together with the isotope effects for the forward reactions determine the isotope effects for the reverse reactions.

Tritium offers the possibility of determining three more independent isotope effects for the hydrogen–iodine reaction. These may be k_{H_2}/k_{T_2}, k_{H_2}/k_{HT} and k_{H_2}/k_{DT}. When these isotope effects are available, an excellent picture of the configuration of the activated complex may be obtained. Eventually, it may be possible to measure the effect of substituting the isotopes of iodine. This will indeed complete the picture.

The author desires to acknowledge the help of Professor Farrington Daniels under whose direction this research was done, and to express appreciation to the National Science Foundation for a pre-doctoral fellowship.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. XIII. Reactions of Some *trans*-Co(AA)$_2$Cl$_2$$^+$ in Methanol[1,2]

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

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Rates of substitution reactions in methanol are reported for a series of *trans*-Co(AA)$_2$Cl$_2$$^+$ complex ions with several anionic reagents. Within experimental error the same rates of reaction are obtained for both basic and non-basic anions with a given complex ion except in one case. Abnormally large rates with basic anions are usually completely repressed by strong buffering, showing that methoxide ion alone produces an increased rate. The rates with methoxide ion in methanol are correlated with the rates of base hydrolysis in water and the rates of reaction with other anions in methanol are correlated with the rates of acid hydrolysis in water. Dissociation mechanisms are indicated in all cases.

In water the direct reaction between an octahedral complex of cobalt(III) and a nucleophilic reagent cannot be studied since an intermediate hydrolysis step invariably occurs. In a weakly complexing solvent such as methanol this complication apparently is absent and a number of direct reactions seem to occur. Thus Brown and Ingold[3] studied the rates of reaction of *cis*-Co(en)$_2$Cl$_2$$^+$ in methanol with several anionic reagents. Their results were very interesting inasmuch as several weakly basic anions such as NO$_3$$^-$, Br$^-$, CNS$^-$ and *Cl$^-$ reacted at the same rate which was independent of the concentration of the reacting anion and equal to the rate of racemization if optically active *cis*-Co(en)$_2$Cl$_2$$^+$ was used. This was interpreted as evidence for a common S$_N$1 or dissociation mechanism in these cases. Certain basic anions, CH$_3$O$^-$, N$_3$$^-$ and NO$_2$$^-$ reacted more rapidly and at a rate roughly proportional to the concentration of the anion. This was assumed to show an S$_N$2 or displacement mechanism for these reactions.

However, it may be pointed out that the methoxide ion reaction in methanol is very likely the analog of the hydroxide ion reaction in water. This latter reaction seems to go by a special dissociation mechanism of the conjugate base of the original complex ion.[4] Thus complexes which do not have acidic protons react at the same rate in acid and in alkali because the conjugate base cannot be formed. Furthermore in cases such as *cis* and *trans*-Co(en)$_2$Cl$_2$$^+$ the reaction with hydroxide ion is so much greater than with water in acid solution that even at *p*H 7 the reaction can involve primarily the hydroxide ion path. Since the previous work in methanol using basic reagents was done in unbuffered systems, it is obvious that the increases in rate observed may be almost entirely due to methanolysis producing methoxide ion, *e.g.*

$$N_3^- + CH_3OH \longrightarrow NH_3 + OCH_3^- \quad (1)$$

Accordingly a study of the reactions of a number of complex ions of cobalt(III) in methanol with several anions has been carried out using buffered systems of variable composition. The results on a series of *trans*-Co(AA)$_2$Cl$_2$$^+$ where AA is a substituted ethylenediamine are presented here

$$trans\text{-}Co(AA)_2Cl_2^+ + X^- \longrightarrow Co(AA)_2ClX^+ + Cl^- \quad (2)$$

Experimental

Preparation of Compounds.—The synthesis of the complex salts [Co(AA)$_2$Cl$_2$]Cl has been described elsewhere.[5] These were purified by converting them to their perchlorate salts with NaClO$_4$ to eliminate cobalt(II) salts and HCl impurities. The purity of the salts was then determined by total chloride analyses which agreed well with theory.

