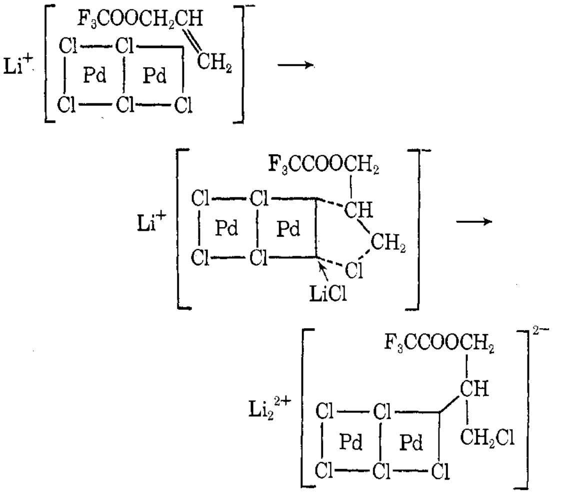

(14)

Support for this scheme comes from the results of the exchange of crotyl and 3-buten-2-ol trifluoroacetate. Thus, the fact that exchange occurs only with isomerization is consistent with chloropalladation–deacetoxypalladation as shown by eq 15 (R, R′ = CH_3 or H).


(15)

The rate expression is consistent with either k_2 or k_3 being the rate-determining step. In symmetrical exchanges, such as radioactive chloride reported in the previous paper of the series,[1] k_2 is rate determining since exchange must occur half the time addition occurs. Most likely k_2 is the rate-determining step since the carbon–chlorine bond is more stable than the carbon–trifluoroacetate bond judging from the fact that the reaction goes to completion even in the presence of a large excess of trifluoroacetate over chloride. In any case, the lack of a trifluoroacetate inhibition eliminates schemes in which k_{-2} is fast compared with k_3 and the trifluoroacetate in solution has a retarding effect on detrifluoroacetatopalladation(II). A scheme involving inhibition of exchange by the group being replaced will, however, be described in the next paper of the series.[5]

The fact that unsymmetrical esters exchange only with isomerization into their allylic isomer eliminates SN2 routes because this type of mechanism would not predict isomerization. No such definite evidence against SN2 attack was available in the vinylic chloride exchange reported in the previous paper.[1] The fact that both rate expressions for exchange are identical suggests that both proceed by the same type of mechanism. SN2 mechanisms for vinylic chloride exchange therefore seem unlikely. On the other hand, the allylic trifluoroacetate exchange gives no clue as to the stereochemistry of chloropalladation. From analogy with vinylic chloride exchange it might be expected to occur by a cis chloropalladation from the Pd(II) coordination sphere as shown in eq 16. The [LiCl] term in the numerator of the rate equation (eq 11) arises from the need for filling the empty coordination site on the Pd(II), which is being formed by the insertion, before transfer can be completed. To determine actual stereochemistry of chloropalladation for allylic trifluoroacetates, exchange of optically active esters would have to be studied.


(16)

The effect of allylic ester structure on rate is qualitatively similar to allylic ester exchange with acetate.[3b] Quantitatively the steric retardation is slightly higher for acetoxypalladation. This result probably reflects

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(5) P. M. Henry, *J. Amer. Chem. Soc.*, in press.

a lower steric requirement for chloropalladation. However, the differences in rate are much less than the rate differences for chloropalladation and acetoxypalladation[3a] of vinylic chlorides and acetates. In this case chloropalladation was much less affected by steric hindrance. The different steric effects in the exchange of allylic and vinylic groups almost certainly reflect the fact that the exchanging group in the vinylic exchange is on the olefinic carbons thus causing vinylic exchange to be more susceptible to steric factors.

One point that deserves comment is whether the value of K_1' ($=k_1/k_{-1}$) in eq 12 has an appreciable value under the reaction conditions. One way to detect K_1' is to measure the rate constant over a broad range of trifluoroacetate concentrations. Of course this is complicated in the present case because of the formation of inactive monomeric π complexes (eq 6). However, a more complete study of the effect of allylic ester concentration on rate was carried out in the work on allylic ester exchange.[8b] It was found that if correction is made for eq 6, using a value of K_2 determined by an ultraviolet spectral study, the rate of exchange of allyl propionate was first order in allyl propionate over a range of allyl propionate concentrations from 0.02 to 0.5 *M*. Since allyl propionate and allyl trifluoroacetate would be expected to have similiar values of K_1', the concentrations of **5** under the reaction conditions will almost certainly be too small to be detected.

