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The Effect of Pressure on the Rate of Hydrolysis of Chloroform. The Nature of the Transition State

Sir:

The dissociation of CCl_3^- to chloride ion and dichlorocarbene is commonly assumed to be the rate-controlling step in the basic hydrolysis of chloroform.¹ The possibility that the chloride ion might be displaced by water has been mentioned by Hine²; on the basis of kinetic arguments this path was held to be an unlikely one, although it could not be ruled out. More recently, a study of the base-promoted methanolysis of chloroform³ showed k_2 to be proportional to h^- . However, the use of acidity functions in assessing the role of solvent molecules is at best highly uncertain, and it remains therefore an open question whether the solvent is to any degree involved in the formation of the intermediate.

Whalley, *et al.*,⁴ and the present authors⁵ have found knowledge of ΔV^\ddagger to be helpful in solving similar problems involving acid catalysis. It therefore appeared to us that a measurement of the pressure coefficient of the rate constant in the hydrolysis of chloroform would reveal to what extent water is involved in the rate-determining step in that reaction. As before, any such participation is expected to lead to a negative activation volume, whereas simple dissociation would be characterized by a volume expansion. The data, essentially obtained by techniques described earlier,⁶ are shown in Table I.

(1) J. Hine, "Divalent Carbon," The Ronald Press Company, New York, N. Y., 1964, pp. 36-42.

(2) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

(3) R. A. M. O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5035 (1963).

(4) For several references, see E. Whalley, "Advances in Physical Organic Chemistry," Vol. 2, V. Gold, Ed., Academic Press, Inc., New York, N. Y., 1964.

(5) W. le Noble and M. Duffy, *J. Phys. Chem.*, **68**, 619 (1964).

(6) W. le Noble, *J. Am. Chem. Soc.*, **85**, 1470 (1963).

TABLE I

THE EFFECT OF PRESSURE ON THE RATE OF BASIC HYDROLYSIS OF CHLOROFORM AT 25° IN WATER CONTAINING 3% METHANOL

Pressure, kbar	$k_2 \times 10^5$, l/mole sec.	Number of observations ^a
0.00	7.39	5
1.07	3.53	4
2.13	2.15	4
3.17	1.62	4
4.21	1.08	4
5.24	0.66	4
6.45	0.70	4

^a The reaction was followed to about 70% completion; the rate constants were reproducible to about 5%. The base concentration was about 1; the chloroform concentration was below the saturation point by a factor of 10.

A plot of $\ln k_2$ vs. p yields a ΔV_0^\ddagger of +16 cm.³/mole, by far the largest positive activation volume reported to date for a reaction in water.⁷ This may be considered conclusive evidence that no water becomes bound in the transition state; the magnitude of the effect strongly suggests, in fact, that water electrostatically bound by the CCl_3^- ion is being released during the reaction and that the transition state goes on to free CCl_2 . We are currently investigating other reactions assumed to go through carbene intermediates, and hope to report those results as well as some of the experimental details later.

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(7) This value is even more remarkable when it is remembered that ΔV^\ddagger tends to be smaller in highly polar solvents: K. R. Brower, *ibid.*, **85**, 1401 (1963).

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