

Solvolysis Rates in Aqueous-Organic Mixed Solvents: Part VII—Enthalpy & Entropy of Activation for Benzoyl Chloride Solvolysis in Methanol-Water Solutions

M. A. ASHY*, E. M. DIEFALLAH, A. M. KHALIL & M. A. MOUSA

Department of Chemistry, Assiut University, Assiut, Egypt and Department of Chemistry
King Abdulaziz University, Jeddah, Saudi Arabia

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The pseudo-first order rate constants for hydrolysis and methanolysis of benzoyl chloride in methanol-water solutions have been measured over the temperature range 15°-45°. The solvolysis rates have been followed by conductance measurements and the reaction product ratios determined by potentiometric titrations after completion of the reaction. When the concentration of water in the solvent is increased, the observed solvolysis rate constant first increases to a maximum at about 0.5 water mole fraction, then decreases. The influence of solvent variation on reaction rate has been examined in terms of changes in the activation parameters. The results do not support any simple correlation between the macroscopic dielectric constant of the medium and the reaction rate constant. The effect of solvent on the enthalpies and entropies of activation has been considered in terms of the electrostatic theory and on the basis of the change in the solvent structure.

THE solvolysis of benzoyl chloride has been studied in aqueous-organic mixed solvents by several investigators¹⁻⁴. However, no detailed study of the solvolysis of benzoyl chloride in alcohol-water mixtures has been undertaken. This led us to study the behaviour of this substrate in a series of methanol-water mixtures including the pure solvents, in order to understand the behaviour of the entropy and enthalpy of activation of solvolytic displacement reactions towards solvent variation. For some reactions the resulting solvent effects were discussed in terms of specific solvation of reactants and transition states^{5,6}. In other solvolytic reactions it was concluded that the behaviour of activation parameters towards solvent variation is determined to a large extent by the process of solvent reorganization in the activation process⁷⁻¹⁰. In the present study, we noted that this last conclusion should especially be used to explain the results of solvolysis of benzoyl chloride in the water-rich solutions.

Materials and Methods

Benzoyl chloride (AR) was distilled and kept out of contact with light. Doubly distilled water and absolute methanol purified according to recommended procedures were used to make the solutions (v/v).

The rate of solvolysis reaction was followed conductometrically. Conductance-concentration calibration curves were constructed using standardized hydrochloric acid solutions, at several experimental temperatures and in the various solvent mixtures, for conversion of measured conductivity to molar concentrations. The range of initial concentrations

suitable for the kinetic studies on the halide was determined by trial and error. In the concentration range 0.01 to 0.1 molar benzoyl chloride, kinetic results were reproducible and exhibited strictly first-order behaviour with small random experimental error.

The products of reaction were determined by acidimetry after completion of the reaction. Analysis of hydrochloric and benzoic acids in the reaction mixtures was done by potentiometric pH titration using a Corning model 12 research pH meter. The equivalence points were determined from the change in potential per 0.05 ml change in volume of reagent. Titrations were generally done at a time which exceeded at least 10 half-lives after the end of reaction while the samples were thermostated at reaction temperatures.

Results and Discussion

The pseudo-first order rate constants, k (sec⁻¹), were determined graphically from measurements covering at least the first half of the reaction. The logarithmic first order plots were strictly linear in all solvent mixtures. Table 1 shows the results of the rate measurements in methanol-water solutions at various temperatures and solvent compositions. Fig. 1 shows the dependence of the observed rate constants on solvent composition for the solvolytic reaction. It is seen that when the concentration of water in the solvent is increased, the rate constant first increases to a maximum at about 0.5 water mole fraction and then decreases. Non-linear dependence of solvolysis rate constants on solvent composition has been observed for other systems in several binary solvent mixtures⁹⁻¹¹.

TABLE 1 — EFFECT OF TEMPERATURE AND SOLVENT COMPOSITION ON THE OBSERVED PSEUDO-FIRST ORDER RATE CONSTANTS IN THE SOLVOLYSIS OF BENZOYL CHLORIDE IN METHANOL-WATER MIXTURES

