Solvolysis Rates in Aqueous–Organic Mixed Solvents. Part 4.‡ Kinetics of the Alkaline Decarboxylation of Trichloroacetate Ion in Water–Methanol Solutions

By **El-Hussieny M. Diefallah,***† Department of Chemistry, Assiut University, Assiut, Egypt
Samir A. Ghonaim, Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia

The kinetics of the alkaline decarboxylation of trichloroacetate ion in water–methanol solutions covering the whole composition range have been studied over the temperature range 30.0—52.0 °C. The results indicate that the rate of reaction is independent of the concentration of the solvoxide ion and point to a mechanism in which the rate-determining step is formation of CCl_3^- carbanion. The rate of reaction varies with methanol concentration in the mixed solvent in a non-linear manner. The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, showed a minimum at a water : methanol mole ratio of *ca.* 3 : 2.

THE alkaline solvolysis of monochloroacetate ion in binary alcohol–water systems proceeds by a direct displacement, a one-step S_N2 mechanism. A detailed study of the alkaline solvolysis of di- and tri-chloroacetate ions in mixed solvents has not been reported. In this paper, we report the alkaline solvolysis of trichloroacetate ion in water–methanol solutions. A

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† *Present address:* Department of Chemistry, King Abdulaziz University, Jeddah, P.O. Box 1540, Saudi Arabia.

‡ Part 3, ref. 2.

comparison of the results observed here with data previously reported for monochloroacetate ion [1,2] shows that the replacement of the two hydrogen atoms attached to the α-carbon atom by chlorine atoms causes a dramatic change in reaction order and mechanism. For trichloroacetate ion it is found that the reaction follows first-order kinetics and the rate of reaction is independent of the concentration of the solvoxide ion. This suggested that the rate of reaction is determined by the breakdown of the trichloroacetate ion into CCl_3^- and CO_2. Trichloromethanide reacts further with base and ultimately yields the products.

It is well known that aqueous binary solvents significantly alter activation parameters and in many solvolysis reactions in alcohol–water mixtures, an extremum in the activation parameters towards the pure water end of the composition scale has been observed.[1-9] This behaviour is also exhibited by other physical properties related to solvent structure, such as solubility,[10,11] viscosity,[12] equivalent conductance,[12] apparent acidity function,[13] and heats of solution [14,15] in aqueous alcohols. The variation in the activation parameters has been discussed in terms of the change in polarity of the substrate in the activation process and more recently in terms of the effect that the addition of cosolvent has on the structure of water.[8,15]

EXPERIMENTAL

VEB Laborchemie Apolda pure trichloroacetic acid and pure sodium hydroxide, carbonate free, were used without further purification. C.P. grade methanol was purified according to recommended procedures.[16]

The rate of reaction was followed by comparison of chloride ion liberated with base used up in the reaction. The results of both methods were in agreement, but the Volhard method is adequate to follow the rate of reaction and gave rise to reproducible data. The initial concentrations of the chloroacid were in the range 0.100—0.050M, while the initial concentrations of the base were in the range 0.80—0.40M.

The products of the alkaline solvolysis of sodium trichloroacetate were identified as salts of hydrochloric, formic, and carbonic acids. The reaction products in completely solvolysed samples were analysed by conventional methods. Chloride was determined by the Volhard method, carbonate gravimetrically by precipitation as barium carbonate in NH_4Cl–NH_4OH buffer, and formate by titration with standardized potassium permanganate solution.

RESULTS AND DISCUSSION

The rate of reaction in a series of water–methanol solutions covering the whole range of solvent composition was found to follow a first-order rate law, being first order in the trichloroacetate ion but independent of the solvoxide ion. Figure 1 shows typical first-order plots in the water–methanol solutions obtained at 30.0 °C.

