[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# The Kinetics of the Decomposition of Trichloroacetic Acid in Formamide–Water Mixtures

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Studies of the decomposition of trichloroacetic acid[1] and of trinitrobenzoic acid[2] in dioxane–water mixtures show that the rates of these decompositions pass through maxima as the proportion of dioxane in the water is increased. In the case of trinitrobenzoic acid the maximum was explained as the result of two opposing effects, based on the assumptions that the decomposing substance in the solution is the acid anion and that it is less stable the less highly it is solvated. One effect, tending to decrease the apparent rate of decomposition, results from the decreased dissociation of the acid into ions in solvents of high dioxane content; the other effect, tending to increase the rate of decomposition, results from the progressive desolvation of the ion as the dioxane content of the solvent is increased. This point of view was confirmed by measurements of the acid dissociation constants in the various solvent mixtures and calculation of the ion concentrations; when the rates were referred to the actually existing ion concentrations, the maximum disappeared and a continuous increase in rate constant with increasing dioxane concentration was observed. Existing data do not permit of such a treatment for the trichloroacetic acid case, but from the parallelism between the behavior of the two acids observed in other cases,[3] it seems likely that the maximum may be explained in a similar fashion.

It is then of interest to investigate the decomposition of one of the acids in a solvent pair in which the dissociation constant of the acid does not change appreciably with change in the composition of the solvent; in this case the whole change in rate must be due to changes in the degree of solvation. A mixture of water and formamide, with dielectric constants of the same magnitude[4] form such a pair. Trichloroacetic acid was chosen for study, since its dissociation constant has been estimated in both water[5] and formamide.[6]

The rate of decomposition of trichloroacetic acid cannot be measured conveniently in formamide–water mixtures by titrating with standard base the acid left undecomposed because hydrolysis of the formamide forms ammonium formate. The amount of ammonium formate produced is of no consequence as far as the composition of the solvent is concerned, its concentration amounting to only 0.25 molar after ten hours at 100° for a 50 mole per cent. formamide–water mixture, but it so buffers the solution that the titrations are unreliable. Accordingly, the reaction was followed by analyzing for trichloroacetic acid through its trichloromethyl group, adapting the colorimetric method devised by Cole[7] for chloroform analysis.

Fifteen milliliter samples of solutions approximately 0.1 molar in trichloroacetic acid in an appropriate solvent mixture were pipetted into twelve individual reaction flasks equipped with an external ground joint to provide an air lock between the thermostat oil and the actual closure on the flask.[8] Six of these were sunk into each of two oil-baths thermostatically controlled at 50 and 60°, or 60 and 70°. Auxiliary heaters were used to compensate quickly for the slight drop in temperature which occurred on immersion of the samples. The first sample was removed after eight to fifteen minutes, and others at suitable intervals thereafter. The samples were cooled in an ice-bath and diluted by a factor of one hundred with distilled water. Air was bubbled for four minutes through a 10-ml. aliquot of this solution to remove chloroform, tests on saturated chloroform solutions having shown no colorimetric test for the latter after sweeping out the solution for this length of time.

A 2-ml. sample of the chloroform-free solution was pipetted into a Pyrex test-tube, and 4 ml. of 20% sodium hydroxide and 2 ml. of pyridine, purified by refluxing over and distilling from barium oxide, added. The test-tube was fitted with a rubber stopper and expansion tube, shaken for two minutes, and immersed in vigorously boiling water at the instant a timer was started. After shaking for sixty seconds in the water, the test tube was removed to a water-bath maintained at 17 ± 1° and shaken until the timer read ninety seconds. At one hundred seconds 10 ml. of alcohol was added and the contents shaken until only one phase was present. At two hundred seconds the solution was poured into the rectangular absorption cell of a Cenco Photelometer, Industrial Model B2, and a reading of the percentage absorption taken at exactly four minutes through a green filter with a maximum transmission at 5300 Å. A calibration curve was prepared according to the same procedure using solutions of trichloroacetic acid in water whose concentrations were known from titration and dilution data. Strict adherence to a time schedule is desirable, since the red color fades on standing. The reproducibility of the technique used is attested by the fact that the average deviation of the points on the calibration curve from the curve itself is 0.94%, for the twelve points taken over the extinction range 0.12 to 0.46 (0.0002 to 0.001 *m*).

Formamide was purified by the chemical and distillation treatment of Verhoek,[6] omitting the fractional crystallizations. The material used boiled at 80–82° at 5 mm. pressure and had a freezing point of 2.3°. Solvent mixtures were made up by adding measured volumes of distilled water to weighed amounts of formamide.

The decomposition products in formamide were shown to be the same as in water by a qualitative test for chloroform from a heated solution of trichloroacetic acid in formamide, and by collecting the gas from the decomposition of a weighed amount of dissolved trichloroacetic acid; 95% of the theoretical amount of carbon dioxide was obtained.

The rate of decomposition was measured at 60° over the range of solvent composition from 0 to 90% formamide, and at 50 and 70° over portions of the range in order to estimate the activation energies. The reaction was first order throughout, as shown in representative experiments in Table I.

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[1] Salmi and Korte, *Ann. Acad. Sci. Fennicae*, **A54**, No. 10 (1940).

[2] Trivich and Verhoek, THIS JOURNAL, **65**, 1919 (1943).

[3] Verhoek, *ibid.*, **61**, 186 (1939); **67**, 1062 (1945).

[4] "International Critical Tables," Vol. VI, p. 83.

[5] Hall, *Chem. Rev.*, **8**, 191 (1931).

[6] Verhoek, THIS JOURNAL, **58**, 2577 (1936).

[7] Cole, *J. Biol. Chem.*, **71**, 173 (1926).

