the ratio (CR)/(C) + (CR)—this is also the fraction of light quanta absorbed by the complex.

By further assuming that the yield of fluorescence of the "640 mμ-intermediate" is approximately the same as that of unreduced chlorophyll, an estimate can be made of the fraction of chlorophyll in the complexed state. This estimate is made by comparing the relative intensities of the fluorescence bands at 640 and 675 mμ, the result being 3% for the concentration of chlorophyll in the complexed state. This is in good agreement with the measured value[13] for the initial yield of photoreduction of chlorophyll by excess ascorbate in aqueous pyridine.

Acknowledgments.—The author wishes to express his appreciation to Dr. T. Bannister and Dr. E. Rabinowitch for several stimulating discussions on the photochemistry of chlorophyll, to Dr. M. Brody for her numerous suggestions which aided the course of this work, to Mr. Krishnan Kumar for his competent assistance in carrying out these experiments and to the members of the Photosynthesis Laboratory of the University of Illinois for their coöperation and interest.

BEDFORD, MASSACHUSETTS

[CONTRIBUTION FROM THE APPLIED CHEMISTRY DEPARTMENT, UNIVERSITY OF KERALA]

Catalyzed Hydrolysis of Benzyl Chloride

BY SARAH KOSHY AND R. ANANTARAMAN

RECEIVED JANUARY 7, 1959

The hydrolysis of benzyl chloride in aqueous acetone with and without mercuric chloride has been examined kinetically under various conditions and the results are discussed. The mercuric chloride-catalyzed reaction has been found to be approximately first order with respect to benzyl chloride and mercuric chloride. A complicating factor, the formation of a complex between mercuric chloride and benzyl chloride, has been noted.

The study of electrophilic catalysis in nucleophilic aliphatic substitution has hitherto been mainly on substances which substitute by the SN1 mechanism.[1,2] Although Hammett and his associates have examined the substitution reactions of some alkyl halides which undergo the normal reaction chiefly by the SN2 mechanism, the reactions in presence of the powerful catalysts they employed (various ionic species derived from mercuric salts) were purely SN1.[3] We have, therefore, decided to examine the hydrolysis of benzyl chloride, which is on the SN2–SN1 border line,[4] in the presence of catalyst mercuric chloride which is relatively weak, since it acts in its un-ionized form.[2]

Results and Discussion

Table I contains the first order rate constants for the normal and mercuric chloride-catalyzed hydrolysis of benzyl chloride, under various conditions. In Table II are given the energies and entropies of activation.

Although the rate constant for hydrolysis in the absence of mercuric chloride is not sensitive to reasonable variations in the benzyl chloride concentration, the rate of the catalyzed reaction decreases slightly with increase in the benzyl chloride concentration, particularly in the more aqueous solvents. This is, however, due, as shown later, to the special circumstance of complex formation between benzyl chloride and mercuric chloride and so it is concluded that the catalyzed reaction is approximately first order with respect to benzyl chloride. The rate of the catalyzed reaction varies linearly with the catalyst concentration in all solvents, over the concentration of catalyst examined. Further, the slopes of the lines do not vary much with the solvent, the respective values being 1.18, 1.00, 1.00, 1.02 and 1.20 10^{-4} l.mole/sec. for 45, 50, 60, 70 and 80% acetone. However, the lines so obtained do not pass through the origin but cut the rate-axis below the origin.[5] This is illustrated in Fig. 1 for 45 and 80% acetone. So, at low catalyst concentrations the linear relationship apparently no longer holds. It is concluded that the catalyzed reaction is strictly first order with respect to mercuric chloride only when the catalyst concentration is not too low.

