

with hydroxyl ions.¹⁷ A theoretical estimation¹⁸ based on the rate of formation of short range ion pairs may be made for the rate of reaction of oppositely charged ions in solution and gives a value

(17) M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 483 (1955); M. Eigen and J. Schoen, *Z. Physik. Chem. (Frankfurt)*, **3**, 126 (1955); M. Eigen and L. de Maeyer, *Naturwissenschaften*, **42**, 413 (1955).

(18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943, pp. 43, 110, eq. (4-7-19).

for the rate constant of approximately 10^{10} l. mole⁻¹ sec.⁻¹ assuming that every collision results in reaction. Presumably in the case of Me₃PH⁺ not every collision results in a reaction.

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High Concentration-Ratio Experiments: Isotope Fractionation at the Methyl Carbon in the Reaction of Cyanide Ion and Methyl Iodide. Isotope Effect under Conditions of Equal Reagent Concentrations

BY K. R. LYNN AND PETER E. YANKWICH

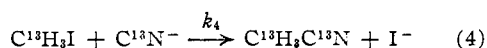
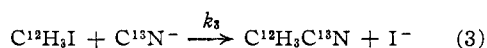
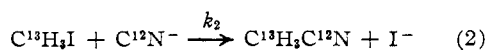
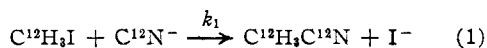
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The C¹³ isotope effect for isotopy at the methyl carbon atom has been measured in the cyanization of methyl iodide in water solution between 11.4 and 58.0°. As a check on these results and those previously reported for isotope fractionation at the cyanide carbon atom, experiments were carried out also in which the reagents were present at equal concentrations instead of one being in large excess; the check experiments yield data of considerably higher quality than either set obtained under high concentration-ratio conditions. There is general agreement among the three sets of results, but it is not sufficiently close to permit detailed speculations concerning the nature of the reaction coordinate motion in terms of simple models. The methyl carbon isotope effect in the cyanization is much larger than that observed in the related hydrolysis, a fact which cannot be explained unless account is taken of the details of activation changes in C-H bonding.

Introduction

In a recent publication¹ we reported results of experiments on the temperature dependence of the isotope fractionation at the cyanide carbon atom in the C-C bond-forming reaction of methyl iodide and cyanide ion. To complete the investigation of carbon isotope effects in this reaction, we have studied isotope fractionation at the methyl carbon over the same range of temperature. In the earlier paper the high concentration-ratio technique was employed, as it was in part of the work to be reported below; to check the results obtained by this method, experiments were carried out under more usual conditions, namely those of equal concentrations of the reacting substances.

The isotopic rate constant ratio measured in the previous study was (k_1/k_3) in the following notation



while the subject of the present investigation is (k_1/k_2). The experimental conditions were such that there was no likelihood of appreciable exchange of methyl nitrile carbon with methyl iodide.^{2,3}

Experimental

Reagents.—Fisher "Certified" sodium cyanide was used without further purification; the methyl iodide samples were center cuts distilled from Eastman "White Label Grade"

(1) K. R. Lynn and P. E. Yankwich, *J. Am. Chem. Soc.*, **83**, 53 (1961).

(2) R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953).

(3) L. Tsai and M. Kamen, *J. Chem. Phys.*, **17**, 585 (1949).

material. Solvent water was de-ionized by passage through a mixed-bed resin ion exchanger. Reagents of analytical grade were employed in the analyses of reactants and products.

Cyanization Runs.—Reactions were carried out at two different concentration ratios: (a) 90 ml. of 0.05 M methyl iodide and 10 ml. of 0.015 M sodium cyanide were mixed and allowed to react for at least fifteen times the calculated half-time of reaction^{4,5} or (b) 90 ml. of 0.05 M methyl iodide and 9 ml. of 0.5 M sodium cyanide were mixed, allowed to react until approximately 3% conversion to methyl nitrile had occurred, then their reaction quenched by addition of excess saturated aqueous zinc sulfate solution (Mallinckrodt A. R.). In either case, aliquots of sodium cyanide solution and freshly prepared methyl iodide solution were brought to the reaction temperature ($\pm 0.1^\circ$), then mixed in glass-stoppered vessels of appropriate volume.