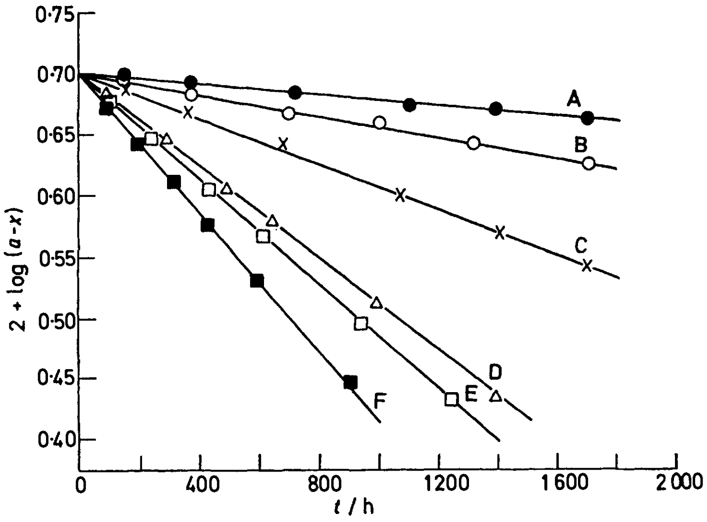

FIGURE 1 First-order plots at 30.0 °C in water–methanol solutions. Mole fraction water: A, 1.00; B, 0.87; C, 0.69; D, 0.00 E, 0.49; F, 0.28.

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[1] Ahmed M. Azzam and El-Hussieny M. Diefallah, *Z. Phys. Chem.* (*Frankfurt*), 1974, **91**, 44.

[2] El-Hussieny M. Diefallah, *Canad. J. Chem.*, 1976, **54**, 1687.

[3] E. Tommila and M. Murto, *Acta Chem. Scand.*, 1963, **17**, 1947, 1957, 1985.

[4] J. B. Hyne and R. Wills, *J. Amer. Chem. Soc.*, 1963, **85**, 3650.

[5] J. B. Hyne, R. Wills, and R. E. Wonkka, *J. Amer. Chem. Soc.*, 1962, **84**, 2914.

[6] J. B. Martin and R. E. Robertson, *J. Amer. Chem. Soc.*, 1966, **88**, 5353.

[7] H. S. Golinkin and J. B. Hyne, *Canad. J. Chem.*, 1968, **46**, 125.

[8] R. E. Robertson and S. E. Sugamori, *J. Amer. Chem. Soc.*, 1969, **91**, 7254.

[9] R. E. Robertson and S. E. Sugamori, *Canad. J. Chem.*, 1972, **50**, 1353.

[10] A. Ben-Naim and S. Baer, *Trans. Faraday Soc.*, 1964, **60**, 1736.

[11] R. W. Cargill and T. J. Morrison, *J.C.S. Faraday I*, 1975, 618.

[12] N. G. Foster and E. S. Amis, *Z. Phys. Chem.*, 1956, **7**, 360.

[13] E. M. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1976.

[14] G. L. Bertrand, F. J. Millero, C. Wu, and L. S. Hepler, *J. Phys. Chem.*, 1966, **70**, 699.

[15] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 1541.

[16] A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 1974, 3rd edn., p. 163.

The rate constants were evaluated from the slopes of the straight lines of such plots and the data obtained in the different temperatures are listed in Table 1. The rate constants are the average of at least four determinations. It can be seen that the rate of the decarboxylation reaction is relatively slow in pure water, increases by increasing the amount of methanol in solution and passes through a maximum for a water mole fraction of 0—0.3.

TABLE 1

Effect of temperature and solvent composition on the rate constants in the alkaline solvolysis of sodium trichloroacetate in methanol–water solutions

Methanol (wt. %)	Water (mole fraction)	$10^8k/s^{-1}$ 30.0 °C	40.5 °C	52.0 °C
0	1.00	1.34 ± 0.05	9.92 ± 0.2	76.4 ± 2
20.9	0.87	2.76 ± 0.06	16.8 ± 0.5	106 ± 2
44.3	0.69	5.76 ± 0.06	32.6 ± 0.5	192 ± 4
64.9	0.49	13.0 ± 0.2	73.6 ± 2	432 ± 6
81.8	0.28	17.6 ± 1	108.8 ± 2	699 ±15
100	0.0	11.5 ± 1	103.6 ± 3	976 ± 20

From a knowledge of the temperature coefficient of the rate constants, the activation parameters, $\Delta H^‡$ and $\Delta S^‡$, were calculated and the results are shown in Table 2.