The catalysed hydrolysis is complicated by the formation of an intermediate complex between benzyl chloride and mercuric chloride, so that the reaction path *via* the complex can be formulated as

$$PhCH_2Cl + HgCl_2 \xrightarrow{K} PhCH_2Cl\cdot HgCl_2 \xrightarrow[H_2O]{k} PhCH_2OH + HgCl_3^- + H^+$$

Complex formation is observed in the solvent range 45–80% acetone, though not in 90% acetone. This is shown by the formation of a yellow color and a turbidity on dissolving the two in the solvent. (However, no heterogeneity is involved in the reaction, since the turbidity vanishes at the reaction temperature.) The complex dissolves on adding more benzyl chloride. Though the complex was isolated, an accurate analysis was not possible because of its instability. The results show, however, that it is probably a 1:1 complex. The intensity of color and turbidity decrease as the solvent becomes drier and vanishes in 90% acetone. Addition of

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(1) E. D. Hughes, C. K. Ingold and co-workers, *J. Chem. Soc.*, 1236, 1243 (1937); 169 (1946); K. Bodendorf and H. Böhme, *Ann.*, **516**, 1 (1935).

(2) C. A. Bunton, E. D. Hughes and R. Anantaraman, unpublished work; see, however, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 359–360.

(3) (a) I. Roberts and L. P. Hammett, THIS JOURNAL, **59**, 1063 (1937); (b) O. T. Benfey, *ibid.*, **70**, 2165 (1948).

(4) S. C. J. Olivier and A. P. Weber, *Rec. trav. chim.*, **53**, 869 (1934); S. C. J. Olivier, *ibid.*, **53**, 891 (1934).

(5) This was kindly pointed out by one of the referees.

TABLE I

KINETICS OF THE HYDROLYSIS OF BENZYL CHLORIDE

(a) Normal hydrolysis—RCl (0.05 *M*)

Acetone %[a]	$10^5 k_1$ (sec.$^{-1}$)				
	55.15°	61.80°	71.50°	76.80°	82.25°
45	0.810	...	...	...	..
50	.490	0.916	2.18	...	5.38
60	.220	.413	1.08	...	2.48
70	...	.151	0.367	0.582	0.930
80	...	...	...	...	0.265

$10^5 k_1$ (sec.$^{-1}$) in 90% acetone at 90.0° was 0.0617

(b) Catalyzed hydrolysis—RCl (0.05 *M*), $HgCl_2$ (0.300 *M*)[b]

45	3.54	...	...	...	..
50	2.66	5.00	12.2	...	30.6
60	1.27	2.39	5.67	...	14.2
70	...	1.19	2.78	4.37	6.77
80	...	...	...	...	3.42

$10^5 k_1$ (sec.$^{-1}$) in 90% acetone at 90.0° was 3.17

(c) Catalyzed hydrolysis—relation between rate of hydrolysis and concentration of catalyst RCl (0.05 *M*)[b]

$HgCl_2$ (*M*)	$10^5 k_1$ (sec.$^{-1}$) 45% acetone (55.15°)	50% acetone (55.15°)	60% acetone (61.80°)	70% acetone (71.50°)	80% acetone (82.25°)
0.150	1.67	1.18	0.90	1.25	1.62
.200	2.29	1.68	1.40	1.75	2.22
.250	2.91	2.18	1.89	2.27	2.84
.350	4.16	3.16	2.88	3.32	4.04

(d) Catalyzed hydrolysis—relation between rate of hydrolysis and concentration of benzyl chloride $HgCl_2$ (0.300 *M*)[b]

Acetone, %	Temp., °C.	$10^5 k_1$ (sec.$^{-1}$) RCl (0.05 *M*)	RCl (0.10 *M*)
50	55.15	2.66	2.43
60	61.80	2.39	2.25
70	71.50	2.78	2.72
80	82.25	3.42	3.40

(e) Catalyzed hydrolysis—effect of adding chloride ions on the rate of hydrolysis $HgCl_2$ (0.300 *M*)[b]

RCl (*M*)	Cl^- (*M*)	$10^5 k_1$ (sec.$^{-1}$) 45% acetone (55.15°)	50% acetone (55.15°)	60% acetone (61.80°)	70% acetone (71.50°)	80% acetone (82.25°)
0.05	0.100	3.32	2.41	2.05	2.33	2.87
.05	.150	3.17	2.23	1.87	2.10	2.57
.05	.200	2.97	2.04	1.69	1.83	2.24
.10	.100	..	2.34	..	2.45	..
.10	.150	..	..	1.92	..	..