Water-Methanol (v/v)	Mole fraction of water	$k \times 10^3$ (sec ⁻¹) at			
		15°	25°	35°	45°
Methanol	0.00	1.55 ± 0.02	4.00 ± 0.05	9.00 ± 0.05	21.0 ± 0.3
4.7: 95.3	0.10	2.42 ± 0.03	6.15 ± 0.03	13.3 ± 0.1	27.6 ± 0.3
16.0: 84.0	0.30	4.20 ± 0.05	10.30 ± 0.1	23.5 ± 0.5	50.0 ± 0.5
30.9: 69.1	0.50	8.30 ± 0.1	18.10 ± 0.02	39.5 ± 0.5	75.0 ± 0.5
51.0: 49.0	0.70	2.19 ± 0.05	4.40 ± 0.05	8.1 ± 0.1	15.5 ± 0.2
64.1: 35.9	0.80	0.740 ± 0.01	1.80 ± 0.01	2.00 ± 0.04	5.25 ± 0.05
80.0: 20.0	0.90	0.270 ± 0.005	0.63 ± 0.01	0.865 ± 0.01	2.00 ± 0.05
Water	1.0	0.182 ± 0.004	0.43 ± 0.01	0.96 ± 0.02	2.03 ± 0.05

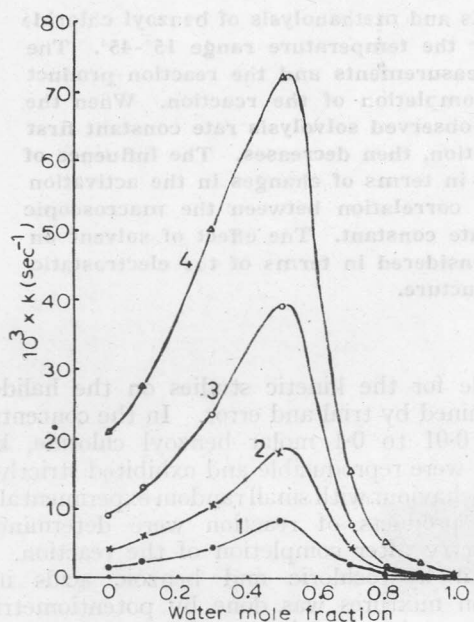
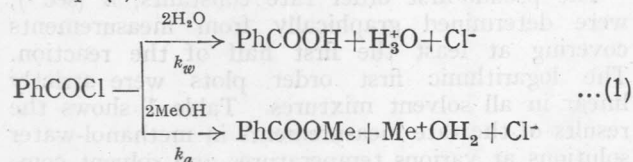


Fig. 1 — Dependence of the observed pseudo-first order rate constants on solvent composition for solvolysis of benzoyl chloride in methanol-water solutions [Curve (1) 15°; (2) 25°; (3) 35°; and (4) 45°]

In a mixture of methanol and water the reaction of benzoyl chloride has been envisaged as shown in Eq. (1),



Hence the observed rate constant (k_{obs}) is the sum of the rate constants for the hydrolysis reaction (k_w) and the rate constant for the alcoholysis reaction (k_a), i.e.

$$k_{\text{obs}} = k_a + k_w \quad \dots(2)$$

In order to analyse the temperature dependence of k_{obs} we realize that the activation parameters $\Delta H_{\text{obs}}^\ddagger$ and $\Delta S_{\text{obs}}^\ddagger$ are composite and each is a function of k_a and k_w which are themselves

temperature dependent. It follows from absolute rate theory¹² that:

$$K_{\text{obs}}^\ddagger = K_a^\ddagger + K_w^\ddagger \quad \dots(3)$$

and after some manipulations of Eq. (3), one obtains:

$$\frac{\partial \ln K_{\text{obs}}^\ddagger}{\partial T} = \frac{K_w^\ddagger}{K_w^\ddagger + K_a^\ddagger} \frac{\partial \ln K_w^\ddagger}{\partial T} + \frac{K_a^\ddagger}{K_w^\ddagger + K_a^\ddagger} \frac{\partial \ln K_a^\ddagger}{\partial T} \quad \dots(4)$$

In Eq. (4) we can substitute for the $\ln K^\ddagger$ s to obtain

$$\Delta H_{\text{obs}}^\ddagger = \frac{k_w}{k_w + k_a} \Delta H_w^\ddagger + \frac{k_a}{k_w + k_a} \Delta H_a^\ddagger \quad \dots(5)$$

Eq. (5) relates $\Delta H_{\text{obs}}^\ddagger$ to the enthalpy of activation for hydrolysis (ΔH_w^\ddagger) and the enthalpy of activation for alcoholysis (ΔH_a^\ddagger).