The details of the gas-chromatographic technique employed in isolation and purification of the methyl nitrile and of the several combustion procedures used to secure carbon dioxide for mass spectrometric analysis are given in the previous paper.¹ The mass spectrometric procedures employed are described in earlier publications from this Laboratory.⁶⁻⁸

Calculations.—Complete reaction of the cyanide ions in the presence of an approximately thirty-fold excess of methyl iodide is equivalent to about 3% reaction of the latter. Under these conditions the isotopic constitution of the residual methyl iodide is not altered significantly, the isotopic constitution of the nitrile carbon is that of the original cyanide reagent and that of the methyl carbon in the product reflects the isotope effect related to (k_1/k_2).

Let R_I be the ratio ($\text{C}^{13}\text{H}_3\text{I}/\text{C}^{12}\text{H}_3\text{I}$) for the original methyl iodide reactant (equivalent to the corresponding ratio of isotopic carbon dioxides obtained by combustion of the reagent material) and X_I the corresponding C¹³ atom fraction ($X = R/[1 + R]$); let X_C be the atom fraction of C¹³ in the reagent cyanide. Further, let $X_{N'}$ be the atom fraction of C¹³ in the carbon dioxide obtained by combustion of

(4) B. W. Marshall and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 2640 (1959).

(5) K. R. Lynn and P. E. Yankwich, *J. Phys. Chem.*, **64**, 1719 (1960).

(6) P. E. Yankwich and R. L. Belford, *THIS JOURNAL*, **75**, 4178 (1953).

(7) P. E. Yankwich and R. L. Belford, *ibid.*, **76**, 3067 (1954).

(8) P. E. Yankwich and J. L. Copeland, *ibid.*, **79**, 2081 (1957).

methyl nitrile product from the experiments in which methyl iodide was present in large excess and $X_{N''}$ be that of the carbon dioxide obtained from combustion of methyl nitrile product from the runs in which the reagents were present at equal concentrations. We assume that $(k_1/k_2) = (k_3/k_4)$.⁹ Then, proceeding as detailed in the previous paper,¹ we obtain

$$(k_1/k_2) = R_I \frac{1 - 2X_{N'} + X_C^{10}}{2X_{N'} - X_C} \quad (5)$$

The results of experiments at equal reagent concentrations cannot be expressed so simply in terms of isotope contents and rate constant ratios. However, one can write an accurate expression for the mean atom fraction of C¹³ in the nitrile product

$$X_{N''} = \frac{(k_2R_I + k_3R_C + 2k_4R_IR_C)}{2(k_1 + k_2R_I + k_3R_C + k_4R_IR_C)} \quad (6)$$

Equation 6 is much more sensitive than eq. 5 to the value of P in the expression $(k_1/k_2) = P(k_3/k_4)$; however, it is not strongly dependent on P . This becomes somewhat more apparent if eq. 6 is written in terms of P and the experimentally observable ratios (k_1/k_2) and (k_1/k_3) . By exchanging the means in the equality defining P , we have $(k_1/k_3) = P(k_2/k_4)$; $(k_1/k_4) = (k_1/k_2)(k_2/k_4) = (k_1/k_2)(k_1/k_3)(1/P)$. The latter substitution and a little manipulation convert (6) to

$$X_{N''} = \frac{\frac{R_I}{(k_1/k_2)} + \frac{R_C}{(k_1/k_3)} + 2P \frac{R_IR_C}{(k_1/k_2)(k_1/k_3)}}{2 + \frac{2R_I}{(k_1/k_2)} + \frac{2R_C}{(k_1/k_3)} + 2P \frac{R_IR_C}{(k_1/k_2)(k_1/k_3)}} \quad (7)$$

It is more convenient for purposes of comparison to express the results of equal concentrations experiments in the form of numbers of the order of unity. To this end, note that the value of $X_{N''}$ if there were no isotope fractionation (*i.e.*, $k_1 = k_2 = k_3 = k_4$) would be N , where

$$N = (X_I - X_C)/2 \quad (8)$$

therefore, a useful representation of the results is the tabulation of values of $(N/X_{N''})$.

