

than 0.001 *M*, it would have been necessary to take this dimerization into account in the quantitative treatment.

Summary

The rate of hydrolysis of β, β' -dichlorodiethyl sulfide (mustard gas) and of β -chloro- β' -hydroxydiethyl sulfide (mustard chlorohydrin) in aqueous solution containing 5% of acetone at 25° has been measured at different concentrations of chloride and monothiophosphate ions and at controlled ionic strength. The rate of liberation of hydrogen ions, measured by the intermittent titration method of Peters and Walker, is identical within the experimental uncertainty with the rate of liberation of chloride ions, followed polarographically with a short-period galvanometer, a fact which shows that neither ethylenesulfonium ions nor any dimeric sulfonium ions accumulate appreciably during reaction.

The results of 17 runs on mustard chlorohydrin and 11 runs on mustard have been interpreted in some detail by means of the mechanistic scheme of eq. 1, involving a rate-determining formation of an ethylenesulfonium ion followed by competition for this ion by water, chloride ion and other competitors such as thiophosphate ion, all at rates much greater than that of the initial cyclization. The "competition factor"

of chloride ion, defined as the ratio of the rate constants for reaction of the ethylenesulfonium intermediate with chloride ion and with water, is shown to be independent of the chloride ion concentration at constant ionic strength, but to depend upon ionic strength in a manner predictable from the Brønsted rate equation and the limiting Debye-Hückel law for the activity coefficient of an ion.

By first determining the strictly unimolecular rate constant ($0.260 \pm 0.016 \text{ min.}^{-1}$) for hydrolysis or displacement of mustard chlorohydrin and then introducing this into the equation for two successive unimolecular reactions, the first rate constant for mustard has been calculated as 0.155 ± 0.010 from the data covering the two steps in its hydrolysis to thiodiglycol, which are not resolvable by any simpler method. From this constant and the data for displacement of the two chlorines successively by monothiophosphate, the constant for cyclization of the S-2-(2-chloroethylthio)-ethyl monothiophosphate ion is determined to be 0.70 ± 0.05 . The fact that this ion cyclizes more than twice as fast as mustard chlorohydrin produced, in earlier experiments, the false appearance of mustard having a faster initial reaction in the presence of thiophosphate than in its absence.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 24, 1948

[CONTRIBUTION FROM THE WOLCOTT GIBBS LABORATORY OF HARVARD UNIVERSITY]

Kinetics and Mechanism of the Reactions of Tertiary β -Chloroethylamines in Solution. III. β -Chloroethyldiethylamine and tris- β -Chloroethylamine¹

BY PAUL D. BARTLETT, SIDNEY D. ROSS AND C. GARDNER SWAIN

In the first² and second³ papers of this series the existence of a general mechanism was established whereby a tertiary β -chloroethylamine undergoes internal cyclization to an ethylene-immonium ion as a first step common to hydrolysis, dimerization and displacement reactions. By quite different methods in the cases of methyl-bis- β -chloroethylamine and ethyl-bis- β -chloroethylamine it was possible to determine the separate rate constants for the steps in this mechanism, and to show how the observed difference between predominating hydrolysis and predominating dimerization rested upon moderate differences between the relative values of the constants for these two homologs.

Two other tertiary β -chloroethylamines have

(1) The work described in this paper was performed under Contract NDCrc-136 between Harvard University and the National Defense Research Committee of the Office of Scientific Research and Development in 1942 and 1943.

(2) Part I: P. D. Bartlett, S. D. Ross and C. G. Swain, *THIS JOURNAL*, **69**, 2971 (1947).

(3) Part II: P. D. Bartlett, J. W. Davis, S. D. Ross and C. G. Swain, *ibid.*, **69**, 2977 (1947).

been examined more briefly and such quantitative information about them as was obtained is here presented. In the case of β -chloroethyldiethylamine the ethylene-immonium ion is comparatively stable and its formation can be observed uncomplicated by other reactions. We have not determined the rates of reaction of this ion with displacing reagents, although such measurements should present no difficulties. In the case of tris- β -chloroethylamine hydrolysis occurs to bis- β -chloroethylethanamine hydrochloride with much less accumulation of the intermediate ethyleneimmonium ion than in the previous cases; in this respect this amine is intermediate between the other "nitrogen mustards" and β, β -dichlorodiethyl sulfide ("mustard gas").⁴ In the presence of alkali to neutralize the liberated hydrochloric acid, the hydrolysis proceeds through successive stages to triethanolamine.⁵

(4) P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949).