Again, from absolute rate theory, we have:

$$\Delta H^\ddagger = -RT \ln \frac{kh}{(R/N)T} + T\Delta S^\ddagger \quad \dots(6)$$

where (R/N) is the Boltzmann gas constant and h is the Planck's constant. Substituting Eq. (6) into Eq. (5), we get:

$$\frac{\Delta S_{\text{obs}}^\ddagger}{R} = \frac{k_w}{k_w + k_a} \left(-\ln \frac{k_w h}{(R/N)T} + \frac{\Delta S_w^\ddagger}{R} \right) + \frac{k_a}{k_w + k_a} \times \left(-\ln \frac{k_a h}{(R/N)T} + \frac{\Delta S_a^\ddagger}{R} \right) + \ln \frac{k_{\text{obs}} h}{(R/N)T} \quad \dots(7)$$

Eq. (7) can be rewritten in the form:

$$\Delta S_{\text{obs}}^\ddagger = \left(\frac{k_w}{k_{\text{obs}}} \right) \Delta S_w^\ddagger + \left(\frac{k_a}{k_{\text{obs}}} \right) \Delta S_a^\ddagger - R \left(\frac{k_w}{k_{\text{obs}}} \ln \frac{k_w}{k_{\text{obs}}} + \frac{k_a}{k_{\text{obs}}} \ln \frac{k_a}{k_{\text{obs}}} \right) \quad \dots(8)$$

Eq. (8) relates $\Delta S_{\text{obs}}^\ddagger$ to the entropy of activation for hydrolysis (ΔS_w^\ddagger) and the entropy of activation for alcoholysis (ΔS_a^\ddagger).

Therefore, in order to allow for a detailed examination of the thermodynamic parameters, analysis of the reaction products at the end of reaction and at each temperature and solvent composition was necessary. The relative rate constant, $\left(\frac{k_w[\text{H}_2\text{O}]}{k_a[\text{CH}_3\text{OH}]} \right)$ is given simply by the relative concen-

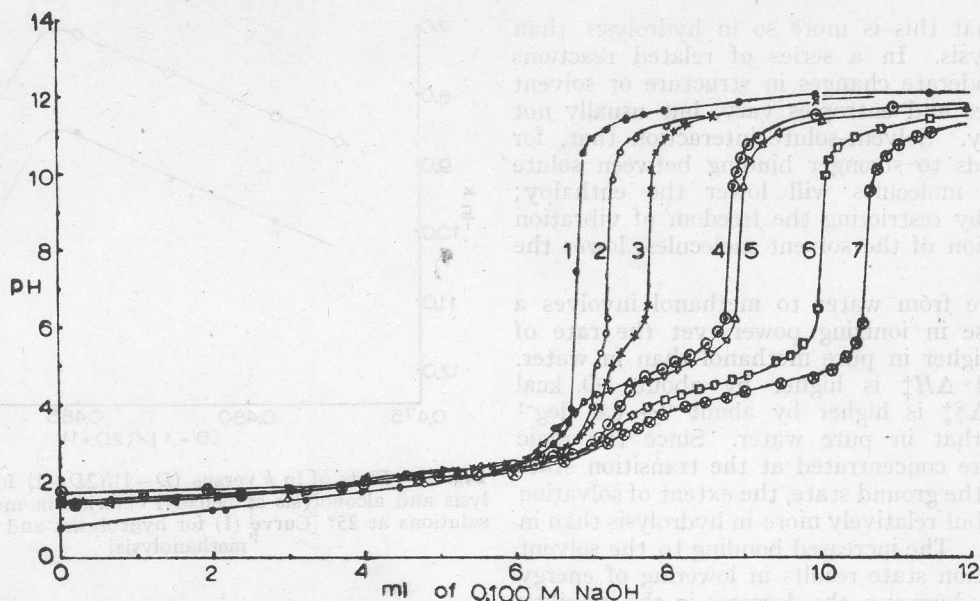


Fig. 2—Potentiometric pH titration curves of the reaction products for solvolysis of benzoyl chloride in methanol-water solutions at 35° [Water mole fraction: (1) 0.0; (2) 0.10; (3) 0.30; (4) 0.50; (5) 0.70; (6) 0.80; (7) 0.90]