Sodium acetate and glacial acetic acid were used without purification. Sodium azide was recrystallized from acidified aqueous solution. Reagent grade absolute methanol was used without further treatment after it was ascertained that up to 0.5% added water had no effect on the measured rates. Radioactive HCl in aqueous solution was obtained on allocation from the Oak Ridge National Laboratory with a specific activity of 0.367 mc./g. It was converted to LiCl with lithium hydroxide and recovered by evaporation.

Acetate buffers were made by mixing stock solutions of acetic acid and sodium acetate. The acetic acid solution was standardized by titration and remade frequently because of the slow methanolysis. Azide buffers were made by adding a methanol solution of *p*-toluenesulfonic acid monohydrate to a methanol solution of sodium azide. Generally a small amount of this acid or methanolic HCl was added to the thiocyanate and chloride solutions to ensure that they were on the acid side.

Kinetic Measurements.—The reactions studied occur in two steps, reaction 2 being followed by

$$Co(AA)_2ClX^+ + X^- \longrightarrow Co(AA)_2X_2^+ + Cl^- \quad (3)$$

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(1) For previous papers in this series see THIS JOURNAL, **79**, 4055 (1957). AA is a substituted ethylenediamine.

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

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

(4) R. G. Pearson, R. E. Meeker and F. Basolo, *J. Inorg. Nuc. Chem.*, **1**, 342 (1955); THIS JOURNAL, **78**, 709 (1956); R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956).

(5) F. Basolo, *ibid.*, **75**, 227 (1953).

Since the substitution of the first chloride is the reaction to be studied, these reactions could only be followed up to the point where the substitution of the second chloride became appreciable. This point was usually under one half-life for one chloride ion removed.

The rates of substitution were most frequently followed by potentiometric titration of the chloride ion. Aliquots of the reaction mixture (10–25 cc.) were transferred to a beaker containing about 150 cc. of acidified acetone which had been previously cooled to 0°. The two electrodes which were placed in this solution were a silver wire coated with silver chloride used as an indicating electrode and a Beckman glass electrode 1190-80 used as a reference electrode. The chloride ion was titrated by a 0.01 *N* silver nitrate solution which was added from a 5-cc. buret calibrated to 0.01 cc. The solution was stirred constantly during the course of the titration with a motor driven stirrer. The potential changes were followed by a model G *p*H meter. End-points could be determined to 0.01 cc. Aliquots of 10 cc. of a reaction mixture 0.0025 *M* in complex ion were used so that 1.5–2.5 cc. of 0.01 *N* silver nitrate were used for complete substitution of the first chloride.

The spectrophotometric method was used in the case where thiocyanate ion was the reagent since this reaction could not be followed by chloride ion titration. Since the spectra of *cis*- and *trans*-$Co(en)_2ClSCN^+$ are known, a wave length could be chosen where the extinction coefficient of both forms are identical, thus giving a D_∞ which is independent of ratios of the geometric isomers formed.[3] The wave length used was 540 mμ at which both forms had a molar extinction coefficient of about 175. The concentrations of the complex ions were 0.001–0.002 *M*. In this work it was assumed that the spectra of all the chlorothiocyanato complexes were the same for different AA groups. A thermostated spectrophotometer controlled to better than 0.1° was used.