(5) C. Columbic, M. A. Stahmann and M. Bergmann, *J. Org. Chem.*, **11**, 550 (1946).

Experimental

Preparation of β -Chloroethyldiethylamine.—Thionyl chloride (166.6 g., 1.4 moles) in 75 cc. of chloroform was added dropwise with external cooling to diethylethanolamine (117 g., 1 mole) in 75 cc. of chloroform. The reaction was extremely vigorous and was moderated by the addition of a further 75 cc. of chloroform. After the addition was complete the reaction flask was removed from the ice-bath and heated for six hours in an oil-bath at 65°. The solvent was removed *in vacuo*; the solid was filtered off, washed with ligroin and acetone, and finally recrystallized from acetone containing a little alcohol after decolorization with Norit. The hydrochloride thus obtained melted with decomposition at 205°. After recrystallization the hydrochloride was used for the preparation of the free amine just before each run in the same manner described for methyl-bis- β -chloroethylamine.²

Isomerization of β -Chloroethyldiethylamine.—The kinetic procedure was essentially that of Part I.² This amine is a strong enough base so that hydrochloric acid can be titrated in the presence of the amine hydrochloride using methyl orange as an indicator. In the run shown in Table I the appearance of chloride ion in 1:1 acetone-water at 25° was followed by Volhard titrations of the aqueous

TABLE I

CYCLIZATION OF β -CHLOROETHYLDIETHYLAMINE IN 2:1 ACETONE-WATER AT 25° (0.0827 M β -CHLOROETHYLDIETHYLAMINE)

Minutes time elapsed	Reaction % based on titration with 0.100 N AgNO ₃	Reaction % based on titration with 0.100 N HCl
0		
3	46.6	44.6
8	81.7	79.5
17	91.5	91.0
25	94.7	93.8
36	95.6	96.4

extract, and the disappearance of basic nitrogen was followed by extracting the benzene extract with standard hydrochloric acid and back-titrating to the methyl orange end-point. The two sets of figures for the degree of reaction agree within 2.5%. The unimolecular rate constant is 0.198 min.⁻¹. Tables II and III show two similar runs with and without the addition of sodium chloride. The

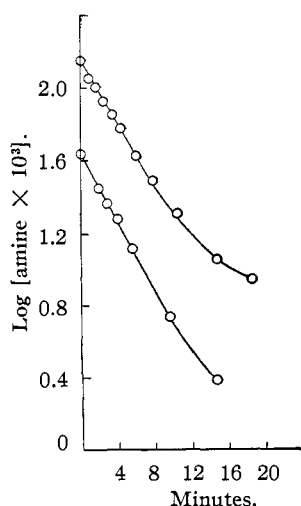


Fig. 1.—Cyclization of diethyl- β -chloroethylamine in 2:1 acetone-water: upper curve, 0.1435 M amine (Table II); lower curve, 0.04405 M amine + 0.0790 M sodium chloride (Table III).

unimolecular plots, shown in Fig. 1, yield rate constants of 0.203 and 0.204 min.⁻¹, respectively. The lack of inhibition by chloride ion is accompanied by normal unimolecular kinetics, but with a slowing beyond 90% reaction which suggests reversibility.

TABLE II

CYCLIZATION OF β -CHLOROETHYLDIETHYLAMINE IN 2:1 ACETONE-WATER AT 25° (0.1435 M β -CHLOROETHYLDIETHYLAMINE)

Minutes time elapsed	Reaction % by titration with 0.100 N AgNO ₃
0	
1	20.5
1.5	28.2
2.4	40.7
3.5	50.0
4.3	58.3
5.9	70.6
7.8	78.4
10.4	85.5
14.6	92.0
18.5	93.8

TABLE III

CYCLIZATION OF β -CHLOROETHYLDIETHYLAMINE IN 2:1 ACETONE-WATER AT 25° IN PRESENCE OF SODIUM CHLORIDE (0.04405 M β -CHLOROETHYLDIETHYLAMINE) 0.0790 M MNaCl

Time elapsed, minutes	Reaction % by titration with 0.100 N AgNO ₃
0	
1.90	33.2
2.77	47.5
4.00	55.9
5.67	69.3
9.62	87.4
14.60	94.3