tration of products, $([\text{PhCOOH}]/[\text{PhCOOCH}_3])_{t=\infty}$. Analysis of the reaction products was done by potentiometric titration of the solution after the completion of the reaction and typical results of titration curves obtained at 35.0°C are shown in Fig. 2 for the different solvent compositions used in this study. If x represents the volume of the base solution equivalent to the first equivalence point in the titration curve and y represents the volume of the base solution at the second equivalence point, then $(y-x/x)$ is the fraction of benzoyl chloride hydrolysed, $(2x-y/x)$ is the fraction alcoholysed, and $(y-x)/(2x-y)$ represents the reaction product ratio, $([\text{PhCOOH}]/[\text{PhCOOCH}_3])_{t=\infty}$. Table 2 lists the product ratios obtained at different temperatures and solvent compositions. At least triplicate experiments were made and the average errors in the product ratios were less than 2% in most cases. The extent of conversion of the ester into acid and alcohol was negligible under our experimental conditions. The results show that the relative amounts of products acid and ester, by reaction with water and with methanol, respectively, are directly proportional to the respective rate constants $k_w[\text{H}_2\text{O}]$ and $k_a[\text{ROH}]$. This experimental result favours the postulation of direct displacement by solvent¹³.

The separation of the observed rate constants into the rate constants for hydrolysis and alcoholysis was done making use of the results of the acidimetry experiments. Energies of activation for hydrolysis and alcoholysis were found from the temperature dependence of the reaction rates according to Arrhenius equation making use of the method of least squares. Activation entropies (ΔS_w^\ddagger and ΔS_a^\ddagger) and enthalpies (ΔH_w^\ddagger and ΔH_a^\ddagger) were calculated from the respective rate constants according to absolute rate theory equations. The activation

TABLE 2—EFFECT OF TEMPERATURE AND SOLVENT COMPOSITION ON THE PRODUCT RATIO IN THE SOLVOLYSIS OF BENZOYL CHLORIDE IN METHANOL-WATER MIXTURES

Mole fraction of water	$([\text{PhCOOH}]/[\text{PhCOOCH}_3])_{t=\infty}$ at		
	25°	35°	45°
0.10	0.025	0.0285	0.038
0.30	0.088	0.0915	0.100
0.50	0.242	0.275	0.317
0.70	0.550	0.530	0.550
0.80	0.617	0.630	0.660
0.90	1.127	1.17	1.24

TABLE 3—ENTHALPIES AND ENTROPIES OF ACTIVATION FOR BENZOYL CHLORIDE SOLVOLYSIS IN METHANOL-WATER SOLUTIONS AT 25°

Mole fraction of water	ΔH_w^\ddagger kcal mol ⁻¹	$-\Delta S$ cal deg ⁻¹ mol ⁻¹	ΔH_a^\ddagger kcal mol ⁻¹	$-\Delta S_a^\ddagger$ cal deg ⁻¹ mol ⁻¹
0.00	—	—	15.03	25.47
0.10	17.36	19.74	13.44	29.92
0.30	15.37	25.46	14.20	26.25
0.50	14.81	25.80	12.26	31.53
0.70	10.84	41.73	11.27	37.42
0.80	9.81	47.26	9.16	45.72
0.90	10.65	46.29	9.75	45.18
1.0	14.04	34.83	—	—

parameters calculated from the experimental data are recorded in Table 3. The high negative entropy values for both hydrolysis and alcoholysis indicate a decrease in the degree of freedom of the system as a whole when the reactants pass into the transition state and are most probably due to the freezing of solvent molecules strongly oriented around the transition state. The data in Table 3

also show that this is more so in hydrolysis than in methanolysis. In a series of related reactions involving moderate changes in structure or solvent the enthalpies and entropies vary, but usually not independently. Solvent-solute interaction that, for example, leads to stronger binding between solute and solvent molecules will lower the enthalpy; it will also, by restricting the freedom of vibration and of rotation of the solvent molecules, lower the entropy¹⁴.

The change from water to methanol involves a large decrease in ionizing power, yet the rate of reaction is higher in pure methanol than in water. In methanol ΔH^\ddagger is higher by about 1.0 kcal mol⁻¹, but ΔS^\ddagger is higher by about 9.4 cal deg⁻¹ mol⁻¹ than that in pure water. Since the ionic charge is more concentrated at the transition state compared to the ground state, the extent of solvation is increased, but relatively more in hydrolysis than in methanolysis. The increased bonding to the solvent at the transition state results in lowering of energy of activation; however, the decrease in the mobility of some solvent molecules more than compensates for the decrease in the entropy of activation and this gives rise to a net increase in reaction rate upon changing the solvent from water to methanol. The abrupt change in reaction rates and activation parameters in the highly aqueous solvents might suggest the operation of a dual mechanism, i.e. a bimolecular substitution and a unimolecular ionization prepondering at high water concentration²⁻⁴.