Experimental Section

Materials.—Preparation and analysis of Pd(II) stock solutions have been described previously[2-4] as have the preparations of the crotyl and 3-butene-2-ol trifluoroacetates.[3c] Similar procedures were used for the preparation of the methallyl trifluoroacetate (bp 97–97.5° (760 mm)).

Kinetic Runs.—Runs were made on a 1-ml scale by procedures described previously.[2,3] All analyses were by vapor-phase chromatography (vpc). For most runs a 6-ft 20% Carbowax 20 M on ABS (70–80 mesh) column programmed from 80 to 200° at 7.5°/min was used. Helium flow rate was 60 ml/min. For some runs a 20-ft 20% Lac 446 on Chromosorb W (60–80 mesh) at 80° was used. Helium flow rate was 100 ml/min.

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CONTRIBUTION FROM THE NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND 20910, AND THE
DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA, WASHINGTON, D. C. 20017

Stoichiometry and Kinetics of the Decomposition of Some Cobalt(III) Ammines in Molten Ammonium Bisulfate and Concentrated Sulfuric Acid[1]

BY RAYMOND A. SUTULA* AND JOHN B. HUNT

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The decomposition reactions of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5SO_4^+$ in molten NH_4HSO_4 and of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5HSO_4^{2+}$, and *cis*-$Co(NH_3)_4(HSO_4)_2^+$ in *ca.* 97% H_2SO_4 have been studied. Complete decomposition of all the complexes studied involves reduction of Co(III) to Co(II) and oxidation of NH_3 or NH_4^+ to N_2. However, proton magnetic resonance (pmr) spectra of partially reacted Co(III) complexes in *ca.* 97% H_2SO_4 reveal that at least three NH_3 ligands of $Co(NH_3)_6^{3+}$, at least two NH_3 ligands of $Co(NH_3)_5HSO_4^{2+}$, and at least one NH_3 ligand of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ are replaced by HSO_4^- ligands prior to the more rapid redox steps. The spectrophotometrically measured first-order rate constants for the replacement of the first NH_3 ligand are $(5.2 \pm 0.4) \times 10^{-5}$ sec^{-1} for $Co(NH_3)_6^{3+}$ and $(3.4 \pm 0.1) \times 10^{-4}$ sec^{-1} for $Co(NH_3)_5SO_4^+$ in molten NH_4HSO_4 at 153°; $(2.0 \pm 0.1) \times 10^{-4}$ sec^{-1} for $Co(NH_3)_6^{3+}$ and $(3.6 \pm 0.2) \times 10^{-4}$ sec^{-1} for $Co(NH_3)_5HSO_4^{2+}$ at 152.6°; and $(7.5 \pm 0.5) \times 10^{-4}$ sec^{-1} for *cis*-$Co(NH_3)_4(HSO_4)_2^+$ at 151.7° in *ca.* 97% H_2SO_4. The activation energies for the replacement of the first NH_3 lie in the range 38–42 kcal mol^{-1} for all complexes studied, and the rates of these substitution reactions are not affected appreciably by the addition of Co^{2+}, by the addition of fuming H_2SO_4 to the H_2SO_4 solvent, or by the addition of $(NH_4)_2SO_4$ to the NH_4HSO_4 solvent.

Introduction

In the course of a search for suitable electrolytes and cathode materials for molten salt batteries we have found that some cobalt(III)–ammonia complexes decompose slowly enough in molten ammonium bisulfate to allow their reactions to be studied in this solvent. For example, the orange color of $Co(NH_3)_6^{3+}$ persists for at least 1 hr after dissolution of $[Co(NH_3)_6][HSO_4]_3$ in molten NH_4HSO_4 at *ca.* 155°. However, if the temperature of the solution is raised to *ca.* 200°, evolution of a gas is observed, the color of the solution changes rapidly to pale blue, and the spectrum is found to be that characteristic of Co^{2+} in this solvent. These observations have prompted us to investigate the stoichiometry and kinetics of the decomposition of the hexaamminecobalt(III) ion in molten ammonium bisulfate. Although the overall decomposition reaction obviously involves reduction of cobalt(III), the high sensitivity of the rate to temperature suggested that the slow step in the reaction might be a substitution reaction. Indeed we have found that several substitution steps precede the redox step in the decomposition of $Co(NH_3)_6^{3+}$ in molten NH_4HSO_4, and very similar behavior has been observed with 95–100% H_2SO_4 as the solvent. The decomposition reaction of $Co(NH_3)_5HSO_4^{2+}$ has been studied also in both solvents, and the decomposition of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ has been

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* To whom correspondence should be addressed at the Naval Ordnance Laboratory.

[1] Based on the Ph.D. dissertation of R. A. Sutula, The Catholic University of America, Jan 1971. Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; see Abstracts, No. INOR 33.