A reaction of β -chloroethyldiethylamine proceeding with first-order kinetics and liberating all of the chlorine of the compound in ionic form might be (a) cyclization to the ethylene-immonium salt, (b) dimerization to a bisquaternary piperazinium salt, or (c) hydrolysis. Only in case (a) would the addition of hydrochloric acid to the solution, followed by evaporation to dryness *in vacuo*, be expected to reverse the reaction and yield β -chloroethyldiethylamine hydrochloride. This experiment was carried out and yielded 93.5% of a solid melting with decomposition at 203–204° (m. p. of β -chloroethyldiethylamine hydrochloride, 205°) and yielding on analysis 21.39% ionic and 39.09% total chlorine (calcd. for β -chloroethyldiethylamine hydrochloride, 20.60% and 41.20%). These results correspond to a mixture of 86% β -chloroethyldiethylamine hydrochloride and 14% diethylethanolamine hydrochloride or the bisquaternary piperazinium dimer, indicating that the solution on which the kinetic study was made contained at the end at least 86% of the unhydrolyzed ethylene-immonium ion.

Comparison of the glass-electrode potentials of half neutralized hydrochlorides by the method described in Part II,² indicated the following ratios of base strengths

$$\frac{K_B \text{triethylamine}}{K_B \text{diethylethanolamine}} = 7.3$$

$$\frac{K_B \text{triethylamine}}{K_B \text{diethyl-}\beta\text{-chloroethylamine}} = 460$$

An attempt to follow the rate of formation of the cyclic intermediate by the thiosulfate titration³ failed, since this

(6) C. Golumbic, J. S. Fruton and M. Bergmann, *J. Org. Chem.*, **11**, 518, 536 (1946).

reagent did not react rapidly enough with the intermediate. The rate of this slow reaction with thiosulfate was later measured by Cohen.⁷

TABLE IV

HYDROLYSIS AND DIMERIZATION OF TRIS- β -CHLOROETHYLAMINE IN 2:1 ACETONE-WATER AT 25° (0.0363 *M* AMINE)

Hours time elapsed	Reaction % based on NaOH	Reaction based on Volhard, %
0		
1.0	15.6	16.8
3.0	28.3	34.4
4.0	36.1	39.4
6.0	42.2	48.7
8.0	49.5	59.4
9.5	53.4	66.6

tris- β -Chloroethylamine.—Table IV gives the results of a run on this amine in which the appearance of chloride ion was followed by Volhard titration while the appearance of hydrogen ion was followed by titration with sodium hydroxide using thymolphthalein as indicator. The figures obtained by the two methods are close together early in the reaction, indicating that the reaction is chiefly hydrolysis. A divergence later between the alkali and silver titers suggests that with low hydroxyl ion concentrations as much as 20% of the total reaction may be dimerization.

Beside the divergence between the curves of chloride ion and hydrogen ion production, and the upward concavity of the latter curve, the plot of these results (Fig. 2) shows two other peculiarities. The reproducibility does not seem

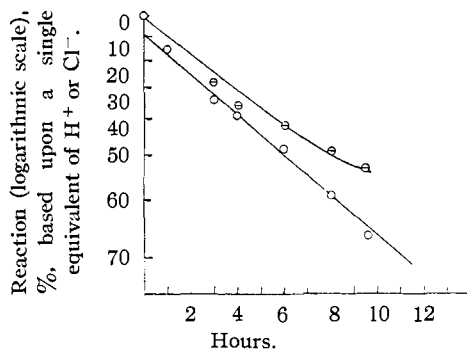


Fig. 2.—Reaction of tris- β -chloroethylamine in 2:1 acetone-water at 25°, followed by titration with sodium hydroxide (\odot) and with silver nitrate (O).

to be as good as that in the slower runs with sodium chloride added and the faster runs with sodium hydroxide, described below. Also in contrast to these other runs, the lines of per cent. reaction against time on a logarithmic plot do not pass through zero at zero time, but rather through about 10% reaction. The probable interpretation of this is as follows. The actual cyclization step (see Fig. 3) is about three times as fast as the liberation of chloride ion in this run, and the reaction proceeds initially at the rapid rate until enough chloride ion is accumulated to make the reversal of the initial cyclization step an important competitor with the hydrolysis. The 10% discrepancy corresponds to the approximate amount of ethylene-immonium ion which accumulates in this earliest stage of the reaction. This immonium ion reacts rapidly with hydroxyl ion in the titration and hence registers as hydrogen ion. The roughness of the "acid" line in this plot suggests that the completeness of the reaction between hydroxyl ion and the immonium ion is a function of the time elapsed during the titration.