It can be seen that the enthalpy and entropy of activation for hydrolysis (ΔH_w^\ddagger and ΔS_w^\ddagger) exhibit a minimum in the water rich solutions at about 0.8 water mole fraction. The depth of this minimum relative to pure water amounts to about 4.2 kcal mol⁻¹ in ΔH_w^\ddagger and 12.4 cal deg⁻¹ mol⁻¹ in ΔS_w^\ddagger . Similarly, it is also observed that the methanolysis reaction exhibits a minimum in the methanol rich solutions at about 0.9 methanol mole fraction. However, the depth of this minimum relative to pure methanol amounts to only about 1.6 kcal mol⁻¹ in ΔH^\ddagger and 4.5 cal deg⁻¹ mol⁻¹ in ΔS^\ddagger . These variations in the enthalpy and entropy of activation are in general agreement with the results in binary alcohol-water systems previously reported for the solvolysis of *t*-butyl chloride^{7,8,15}, benzyl chloride¹⁶ and for mono- and tri-chloroacetate ions^{9,10}. This behaviour is observed not only for activation parameters in solvolysis reactions, but also for many of the physical properties of solutes in mixed solvents¹⁷.

It is well known that the addition of a small amount of methanol to water increases the structure making power of the solution and that the extrema in ΔH^\ddagger and ΔS^\ddagger are related to the accompanying solvent reorganization attending the activation process for solvolysis in binary alcohol-water systems^{8,17}. The results in the methanol-rich solutions point to a similar situation where the addition of a small amount of water to methanol increases the degree of structuredness of the solution, although the sensitivity of the activation parameters to the solvent-structural effects seems to be lower in the alcoholysis than in the hydrolysis reaction.

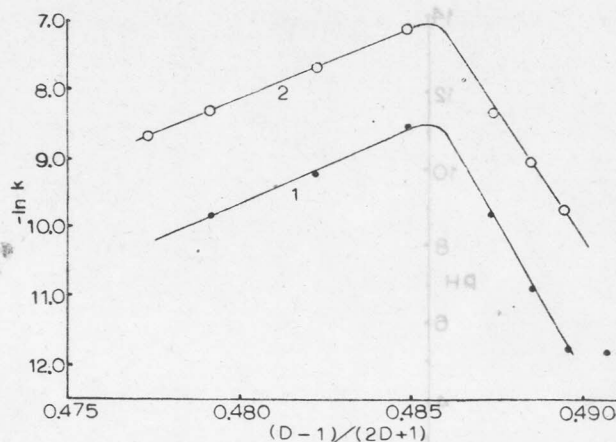


Fig. 3 — Plots of $\ln k$ versus $(D-1)/(2D+1)$ for the hydrolysis and alcoholysis of benzoyl chloride in methanol-water solutions at 25° [Curve (1) for hydrolysis; and curve (2) for methanolysis]

The results do not support any simple correlation between the dielectric constant of the medium, D , and the reaction rate constants. A linear relation between $\log k$ and $(D-1)/(2D+1)$ follows from Kirkwood's treatment of dipole solvation by assuming that the reagent molecules and the transition states can be regarded as electric dipoles immersed in a structureless medium of dielectric constant D and that all non-electrostatic interactions are unimportant¹⁸. In the present study, the transition state has a larger dipole moment than the reactant molecule and hence it is expected that the reaction should be accelerated in solvents of high dielectric constant. However, the plot of $\log k$ versus $(D-1)/(2D+1)$, shown in Fig. 3, shows that a linear relation of the type mentioned holds for media containing less than about 0.5 water mole fraction. On extrapolation of the curve to more aqueous media, a departure from such linearity appears to set in fairly suddenly. Of course, solvents are not continuous media and in the vicinity of the reacting species individual solvent molecules would undoubtedly play an important role. The predictions of the dielectric constant theory sometimes fit and sometimes fail to fit the actual behaviour of polar reaction^{19,20}. Here, it is concluded that the simple electrostatic theory is inadequate to account for the result for the whole range of solvent composition. On this basis one would conclude that over the linear portion of the curve (for media containing less than about 0.5 water mole fraction) the solvolysis reaction occurs in a structureless medium and that the dielectric theory of medium effects holds good. In the water-rich solutions, the structure of the solvent and the increased amount of hydrogen-bonded structures play a more important role.