[a] Percentage acetone signifies solvent made up of x volumes of dry acetone and $(100 - x)$ volumes of water.

[b] The rates given for the catalyzed hydrolysis are the difference between the total rate in presence of catalyst and the rate of the normal hydrolysis.

TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION

Solvent	ΔH^* (kcal./mole) (82.25°)	ΔS^* (e.u.) (82.25°)
(a) Normal hydrolysis		
50% Acetone	19.79	−22.5
60% Acetone	20.12	−23.1
70% Acetone	20.40	−24.3
(b) Catalyzed hydrolysis (catalyst, 0.3 *M*)		
50% Acetone	20.25	−17.8
60% Acetone	19.91	−20.2
70% Acetone	19.41	−23.1

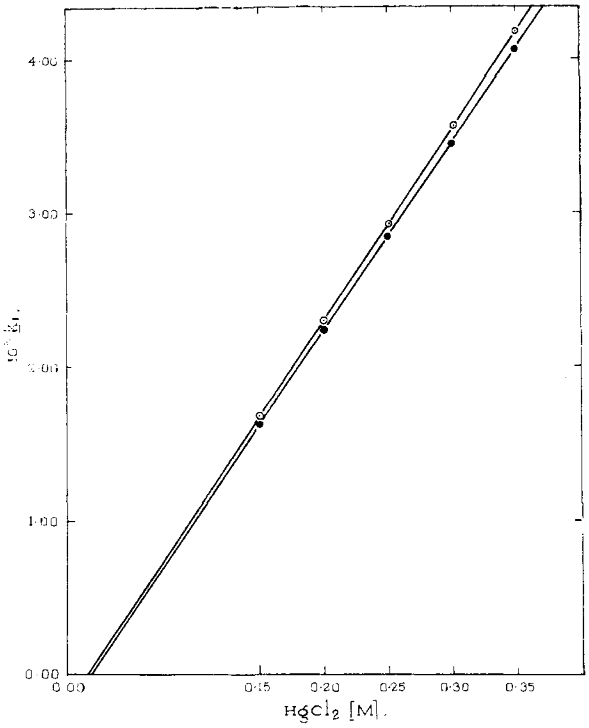

Fig. 1.—Relation between rate of hydrolysis and mercuric chloride concentration: —⊙—, 45% acetone (55.15°); —●—, 80% acetone (82.25°).

chloride ions also causes such a decrease in intensity. This is taken to mean that chloride ions and benzyl chloride compete for the mercuric chloride. It has been shown that in the solvent range, and mercuric chloride and added chloride ion concentrations used here, the reduction in the rate of the catalyzed reaction on the addition of chloride ions can be calculated to a good approximation by assuming that the catalyst is inactivated thus[2]: $HgCl_2 + 2Cl^- \rightarrow HgCl_4^{=}$. In the present case, the calculated reduction is greater than that observed in the more aqueous solvents, and this difference decreases gradually as the solvent becomes less aqueous and becomes small in 80% acetone. Also, the reduction caused by a fixed quantity of chloride ions (catalyst concentration being constant) is reduced by an increase in the benzyl chloride concentration. This effect also decreases

TABLE III

EFFECT OF ADDED CHLORIDE IONS ON THE RATE OF CATALYZED HYDROLYSIS[a]

RCl, *M*	Cl^-, *M*	Temp., °C.	Solvent, % acetone	% Reduction in rate Found	Calcd.[b]
0.05	0.100	55.15	50	9.4	16.7
.05	.150	55.15	50	16.3	25.0
.05	.200	55.15	50	23.2	33.3
.10	.100	55.15	50	3.7	16.7
.05	.100	71.50	70	15.2	16.7
.05	.150	71.50	70	23.6	25.0
.05	.200	71.50	70	23.3	33.3
.10	.100	71.50	70	9.6	16.7

[a] Catalyst concn. 0.300 *M* throughout. [b] Calculated, assuming that the catalyst is inactivated according to $HgCl_2 + 2Cl^- \rightarrow HgCl_4^{=}$.

as the solvent becomes drier. These points are illustrated in Tables I and III.