In predominance of hydrolysis and in relatively slight

(7) Barnett Cohen, N. D. R. C. reports, 1943.

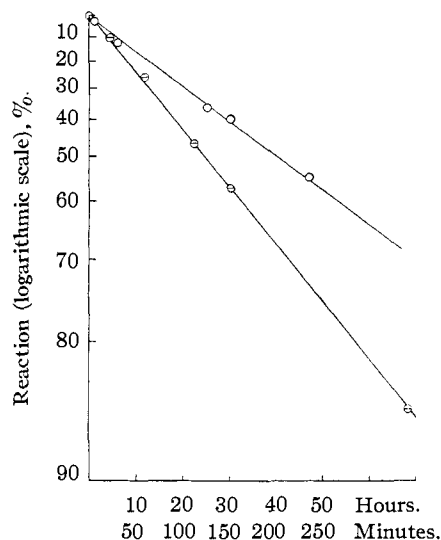


Fig. 3.—Upper curve, hydrolysis of tris- β -chloroethylamine in 2:1 acetone-water containing sodium chloride (upper time scale); lower curve, hydrolysis of tris- β -chloroethylamine in 2:1 acetone-water containing sodium hydroxide (lower time scale).

accumulation of the cyclic intermediate, tris- β -chloroethylamine is more like β, β' -dichlorodiethyl sulfide (mustard gas) than are the other amines, and forms a connecting link between the comparatively simple kinetics of hydrolysis of mustard and the complex situation with methylbis- β -chloroethylamine. The lower basic strength (and perhaps also the greater branching in space) of the trichlorinated amine causes a decrease in k_2 (and also k_1) relative to k_w .⁸

The basic dissociation constants measured in this medium in the same way as in the case of diethyl- β -chloroethylamine, are

$$\frac{K_B \text{ triethylamine}}{K_B \text{ triethanolamine}} = 210$$

$$\frac{K_B \text{ triethylamine}}{K_B \text{ tris-}\beta\text{-chloroethylamine}} = 1.5 \times 10^7$$

These results indicate a ratio of basic strengths in 2:1 acetone-water of 3.3×10^4 for diethyl- β -chloroethylamine and tris- β -chloroethylamine, as compared with the ratio of 2.7×10^4 in water.⁹

With sodium chloride added to the solution the reaction became very much slower and truly unimolecular with no initial rapid reaction. There was certainly less than 3% cyclic intermediate concentration at any time in the run at an initial amine concentration of 0.0384 with 0.0955 *M* sodium chloride added. The rate in this run was 5.2% of that in the likewise unimolecular run with 0.208 *M* hydroxyl ion added, which practically eliminated reversal of the first step (Fig. 3). The latter run gives k_1 as $5.5 \times 10^{-3} \text{ min.}^{-1}$.

In pure unbuffered water as a solvent, bis- β -chloroethylamine hydrochloride is the principal final reaction product. However, the ethyleneimmonium ion (called "B" in Part I² and below) accumulates to a substantial extent in water. This is shown by the fact that hydrogen ion production did not become appreciable until the chloride ion concentration had reached 0.006 *M* in a solution kept saturated with amine. The difference between chloride and hydrogen ion concentration at this point cannot be due to cyclic dimer, for this would not

(8) See the mechanism presented in Part I (ref. 2).

(9) B. Cohen, E. R. VanArtsdalen and J. Harris, THIS JOURNAL, 70, 282 (1948).

give rise to hydrogen ion later; therefore this difference between titers is largely a measure of cyclic intermediate.

The reaction in water was studied by the technique which was successfully applied by Wilson¹⁰ and more recently by Northrop¹¹ to the kinetic study of mustard. This technique consists in simplifying the kinetics by keeping the solution essentially saturated with starting material at all times by means of vigorous stirring of the solution with pure amine. In the presence of sufficient amounts of added chloride or hydroxyl ion the reaction shows zero-order kinetics; without any added electrolyte the rate of production of chloride ion decreases during reaction on account of the reversibility of the initial step and the diminution of the steady-state concentration of the cyclic intermediate B. Figure 4 shows the data for a typical run.