Results

High Concentration-Ratio Experiments.—Average values of (k_1/k_2) obtained from thirty-one experiments are given in Table I. Because of the large number of runs, the primary data are shown only for one temperature, 11.4°. A convenient representation of these results is a plot of $L(k_1/k_2)$ versus $(1000/T)$ ¹¹; the equation of the least-squares fitted line through this plot is

$$L(k_1/k_2) = (0.56 \pm 0.56)(1000/T) + (4.95 \pm 1.52) \quad (9)$$

the average deviation of the experimental points from the calculated line being 0.49.

Equal Concentrations Experiments.—Average values of $(N/X_{N''})$ obtained from forty experiments are shown in Table II; again, the primary data are shown only for 11.4°. The least-squares fitted line through a plot of values of $L(N/X_{N''})$

(9) These are the isotopic rate constant ratios for fractionation of methyl carbon reacting with different cyanides. Since the isotope effect for methyl carbon fractionation is much larger than that for cyanide carbon fractionation, the equality assumed should be valid to a high degree of approximation. Calculations based on a number of simple models for the reaction coordinate motion indicate that the equality is better than 0.1%.

(10) Values of (k_1/k_2) obtained from application of eq. 5 are relatively insensitive to the approximation $(k_1/k_2) = (k_3/k_4)$. This was tested by using the rigorous relation $(k_1/k_2) = P(k_3/k_4)$, where P is a proportionality constant. With $(0.9 < k_3/k_4 < 1.1)$ and $(0.7 < P < 1.3)$ the calculated values of (k_1/k_2) are shifted by less than the effect of the average deviations in the experimental isotope ratios. For the range of (k_3/k_4) indicated, P must differ from unity by more than 0.1 to affect the calculated value of (k_1/k_2) in the fifth significant figure.

(11) $L(x) = 100 \ln(x)$. Throughout this paper the errors appended are average deviations.

TABLE I

C¹³ ISOTOPE EFFECTS IN THE CYANIZATION OF METHYL IODIDE

Temp., °C.	$X_{N'} \times 10^6$	(k_1/k_2) eq. 5	$R_I \times 10^6 = 9943 \pm 2$	Ave. (k_1/k_2)
11.4	9950	1.0648		
	9976	1.0605		
	9894	1.0799		
	9889	1.0816		
	9905	1.0772		
	9916	1.0746		
	9913	1.0756		
	9927	1.0725	1.0733 ± 0.0056	
	31.0	10 expts.		1.0713 ± .0046
	43.2	8 expts.		1.0741 ± .0033
58.0	7 expts.		1.0692 ± .0026	

vs. $(1000/T)$ has the equation

$$L(N/X_{N''}) = (1.123 \pm 0.123)(1000/T) - (0.409 \pm 0.502) \quad (10)$$

the average deviation of the experimental points from the calculated line being 0.13. In the last column of Table II average values of $(N/X_{N''})$ calculated by eq. 7 are shown; the actual average values of (k_1/k_2) and (k_1/k_3) at each temperature were employed in the computation.

TABLE II

FRACTIONATION OF C¹³ IN REACTION OF EQUAL CONCENTRATIONS OF CYANIDE ION AND METHYL IODIDE

Temp., °C.	$X_{N''} \times 10^6$	$2N \times 10^6 = 20509 \pm 5$	Ave. $(N/X_{N''})$ eq. 7 with $P = 1$	$(N/X_{N''})$ calcd.	
11.4	7 expts.		1.0372 ± 0.0008		
	9921	1.0336			
	9904	1.0354			
	9920	1.0337			
	9889	1.0371			
	9890	1.0369			
	9901	1.0357			
	9901	1.0357	1.0354 ± 0.0010	1.0417 ± 0.0036	
	19.5	6 expts.		1.0357 ± .0005	
	31.0	7 expts.		1.0343 ± .0009	1.0377 ± .0057
43.2	6 expts.		1.0318 ± .0022	1.0406 ± .0047	
58.0	7 expts.		1.0297 ± .0012	1.0366 ± .0042	

Discussion

The values of (k_1/k_2) shown in Table I are somewhat larger than one would have expected from the work of Bender and Hoeg¹² on C¹⁴ isotope effects in nucleophilic substitution reactions. The scatter at each temperature is not as wide as observed with (k_1/k_2) measured in similar experiments¹ but is still three to seven times as great as that encountered in isotope fractionation studies of a more conventional nature. It will become apparent below that the scatter of the data is not, as we indicated in the previous paper, to be attributed to the vagaries of the complex analytical procedures employed in these high concentration-ratio experiments. It seems certain that the scatter of the data reflect the occurrence of side reactions which become important and irreproducible under the concentration conditions employed, for the results obtained with equal reagent concentrations are of very good quality.