These observations are consistent with the assumption of complex formation between mercuric chloride and benzyl chloride. Further, it is also clear that the extent of complex formation decreases with decrease in the water content of the solvent.

Spectrophotometric studies show that the equilibrium concentration of the complex is small and this fact together with what has been said about the effect of added chloride ions indicates that the complex plays an important part in the hydrolytic process particularly in the more aqueous solvents. This, however, does not exclude the possibility of a parallel path without involving the complex.

With regard to the identity of the catalytic agent, the evidence points to the un-ionized mercuric chloride molecule rather than to any of its ionized forms. First, since mercuric chloride ionizes only slightly even in water,[6] the extent of ionization in the solvents of fairly low dielectric constant used here is likely to be too small to account for the catalysis. Further, addition of the rather high concentrations of chloride ions employed here will certainly suppress the ionization and so would completely inactivate the catalyst, which is not what has been observed. If ionic catalysts are the active agents, the slopes of the rate–catalyst concentration lines should vary with the solvent. Also, this relationship in any one solvent would be different from that observed, since the concentration of ionic species will not be proportional to the formal concentration of mercuric chloride. For example, in the mercuric nitrate-catalyzed hydrolysis of benzyl chloride, it has been observed that the second order rate actually decreases with increase in the catalyst concentration.[3a]

Experimental

Materials.—Kauffman C.P. benzyl chloride was fractioned and the fraction of b.p. 89–90° (40 mm.) was collected. Acetone was purified by the method of Conant and Kirner.[7]

Kinetic Method.—The appropriate quantity of benzyl chloride was taken in a 100 ml. measuring flask. Accurately weighed quantities of mercuric chloride and other salts were quantitatively transferred to the flask with the solvent. After making up the solution to 100 ml., 5-ml. portions were pipetted out into ampoules which were sealed. The reaction was followed by titration against standard alkali with brom thymol blue indicator. When mercuric chloride was present, it was destroyed by the addition of a slight excess of potassium iodide. The rate coefficients given are the mean of duplicate runs; the duplicate values differed by less than 1.5%.

It has been observed that the auto-anticatalysis of chloride ions formed during the hydrolysis is less than that calculated in accordance with the equation $HgCl_2 + 2Cl^- \rightarrow HgCl_4^=$. This is at least partly due to the failure of this equation at low chloride ion concentrations.[8] Details of a sample run are given in Table IV, from which it can be seen that the rate remains sufficiently constant for the purpose of obtaining a value of reasonable accuracy for the initial rate. These are the rate values used in this paper.

TABLE IV

DATA FOR THE MERCURIC CHLORIDE-CATALYZED HYDROLYSIS OF BENZYL CHLORIDE IN 80% ACETONE AT 82.25°

[RCl] = 0.0495; $[HgCl_2]$ = 0.150; titers are expressed in ml. of 0.0232 *Na*NaOH per 5 ml. reaction mixture.

t (sec.)	Titer	$10^5 k_1$ (sec.$^{-1}$)
0	0.23	..
7200	1.60	1.95
10200	2.14	1.98
11400	2.31	1.95
13800	2.71	1.97
15600	3.00	1.98
16800	3.16	1.96
18000	3.38	2.00
20400	3.68	1.97
21600	3.87	1.99
33000	5.07	1.89
47400	6.24	1.80
76800	7.97	1.76
∞	10.67	..

Acknowledgment.—The authors thank the referees for valuable suggestions and criticism.

TRIVANDRUM, INDIA

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