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The kinetics of oxidation of cyanide ion by 2,8-dioxy-p-cresol (C₆H₃(OH)₂SO₃) in alkaline medium has been studied at 0°. The rate shows a first order dependence on CAT and KCN, independent of [OH⁻] in the range 0.04-0.06M, but shows an inverse fractional order at lower alkalinities (0.01-0.03M). The ionic strength effect is positive and addition of the product p-toluenesulphonamide has no influence on the rate. The activation parameters are: E_a = 54.43 kJ mol⁻¹; ΔS‡ = -43.22 JK⁻¹. The results are interpreted on the basis of a two process reaction. The alkali independent path involves interaction of chloramine-T anion and cyanide ion forming a reaction intermediate which subsequently hydrolyses in a last step to give the products. The free acid RNHCl is assumed to be the reactive species in the alkali dependent path.

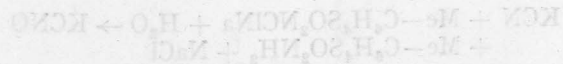
and 2,8-dioxy ion in methyl cyanide solution has been investigated by Anand²². The rate shows a first order dependence on the reactants. Oxidation of cyanide ion in aqueous alkaline solution and rate = k[CN]²[O₂]. An activation energy of 44.2 kJ/mol has been obtained²².

Materials and Methods

All solutions were prepared in triply distilled water. Analytical KCN (Hungary) was employed and its standard solution (0.05M) was standardized by the iodometric method. Chloramine-T (E. Merck) was purified by the method of Morris et al.²³ An approximately decimolar aqueous solution of the compound was prepared and standardized by the iodometric method. All other reagents were of accepted grades of purity. The ionic strength was kept constant at a high value using a constant solution of sodium perchlorate.

Requisite amounts of cyanide, NaOH, and NaClO₂ solutions and water (to keep the total volume constant for all runs) were taken in a dry boiling tube and thermostated in an ice bath maintained at 0°C. A measured amount of chloramine-T solution also cooled to 0°, was added to the mixture and the progress of the reaction followed for two half lives by iodometric estimation of CAT in a measured aliquot of the reaction mixture at various time intervals. The pseudo first order rate constants calculated were reproducible within ± 3%.

Stoichiometry—Reaction mixtures containing excess CAT over KCN were kept at room temperature (27 ± 3°) and at 0° in the presence of 0.05M NaOH for 24 hr. Estimation of the unchanged CAT showed that one mol of KCN consumed one mol of CAT (Eq. 1).



CHLORAMINE-T (CAT) (sodium N-chloro-p-toluenesulphonamide) behaves as an oxidizing agent in both acidic and alkaline media. The oxidation potential of CAT-sulphonamide system is pH dependent, and decreases with increase in pH of the medium. Although CAT has been widely used as a volumetric reagent in the determination of a variety of compounds, very few kinetic studies of these reactions are reported. The decomposition of H₂O₂ by CAT in the presence of HCl was the first reaction to be kinetically investigated by Coll and coworkers.²⁴ Recently a number of papers have appeared on the kinetics of reactions involving CAT, such as chlorination of p-cresol,²⁵ catalyzed oxidation of a hydroxy acid,²⁶ oxidation of glycerol, ketones,²⁷ aldehydes,²⁸ sugars,²⁹ alcohols,³⁰ amino acids,³¹ dimethyl sulfoxide,³² thioacetamide³³ and EDTA.³⁴ As a part of our broad programme on the kinetics of reactions involving CAT, we report in this paper the results of studies on the kinetics of oxidation of KCN by CAT in aqueous alkaline medium (0.01 to 0.06M NaOH) at 0°. The reaction was too rapid for rate measurements in neutral or acidic medium at room temperature.

The kinetics of oxidation of cyanide ion by aqueous KMnO₄ in alkaline solution has been reported by Freund.³⁵ At lower [OH⁻] the rate is first order each in MnO₄⁻ and CN⁻ ions, but a slight dependence on [OH⁻] was noticed at higher alkalinities. A detailed investigation of this reaction has been carried out by Stewart and Vander Linden.³⁶ At pH > 12 the authors³⁶ assume the operation of two parallel reactions. The first reaction is independent of [OH⁻] and depends on [MnO₄⁻] and [CN⁻] but the second reaction at higher pH is independent of [OH⁻] and rate is equal to k[MnO₄⁻][CN⁻]. [OH⁻] = k[MnO₄⁻][HCN]. Smith³⁷ reports the oxidation of CN⁻ ion by iodine in aqueous acid medium. Oxidation of cyanide ion by 2,8-dioxy-