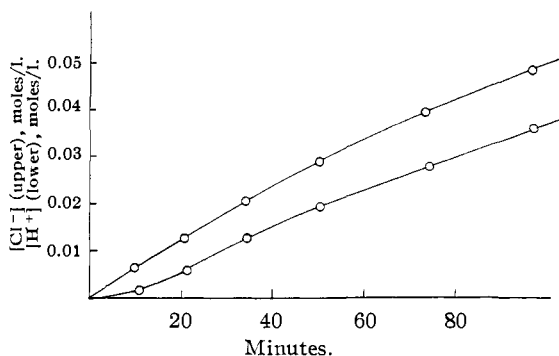


Fig. 4.—Reaction of tris- β -chloroethylamine in saturated aqueous solution at 25°, followed by titration with sodium hydroxide (lower) and with silver nitrate (upper curve).

After hydrogen ion production has begun and approximately reached the rate of further chloride production we can set the rate of change of (B) equal to zero and derive the approximate relation

$$(B) = \frac{k_1 c}{k_{-1}(\text{Cl}^-) + k_w}$$

where c is the solubility of the amine in water. The rate of appearance of chloride ion is

$$\frac{d(\text{Cl}^-)}{dt} = k_1 c - k_1(B)(\text{Cl}^-) = k_1 c \frac{k_w}{k_{-1}(\text{Cl}^-) + k_w}$$

This derivative is equal to the slope of the curve of (Cl^-) as a function of time. If we denote this slope by S , and its value at zero time by S_0 , then by substitution in this equation we get

$$\frac{S_0 - S}{S} = \frac{k_{-1}}{k_w} (\text{Cl}^-)$$

from which the ratio k_{-1}/k_w can be estimated graphically. The average of a number of such determinations in a run without added chloride was 17, the maximum deviation from the mean being about 10%. From a run with 0.1433 M sodium chloride added, the ratio was estimated to be 18.

From the extent to which hydrogen ion production lags behind chloride ion, the concentration of intermediate at the steady state can be estimated as of the order of 0.012 molar.

Because of the reactivity of tris- β -chloroethylamine toward water, its solubility cannot be determined by the usual methods. The solubility was determined by combining the value $k_1 c = 0.00062$ mole/liter min., which is the initial slope of a plot of chloride ion concentration *vs.* time, with the value of $k_1 = 0.310$ min.⁻¹ at 25° determined by Cohen.⁷ The solubility in water at 25° is thus found to be 0.0020 mole per liter.

In all these runs, there being no buffer present, the reaction comes to a virtual stop when one equivalent of chloride has been produced per mole of reacting amine. Because a hydroxyethylamine is a somewhat stronger base than a chloroethylamine and will hence combine preferentially with the acid present, the bulk of the product would be expected to be the bis- β -chloroethylethanolamine hydrochloride. This product has been isolated as the picrylsulfonate in yields of 93%.¹²

Discussion

In Table V are summarized the rate constants in 2:1 acetone-water solution which have been determined for the four *t*- β -chloroethylamines studied in this series of researches. Among the three successively chlorinated triethylamines the rate of initial cyclization falls, and the reactivity of the ethylene-immonium ion rises, with decreasing basicity of the original amine. (This fact is apparent qualitatively from the stability, partial accumulation, and non-accumulation of the ethylene-immonium ion, respectively, in the successively chlorinated triethylamines.) From this regularity it might be guessed that β, β' -dichlorodiethyl sulfide, which is still less basic than tris- β -chloroethylamine and otherwise chemically analogous to it, would show still less accumulation of cyclic intermediate during its reaction in aqueous media, as is the case. The steady decrease in rate of cyclization (k_1) is in accord with the picture of an intramolecular displacement of the $\text{S}_{\text{N}}2$ type,¹³ since successively weaker bases are being used as nucleophilic reagents. The steady increase in reactivity of the ethylene-immonium ions with chloride ion (k_{-1}) may be due to the increased electron deficiency on the ring carbon atom being attacked, caused by increasing chlorination of the molecule.

The differences shown in the table between methyl- and ethyl-bis- β -chloroethylamine are substantial, and one might be inclined to question their reality in view of the entirely different ways in which the constants were determined in the two cases. However, differences of this magnitude must necessarily exist between two compounds which show the qualitative differences in behavior in solution noted with these two homologs. The differences can be summarized by saying that the ethylene-immonium ion of the ethyl compound is formed faster than that of the methyl compound and reacts faster toward every reagent except the parent amine (k_2). The latter reaction is an alkylation of a methylamine in the one case and of an ethylamine in the other, and rate differences attributable to steric hindrance have been observed in such cases. On the other hand, steric hindrance of this type does not appear to be so important a factor in ring closure,¹⁴ and would not be expected to dominate the opening of a three-membered ring by water or by a small ion at an

(12) Ref. 5, p. 556.