TABLE 2

Activation parameters in the alkaline solvolysis of sodium trichloroacetate in methanol–water solutions at 30.0 °C

Water (mole fraction)	E_a/ kJ mol^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	$\Delta G^‡$/ kJ mol^{-1}
1.00	150.6 ± 1.4	148.2 ± 1.4	92.5 ± 5	120.1 ± 2.9
0.87	136.0 ± 1.8	133.5 ± 1.8	50.6 ± 6	118.0 ± 3.6
0.69	130.5 ± 0.9	128.0 ± 0.9	38.9 ± 3	116.3 ± 1.8
0.49	130.5 ± 1.6	128.0 ± 1.6	45.6 ± 5	114.2 ± 3.2
0.28	137.2 ± 3	134.7 ± 3	69.9 ± 10	113.4 ± 6
0.0	165.7 ± 5	163.2 ± 5	160.4 ± 16	114.6 ± 10

The average errors in the activation energies and enthalpies are *ca.* 1—3%. The listed errors in $\Delta S^‡$ and $\Delta G^‡$ are the maximum expected using average errors in $\Delta H^‡$ and the rate constant data at 30.0 °C. The most irreproducible data were obtained in pure methanol. The plot of $\Delta H^‡$ and $\Delta S^‡$ *versus* water mole fraction in the solvent mixtures (Figure 2) shows that these activation parameters pass through a minimum at a water : alcohol mole ratio of *ca.* 3 : 2. For many solvolysis reactions in aqueous–organic binary mixtures, the activation parameters showed an extremum towards the pure water end of the composition scale.[1-9] The calculated entropies of activation (listed in Table 2) are positive over the whole solvent composition range. It is shown below that the rate-limiting step in the reaction involves the release of CO_2 and the formation of a carbanion intermediate, there is a decrease in electrostriction when the activated complex is formed, the extent of activation is reduced, and there is a corresponding positive entropy of activation.

Since the rate of reaction was found to be independent of the hydroxide ion concentration, this points to a mechanism in which the rate-determining step is the breaking of the carbon–carbon bond, the release of carbon dioxide, and the formation of trichloromethanide as intermediate. The presence of three chlorine atoms on a carbon atom adjacent to a carbonyl group causes the C–C bond to break very easily.[17] The CCl_3^- intermediate in turn eliminates chloride ion to yield dichloromethylene which in turn reacts with base and ultimately yields chloride and formate ions. In fact, it is believed that CCl_3^- and CCl_2 intermediates are produced in the alkaline hydrolysis of chloroform;[18] there is no reason not to believe that the same intermediates are formed in the decomposition of trichloroacetic acid by base.[19] Our kinetic results and other evidence cited in the literature[17-19] are in agreement with the mechanism in the

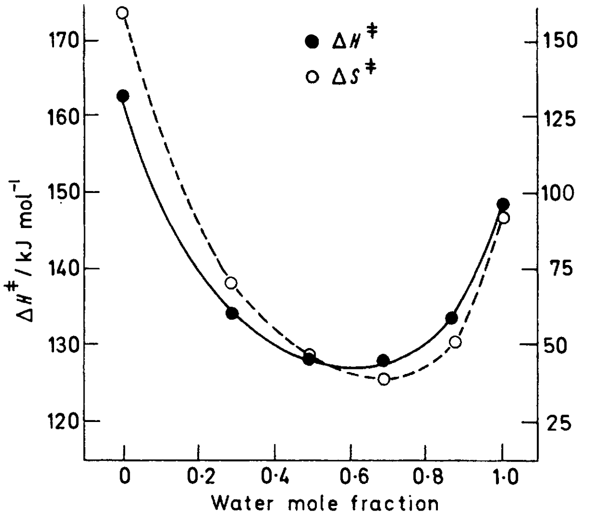

FIGURE 2 Dependence of $\Delta H^‡$ and $\Delta S^‡$ on solvent composition at 30.0 °C