An isotopic rate constant ratio such as (k_1/k_2) is the product of a temperature independent factor

(12) M. L. Bender and D. F. Hoeg, THIS JOURNAL, 79, 5649 (1957).

(TIF, which is the high temperature limit of the ratio) and a temperature dependent factor (TDF).¹³⁻¹⁶ The *ab initio* calculation of the former (it is the contribution of the reaction coordinate motion to over-all isotope effect) is a much more formidable task than that of the latter (which seems to be reproduced quite easily by computations based on models which have little to recommend them in the way of chemical and physical reasonableness). An "experimental" estimate of TIF can be obtained by a semi-empirical method^{17,18}; the temperature dependence of (k_1/k_2) as expressed in eq. 9 corresponds to TIF = 1.057 ± 0.010 . At the mid-temperature of the experimental range ($1000/T = 3.25$), $(k_1/k_2) = 1.070 \pm 0.007$, and there TDF = 1.012 ± 0.010 .¹⁹ In the previous publication¹ the experimental indicated value of TIF for (k_1/k_3) was 0.988 ± 0.011 , and TDF at mid-temperature was 1.022 ± 0.009 ; that situation is abnormal, while that observed for (k_1/k_2) is quite reasonable insofar as the relative magnitudes of TIF and TDF are concerned. In comparison with the C¹⁴ isotope effects reported by Bender and Hoeg¹² for reactions of this type, (k_1/k_2) seems rather large; in particular, TIF seems to be quite large for a reaction which is apparently S_N2. This problem can be explored conveniently in terms of the three-particle model for such reactions suggested by Bigeleisen and Wolfsberg.¹⁵

Bigeleisen and Wolfsberg considered the system A-B-C in which the B-C bond is being broken and one is being formed between A and B. The calculation of TIF is based on an equation of Slater²⁰ and is a function of the masses of the three particles, the angle ABC and a reaction parameter p which is the square of (amount of bond formation between A and B)/(amount of bond extension between B and C); $p = 0$ for S_N1 and $p = 1$ for S_N2. Slater's original notions were that A, B, and C were the atoms involved in the primary bonding changes occurring during the reaction; more recently, Bigeleisen and Wolfsberg²¹ have suggested that the masses of molecular fragments containing the atoms among which primary bonding changes occur be employed in the calculation of TIF instead of the masses of the atoms themselves. In Table III are collected values of TIF for the three isotope effects of interest in the present study, calculated after Bigeleisen and Wolfsberg and Slater using both "atomic" and "molecular fragment" masses.²² Neither basis of calculation furnishes a value for the (k_1/k_2) TIF as large as the apparent experimental lower limit: 1.047. Further, in the range of p

values descriptive of an S_N2 mechanism (about 0.7-1.0) TIF is not strongly dependent upon the basis employed. The situation is further complicated by the fact that the same value of p must apply to (k_1/k_2) and (k_1/k_3) , and no value of p brings both sets of results into consonance. For similar reasons it is interesting to compare the hydrolysis and cyanization methyl carbon isotope effects. In the earlier investigation of the hydrolysis reaction¹ the apparent experimental TIF was 1.031 ± 0.007 (to be compared with 1.057 ± 0.010 for cyanization), while TDF at the mid-temperature of the experimental range was 1.003 ± 0.007 (the corresponding cyanization TDF being 1.012 ± 0.012). While the TDF values overlap in the two reactions, the TIF's are different by 0.026 ± 0.012 . In terms of three-particle models for these S_N2 reactions, such a difference cannot be explained on the basis of the different masses of O and C or of OH and CN. These difficulties of correspondence and interpretation suggest that the three-particle models are over-simplified. If such is the case, the most likely explanation of the relatively high TIF values is that the modification of C-H bonding upon activation, with concomitant contributions to the over-all isotope effect, is not insignificant (it is neglected completely in the three-center approximation); the greatest difficulty attending such an inference is that there does not appear to be any justification for an assumption that such a contribution will be strongly influenced by the nature of the incoming group—particularly when two relatively so similar as CN⁻ and OH⁻ are compared.