To follow the rate of radioactive chloride exchange, 5.00 cc. of a solution 0.002–0.005 *M* in complex ion and 0.02–0.07 *M* in radioactive lithium chloride was prepared and thermostated at 25 ± 0.05°. At intervals, 0.50-cc. aliquots were withdrawn and the chloride ion precipitated with silver nitrate, a 10% excess being employed. The mixture was centrifuged for 5 minutes and the supernatant liquid was removed with a pipet and evaporated on an aluminum disk in the middle of which was placed a small piece of filter paper to absorb the methyl alcohol. These evaporated samples were counted on a tracer-lab T. G. C.-2 end-window Geiger-Müller counter. Infinity readings were taken after 7 or 8 half-lives, or about 2 weeks. This infinity reading was checked by evaporating 0.02 cc. of the reaction mixture on an aluminum disk and measuring its activity. From this the total activity of each aliquot could be calculated. From this and the known concentrations of the complex ion and radioactive chloride, an infinity reading could be calculated. In all cases the agreement was within 5%. Log $(C_\infty - C)$ was plotted against time and the rate constant obtained from the slope by the relation

$$(2.303)(\text{slope}) = -k(2[\text{complex}] + [\text{Cl}^-])/2[\text{Cl}^-] \quad (4)$$

Determination of the pK_a of Hydrazoic and Acetic Acids in Methanol.—The pK_a's of these acids were determined spectrophotometrically using brom cresol green as an indicator. The absorbancy of the acid and base forms of the indicator was found by measuring the spectra in strongly acid and strongly basic solution. The concentrations of the acid and base forms can then be found in the buffer solutions of the acid and its corresponding base. A stock solution containing 0.04% indicator was made up and one cc. of this was used for 35 cc. of buffer solution.

If $K_{a(c)}$ is the concentration ionization constant of the acid and $K_{I(c)}$ is the concentration ionization constant of the indicator, then

$$pK_{a(c)} = pK_{I(c)} - \log(\text{HI}/\text{I}^-)(\text{A}^-/\text{HA}) \quad (5)$$

where HI and I^- are the acid and base forms of the indicator, respectively, and HA and A^- are the corresponding forms of the acid. Since $[A^-]/[HA]$ is known in the buffer solution and $[HI]/[I^-]$ can be found, then $pK_{a(c)}$ can be determined if $pK_{I(c)}$ is known. Values of $pK_{I(c)}$ for brom cresol green were taken from Kolthoff and Guss.[6] This method was used to determine the $pK_{a(c)}$ of acetic acid at several concentrations. The values obtained were in excellent agreement with those given by Kolthoff and Guss. At infinite dilution a value of K_a of 2.2×10^{-10} for acetic acid and of 6.3×10^{-10} for hydrazoic acid was found.

Results

Table I gives the data on the rates of reaction with thiocyanate ion and radioactive chloride ion for several complexes.

TABLE I

RATES OF REACTION OF *trans*-$Co(AA)_2Cl_2^+$ WITH SCN^- AND $*Cl^-$ IN METHANOL AT 25°

AA[a]	SCN^-, *M*	$*Cl^-$, *M*	$k \times 10^4$, min.$^{-1}$
en	0.02		2.2
	.04		3.0
	.06		3.3
	.08		3.6
		0.069	3.0
		.028	3.7
		.0094	2.9
pn	.10		3.9
		.021	4.4
d,l-bn	.10		8.1
i-bn	.20		88
N-meen		.026	0.43
tetmeen	.01		Instantaneous

[a] en = ethylenediamine, pn = propylenediamine, bn = butylenediamine, N-meen = N-methylenediamine, tetmeen = C-tetramethylethylenediamine.

In the case of basic anions it was found that in all cases a very rapid reaction occurred if an unbuffered solution was used. However adding the acid corresponding to the base caused a sharp drop in the rate of chloride ion release. Table II shows the typical results obtained for the ethylenediamine complex with sodium acetate.

TABLE II

RATE CONSTANTS FOR THE RELEASE OF CHLORIDE ION FROM *trans*-$Co(en)_2Cl_2^+$ IN ACETATE–ACETIC ACID BUFFERS IN METHANOL AT 25°, $[OAc^-] = 0.05$ *M*

[HOAc], *M*	$k \times 10^3$, min.$^{-1}$	[HOAc], *M*	$k \times 10^3$, min.$^{-1}$
None	~100	0.01	1.77
0.003	5.00	.02	0.79
.004	3.68	.05	.42
.005	2.99	∞	.35

The data were analyzed by plotting the observed pseudo-first-order rate constant against the reciprocal of the acetic acid concentration as shown in Fig. 1. The extrapolated value corresponding to infinite acetic acid concentration is shown in Table II.