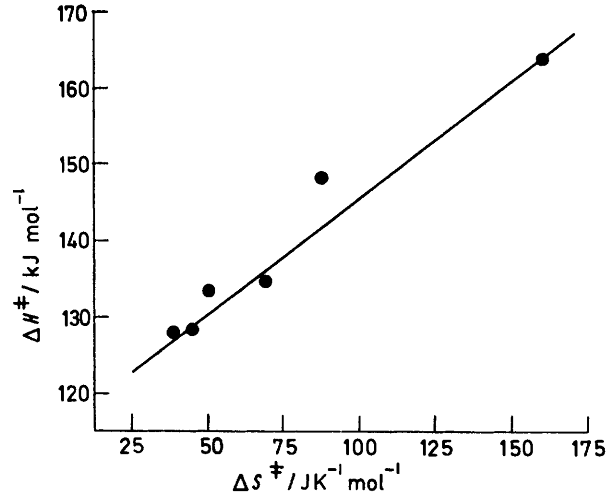

FIGURE 3 Plot of $\Delta H^‡$ *versus* $\Delta S^‡$

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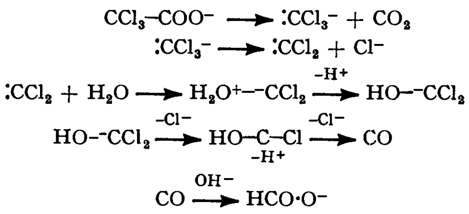
[17] I. L. Finar, ' Organic Chemistry,' Longman, London, 1973, vol 1, 6th edn., p. 240.

[18] W. J. Le Noble and M. Duffy, *J. Amer. Chem. Soc.*, 1964, **86**, 4512; J. Hine and A. M. Dowell, jun., *ibid.*, 1954, **76**, 2688.

[19] H. Höver, ' Problems in Organic Reaction Mechanisms,' Wiley, New York, 1970, p. 137; F. H. Verhoek, *J. Amer. Chem. Soc.*, 1934, **56**, 571.

Scheme where the first step is the rate-determining step and the $:CCl_3^-$ intermediate is stabilized by *d* orbital resonance.[17]



$$CCl_3{-}COO^- \longrightarrow :CCl_3^- + CO_2$$
$$:CCl_3^- \longrightarrow :CCl_2 + Cl^-$$
$$:CCl_2 + H_2O \longrightarrow H_2O^+{-}{-}CCl_2 \xrightarrow{-H^+} HO{-}{-}CCl_2$$
$$HO{-}{-}CCl_2 \xrightarrow{-Cl^-} HO{-}\underset{-H^+}{C}{-}Cl \xrightarrow{-Cl^-} CO$$
$$CO \xrightarrow{OH^-} HCO{\cdot}O^-$$

SCHEME

The pattern of change in $\Delta H^‡$ and $\Delta S^‡$ with change in water mole fraction (Figure 2) is similar to the pattern found for the solvolysis of monochloroacetate ion,[1,2] benzyl chloride,[7] and t-butyl chloride [8,9] in water–alcohol mixtures. Such extrema are thought to reflect corresponding structural changes in binary mixtures.[15] The changes in structural features in the solvent zones surrounding the reactants in their transition state as well as structural effects in the transition state are specifically influential in controlling the magnitude of $\Delta H^‡$ and $\Delta S^‡$ for the overall process. The observed extrema in the activation parameters in the high water mole fraction region of the solvent mixture suggest that structure breaking of the solution in the activation process parallels the sensitivity to changes in the solvent composition.[8,15] Furthermore, the minimum in this case may possibly point to a critical solvent structure or a molecular complex between methanol and water with the general formula $[(CH_3OH)_2(H_2O)_3]_n$, where the value of n is expected to be temperature dependent.

The free energy of activation, $\Delta G^‡$, shows, within experimental errors, little changes with solvent composition and a plot of $\Delta S^‡$ against $\Delta H^‡$ (Figure 3) is approximately a straight line. This compensation effect is frequently the case for a given reaction investigated in a series of solvents and is possible because there is a general tendency in solution for enthalpy and entropy to compensate each other, so that the changes in free energy are much smaller.[20]

[6/478 *Received*, 10*th March*, 1976]

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[20] K. J. Laidler, ' Chemical Kinetics,' McGraw-Hill, New York, 1965, 2nd edn., ch. 5.