TABLE III

TIF CALCULATIONS FOR THE BIGEISEN-WOLFSBERG-SLATER THREE-PARTICLE MODEL: COMPARISON OF USE OF "ATOMIC" AND "MOLECULAR FRAGMENT" MASSES

(The asterisk indicates the atom which is C¹² or C¹³)

	A	B	C	0	TIF for $p =$	
					1	∞
k_1/k_2	C ¹²	C*	I	1.0371	1.0316	1.0198
	NC ¹²	C*H ₃	I	1.0292	1.0278	1.0207
k_1/k_3	C*	C ¹²	I	1.000	1.0076	1.0198
	NC*	C ¹² H ₃	I	1.000	1.0023	1.0069
k_3/k_4	C ¹³	C*	I	1.0371	1.0321	1.0206
	NC ¹³	C*H ₃	I	1.0292	1.0279	1.0204

The scatter of the data for (N/X_N'') is only about a third as great, on the average, as that for (k_1/k_2) at similar temperatures and about a fourth as great as the scatter in the data for (k_1/k_3) . The values for (N/X_N'') computed from the averages of (k_1/k_2) and (k_1/k_3) are larger at each temperature than the experimental average value of (N/X_N'') . Two obvious explanations for this discrepancy can be offered: first, the value of P (eq. 7 and ref. 10) is not essentially unity as concluded above; second, one or both of the input average values of (k_1/k_2) and/or (k_1/k_3) is consistently in error.

The first possibility can be disposed of quickly because the values of P required to produce correspondence between the calculated and observed (N/X_N'') 's lie in the range 1.55-1.75, which is ridiculous. If we assume that the observed magnitude of (k_1/k_2) , 1.07, is approximately correct it

(13) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(14) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

(15) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1927 (1953); **22**, 1264 (1954).

(16) H. S. Johnston, W. A. Bonner and D. J. Wilson, *ibid.*, **26**, 1002 (1957).

(17) P. E. Yankwich and H. S. Weber, *THIS JOURNAL*, **78**, 564 (1956).

(18) P. E. Yankwich and R. M. Ikeda, *ibid.*, **81**, 1532 (1959).

(19) All these values are based on eq. 9.

(20) N. B. Slater, *Proc. Roy. Soc. (London)*, **194A**, 113 (1948).

(21) J. Bigeleisen and M. Wolfsberg, *Advances in Chemical Physics*, **1**, 30 (1958).

(22) Note that for these models the proportionality constant P^{10} never deviates from unity by more than 0.001; the situation is similar with four-center models (which, however, would be expected to yield similar results because of the great strength of the C-N bond).

seems unlikely that P would differ from unity by more than 0.02, and the shift in $(N/X_{N'})$ ascribable to such a P is only ± 0.0002 . P may not be unity, but its deviation from unity is not the source of the discrepancy under discussion.

It seems much more likely that the results of experiments with a high ratio of reagent concentrations are in error, the most likely source of error being the occurrence of side reactions which are irreproducible in effect under the conditions employed. We have examined a number of possibilities (hydrolyses and solvation equilibria of reagents and products, etc.), and none seem to account for both the direction and magnitude of the discrepancy between the equal and unequal concentrations experiments or are ruled out on the basis of relative rate^{4,5,23} or would produce products easily detectable and identifiable on the analytical chromatogram of the reacted samples.

(23) E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **164A**, 295 (1938); **196A**, 540 (1949); **220A**, 386 (1953).