Assuming the observed rate constant to be given by

$$k_{\text{obs}} = k_1 + k_2[\text{OCH}_3^-] + k_3[\text{OAc}^-] \quad (6)$$

and since $[OCH_3^-] = (K_s/K_a)[OAc^-]/[HOAc]$ where K_s is the ionization constant of methanol[7] equal to 2.2×10^{-17} at 25°, then the linear plot shown in Fig. 1 is expected. The slope is equal to $k_2[OAc^-](K_s/K_a)$ when the acetate ion concentration is, of course, constant in any set of experiments. Hence the rate constant k_2 for the reaction of methoxide ion can be calculated, if the as-

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(6) I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **61**, 330 (1939).

(7) A. Unmack, *Z. physik. Chem.*, **133**, 45 (1928).

sumption is made that the ratio (K_s/K_a) is independent of medium effects due to changing ionic concentrations.

The intercept in Fig. 1 is equal to $k_1 + k_3[\mathrm{OAc}^-]$ where the first term is equal to the spontaneous rate of dissociation and the second term is a reaction due to acetate ion *per se*. Table III shows the results for several complexes analyzed in terms of the intercept and the rate constant for reaction with methoxide ion derived from linear plots such as Fig. 1. In the case of the propylenediamine complex the same procedure was followed using hydrazoic acid–azide ion buffers and the measured value of K_a for hydrazoic acid. The agreement of the k_2 values from acetate buffers and azide buffers confirms the interpretation given to the slopes of the lines obtained.

TABLE III

VALUE OF THE INTERCEPT RATE CONSTANT AND RATE CONSTANT FOR REACTION WITH METHOXIDE ION OF SOME *trans*-Co(en)$_2$Cl$_2^+$ IN METHANOLIC BUFFERS OF 0.05 *M* ACETATE ION AT 25°

AA	$k_1 + k_3[\mathrm{OAc}^-]$, min.$^{-1}$	k_2, M^{-1} min.$^{-1}$
en	3.5×10^{-4}	2.7×10^3
pn	4.0×10^{-4}	3.3×10^3
d,l-bn	6.8×10^{-4}	4.7×10^3
i-bn	144×10^{-4}	17.6×10^3
N-meen	20×10^{-4}	54×10^3
N-pren[a]	20×10^{-4}	55×10^3
pn[b]	7.8×10^{-4}	3.2×10^3

[a] N-pren = N-propylethylenediamine. [b] 0.02 *M* azide ion buffers used in place of acetate ion.

Discussion

In the case of the ethylenediamine and propylenediamine complexes with SCN$^-$ and *Cl$^-$ it is found, as in the results of Brown and Ingold[3] with the *cis* isomer, that there is an essential identity of the rates of reaction. Furthermore in the case of the ethylenediamine complex there is very little dependence of the rates on the concentration of the entering anion. There is an increase in rate in the case of the thiocyanate ion which may be explained in part by chloride ion inhibition at low [SCN$^-$] and by medium effects at high [SCN$^-$] as was done in reference 3. Presumably this means that we are measuring the spontaneous rates of dissociation of a chloride ion from the complex under these conditions.

It is seen easily from Fig. 1 that the greater rates in solutions of acetate ion and azide ion are primarily due to methoxide ion as generated in equation 1. Strong buffering leaves a residual rate which should be at least as great as the rate of dissociation, *i.e.*, k_1 in equation 6 should be the same as the rate constant of the reaction with SCN$^-$ and *Cl$^-$, and may be greater if an acetate ion reaction is present. A comparison of the intercepts shown in Table III with the data given in Table I, shows that in several cases these rates are so closely the same that it may be safely concluded that there is no direct reaction of these complexes even with 0.05 *M* acetate ion. This observation is similar to the results obtained in acetate buffers in water for the ethylenediamine complex,[8] where only reactions with water and hydroxide ion were observed.