[8] Trivich, Ph.D. Thesis, the Ohio State University, 1942.

TABLE I

TEST OF THE FIRST-ORDER RATE LAW

| Time, min. | 60 mole per cent. formamide at 70° Concn. m./liter | $-\frac{\Delta \log C}{\Delta t}$ | Time, min. | 75 mole per cent. formamide at 50° Concn. m./liter | $-\frac{\Delta \log C}{\Delta t}$ |
|---|---|---|---|---|---|
| 10 | 0.0740 | 0.0119 | 15 | 0.0845 | 0.00114 |
| 25 | .0490 | .0123 | 145 | .0600 | .00108 |
| 40 | .0320 | .0120 | 275 | .0435 | .00108 |
| 57 | .0200 | .0119 | 405 | .0315 | .00112 |
| 70 | .0140 | .0128 | 535 | .0225 | .00111 |
| 85 | .0090 | | 693 | .0150 | |

First-order rate constants obtained from graphs of log concentration against time are recorded in Table II, together with calculated activation energies, and a graph of log $k$ against solvent composition is given in Fig. 1.

TABLE II

VARIATION OF THE VELOCITY CONSTANT AND ACTIVATION ENERGY WITH SOLVENT COMPOSITION

| Mole per cent. formamide | Initial concn. (m./liter) | Velocity constants (sec.$^{-1}\times10^5$) 50° | 60° | 70° | Activation energy kcal./mole 50-60 | 60-70 |
|---|---|---|---|---|---|---|
| 0 | | | 0.348[a] | 1.713[a] | | 36.2[a] |
| 20 | 0.0886 | | 1.40 | | | 35.2 |
| 20 | .0935 | | | 6.58 | | |
| 40 | .1000 | 0.992 | | | 33.6 | |
| 40 | .1050 | | 4.77 | | | 34.6 |
| 40 | .1050 | | | 21.9 | | |
| 60 | .1003 | 2.29 | | | 33.2 | |
| 60 | .0882 | | 10.8 | | | 33.1 |
| 60 | .0882 | | | 46.4 | | |
| 75 | .0905 | 4.25 | 19.1 | | 32.1 | |
| 85 | .0923 | 5.82 | 26.5 | | 32.4 | |
| 90 | .0878 | 6.86 | 29.4 | | 31.1 | |

[a] Data of Verhoek, THIS JOURNAL, 56, 571 (1934), for sodium trichloroacetate.

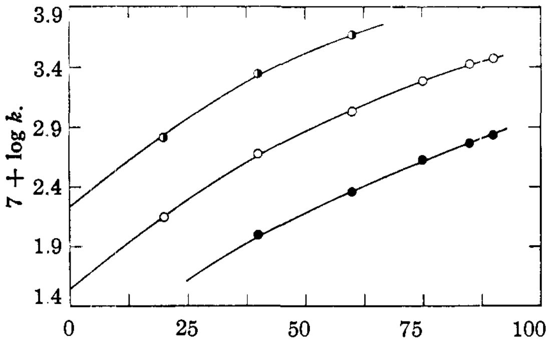

Fig. 1.—Variation with solvent composition of the velocity constant for the decomposition of trichloroacetic acid in formamide–water mixtures: ●, 50°; ○ 60°; ◑, 70°.

It is evident from Fig. 1 that there is no evidence for a maximum similar to that found by Salmi and Korte[1] for the decomposition in dioxane–water mixtures, confirming the hypothesis that the maximum they found is due to the changing dissociation of the acid as the composition of the solvent is changed. This explanation of their data was apparently missed by these authors.[1,9]

According to the recorded values of the dissociation constants,[5,6] trichloroacetic acid at room temperature is slightly less dissociated in formamide than in water. If these $pK$ values are used, with straight line interpolation between the two extremes, and the data of Table II recalculated to give velocity constants for the decomposition of the trichloroacetate ion, curves for log $k_{\text{ion}}$ *vs.* solvent composition give lines more nearly straight than those shown in Fig. 1. The change is not great, however, since the calculated $k_{\text{ion}}$ is only twice the observed velocity constant even at 90 mole per cent. formamide.

Comparison of the data with those for trinitrobenzoate ion in water–dioxane mixtures[2] indicates that, even over the smaller range of solvent composition investigated in that case, the increase in velocity constant and the decrease in activation energy are much greater than in the present case. This difference is to be attributed to the greater solvation of the decomposing ion by formamide as compared to dioxane—or at least to the greater difference between the solvation of the ion and that of the activated complex, for formamide as compared to dioxane. Comparison with the data for the decomposition of trichloroacetate ion in water–alcohol mixtures[10] shows that the change in activation energy is about the same in the two cases. If the change in the rate of decomposition is due mainly to changes in the solvation energy, this would indicate that the difference in solvation energy between water and alcohol, and water and formamide, is the same. For each of the three solvent pairs, the decrease in activation energy is accompanied by a decrease in the factor $C$ in the equation $\log k = -E/2.3RT + C$; further, the decrease in $C$ is nearly the same in the three cases, when the comparison is made for equal changes in the activation energies.

## Summary

1. The decomposition of trichloroacetic acid is first order in water–formamide mixtures up to 90 mole per cent. formamide.

2. The velocity constant increases uniformly with increasing formamide content, with no evidence for a maximum over the range studied.

3. The activation energy decreases uniformly with increasing formamide content.

4. The change in rate and activation energy is attributed to a decrease in the extent of solvation of the trichloroacetate ion as the water content of the solvent decreases.

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[9] Salmi and Korte, *Suomen Kemistilehti*, **18B**, 28 (1945).

[10] Hall and Verhoek, THIS JOURNAL, **69**, 613 (1947).