Actually, the least-squares *calculated* values of $(N/X_{N'})$ average only 0.0047 ± 0.0047 higher than the least-squares *experimental* values; though this is a difference in isotope effect of $14 \pm 14\%$, on the average, it is not very large. It is not possible, on the evidence available, to ascribe to either (k_1/k_2) or (k_1/k_3) the major part of the discrepancy. It is not to be expected that this state of affairs would be general to the application of the high concentration-ratio technique. Some insight into the experimental limitations operating in the cyanization of methyl iodide may be obtainable from studies on the cyanizations of methyl bromide and methyl chloride, and we have projected such investigations. Additionally, these would furnish further information as to "leaving group" effects, including the effect of "particle" mass.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

Kinetics of Some Electron Transfer Reactions of Cobalt(III)

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The rates of reaction of V_{aq}^{++} with complexes RL ($R = Co^{III}(NH_3)_5$; $L = OH_2, NH_3, Cl^-$) have been studied in H_2O and in D_2O . The rate of reaction of Cr_{aq}^{++} with RNH_3^{+++} has been studied in the two media. Rates, ligand and isotope effects are compared with those found in reactions, the nature of whose activated complexes are more definitely understood.

Cr(II), both as an aquo ion and as the tris- α, α' -bipyridine complex, has received much attention as a reductant for Co(III) complexes of the type RL . These reactants have been shown to exemplify two kinds of activated complexes. $Cr(bip)_2^{++}$ ($bip = \alpha, \alpha'$ -bipyridine) has been found to react by an outer sphere activated complex, the coordination spheres of both oxidant and reductant apparently remaining intact in the activated complex,¹ while Cr_{aq}^{++} has been shown to exploit the bridged activated complex² (for $L = OH^-, OH_2, SCN^-, N_3^-, PO_4^{=}, acetate, oxalate, etc.$), wherein the one ligand on the oxidant which is not NH_3 occupies a coordination position of each metal center in the activated complex.

The demonstration of the operation of the bridged activated complex depends upon the slowness with which Cr(III) complexes reach substitution equilibrium. V(III) rapidly equilibrates with solution, and thus the mechanism of reaction of V_{aq}^{++} cannot be determined by the methods which availed for Cr_{aq}^{++} . An attempt is here made to elucidate the mechanism of reaction of V_{aq}^{++} with complexes of Co(III) by arguments based upon the chemical and isotopic effects characteristic of the two activated complexes as calibrated by Cr(II). The reaction of Cr_{aq}^{++} with RNH_3^{+++} has been studied for inclusion in the comparisons.

(1) A. Zwickel and H. Taube, *Discussions Faraday Soc.*, in press (1960).

(2) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959, Chapter 1.

Experimental

The reductants are air-sensitive and all work was done in an atmosphere of nitrogen scrubbed by Cr_{aq}^{++} to remove any traces of oxygen. Cr_{aq}^{++} was generated both electrolytically and by reduction with amalgamated zinc. The solutions of Cr(III) were prepared by reducing a solution of recrystallized potassium dichromate with hydrogen peroxide. V_{aq}^{++} was generated by reduction with amalgamated zinc of solutions of V(IV) which were obtained by reaction of vanadium pentoxide with hydrochloric acid. The vanadium pentoxide was prepared by roasting recrystallized ammonium metavanadate. Crystalline vanadyl perchlorate, prepared by W. J. Pendergast, was also used as source of V(IV). The Co(III) compounds were prepared by standard methods.

The reductant was added to deoxygenated solutions containing oxidant, neutral salt to maintain the ionic strength and other reactants (*e.g.* acid). The mixture was stirred by bubbling with nitrogen and pumped into a deoxygenated spectrophotometer cell, the cell and the mixing vessel being thermostatted by immersion in a water-bath. After filling, the cell was isolated, dried and transferred to the thermostatted cell compartment of a Cary Model 14 spectrophotometer, where the optical density of the solution was recorded as a function of time at a chosen wave length. One of the maxima in the visible region of the Co(III) complex was used in all cases. After appropriate correction for absorption by species other than Co(III), the second order rate law (first order in oxidant and in reductant) was used in the form

$$\frac{d}{dt} \ln \frac{(V^{++})}{(Co^{III})} = -k(Co_0^{III} - V_0^{II})$$

the differentiation being performed graphically. Linearity of plots of the logarithmic ratio *vs.* time was taken as evidence of the validity of the treatment of data and specifically of the second order rate law. The wave lengths chosen and extinction coefficients used are shown in Table I.