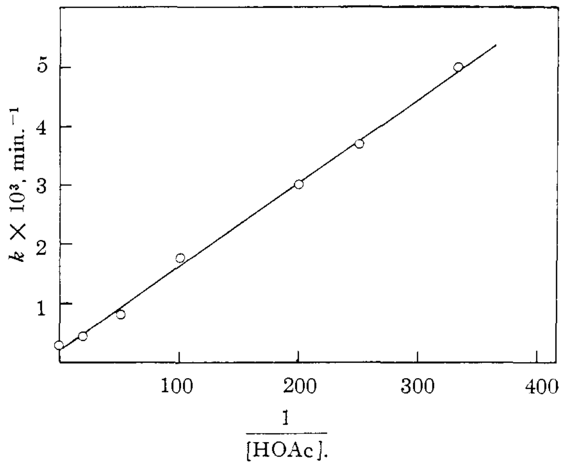

Fig. 1.—Rate of release of chloride ion of *trans*-Co(en)$_2$Cl$_2^+$ in the presence of 0.05 *M* acetate ion and varying acetic acid concentration at 25°.

In several other cases the intercept rate is somewhat greater than the rate of reaction with SCN$^-$ or *Cl$^-$. However, Fig. 1 shows that the intercept is so close to zero in all of these studies that the error of locating it is relatively large. This is particularly true in the case of the isobutylenediamine and the N-alkyl-ethylenediamine complexes where the rate of reaction with methoxide ion is large. Furthermore an uncertainty of a factor of two in the intercept rate exists because it may be that the intermediate Co(AA)$_2$ClX$^+$ is very reactive, in which case two chloride ions would be released each time Co(AA)$_2$Cl$_2^+$ dissociates. With these limitations in mind it may be said that only in the case of the N-methyl derivative is the intercept rate enough greater than the rate of radioactive chloride exchange (factor of 50) so that evidence for a direct reaction with acetate ion exists.

Table IV summarizes a number of rate constants obtained in methanol and in water for dichloro complexes of cobalt(III). The rates of dissociation in methanol from the reactions with SCN$^-$, *Cl$^-$ or the intercept rates with OAc$^-$ are given as $k_{\mathrm{CH_3OH}}$.

TABLE IV

RATE CONSTANTS FOR SOME REACTIONS OF *trans*-Co(AA)$_2$Cl$_2^+$ IN METHANOL AND IN WATER AT 25°

(AA)	$k_{\mathrm{CH_3OH}}$, min.$^{-1}$ $\times 10^4$	$k^c_{\mathrm{H_2O}}$, min.$^{-1}$ $\times 10^3$	$k_{\mathrm{OCH_3^-}}$, M^{-1} sec.$^{-1}$ $\times 10^{-1}$	$k^c_{\mathrm{OH^-}}$,[c] M^{-1} sec.$^{-1}$ $\times 10^{-3}$
en	3.2	1.9	4.5	3.0
pn	4.0	3.7	5.5	2.7
d,l-bn	7.5	8.8	8	2.1
i-bn	115	130	29	9.8
tetramen	instant.	instant.	...	...
N-meen	0.4 ?	1.0	90	11
N-pren	2	7	92	21
en[a]	20[d]	15	~2[e]	1
trien[b]	13[e]	9	...	200

[a] *cis*-Isomer. [b] *cis*-Triethylenetetramine isomer. [c] See ref. 4 for sources. [d] From ref. 3. [e] Data from following paper in this series.

The rates of acid hydrolysis in water are given as $k_{\mathrm{H_2O}}$. Also the rate constants for reaction with methoxide ion in methanol and with hydroxide ion

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[8] R. S. Meeker, Ph.D. Thesis, Northwestern University, 1956.

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

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

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

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

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

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

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

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

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

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

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

Experimental

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

Results

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

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

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

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

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