(13) Ref. 2, p. 2975.

(14) Sebelius, Inaugural Dissertation, Lund, 1927; see Hückel, "Theoretische Grundlagen der organischen Chemie," 2nd ed., Leipzig, 1935, Vol. 2, p. 259.

(10) R. E. Wilson, E. W. Fuller and M. O. Schur, THIS JOURNAL, 44, 2762 (1922).

(11) J. H. Northrop, N. D. R. C. Reports, 1943.

TABLE V

COMPARISON OF KINETIC CONSTANTS OF SOME β -CHLOROETHYLAMINES $\text{ClCH}_2\text{CH}_2\text{NRR}'$ IN 2:1 ACETONE-WATER SOLUTIONS AT 25°

R	R'	ΔpK_A^a	Principal reaction	Constants in 2:1 acetone-water (time in minutes)			
				k_1	k_{-1}	k_2	k_w
C_2H_5	C_2H_5	-2.66	I^b	0.202	<0.02	<1.0	<0.05
ClCH_2CH_2	CH_3	-4.76	D^c	.02	1.35'	0.4	0.0012
ClCH_2CH_2	C_2H_5	-4.87	H^d	.085	1.5 ^e	0.08	0.0057
ClCH_2CH_2	ClCH_2CH_2	-7.18	H^d	.0055	~200	≤20	~1

^a ΔpK_A is defined in Part II, THIS JOURNAL, 69, 2977 (1947). ^b I = internal cyclization. ^c At the ionic strength prevailing when initial amine concentration = 0.1501. ^d H = hydrolysis. ^e D = dimerization. ' At the ionic strength prevailing when initial amine concentration = 0.118.

unbranched carbon atom, in the reactions to which k_{-1} and k_w refer. The greater rate of cyclization of the ethyl over the methyl compound in water is largely a matter of entropy of activation;⁹ there may even be some release of steric interference with the ethyl group associated with the conversion of one of its neighbor groups into a ring.

Summary

In connection with the mechanism of hydrolysis, dimerization and displacement reactions of methyl-bis- β -chloroethylamine and ethyl-bis- β -chloroethylamine, studied in Parts I and II of this series, respectively, two related compounds have been examined kinetically. β -Chloroethyldiethylamine in 2:1 acetone-water solution undergoes

cyclization to diethylethylene-immonium chloride without complicating reactions, and more rapidly than its analogs previously studied. tris- β -Chloroethylamine is hydrolyzed slowly, with 10% or less accumulation of bis- β -chloroethylethylene-immonium chloride as an intermediate in the reaction in 2:1 acetone-water solution. The kinetics of its hydrolysis has also been studied in water kept saturated with the amine by vigorous stirring. A table is given comparing the individual rate constants in the reactions of the several amines studied in 2:1 acetone-water solution, and the variation of these rate constants with structure is interpreted in part.

CAMBRIDGE 38, MASSACHUSETTS

RECEIVED NOVEMBER 4, 1948

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of the Decomposition of Potassium Persulfate in Aqueous Solutions of Methanol

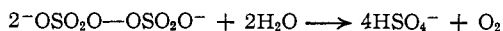
BY PAUL D. BARTLETT AND JOHN D. COTMAN, JR.

Introduction

It has been known for some time that the decomposition of a diacyl peroxide in an organic solvent may be, in its over-all course, a reaction between the peroxide and the solvent.¹⁻⁶ Recently three lines of evidence have pointed to the fact that often this participation of the solvent has the character of a chain reaction, free radicals arising in the process being able to induce the decomposition of further peroxide.⁴⁻⁶ Such chain-induced decomposition is revealed (1) by great differences in the rates of decomposition of the same peroxide in different solvents, (2) by characteristic order of reaction, (3) by inhibition of the chain reaction by typical inhibitors, and (4) by the nature of the products.

The decomposition of potassium persulfate, an analog of the diacyl peroxides, has been much

studied in water.⁷⁻¹⁰ In solutions buffered against the accumulation of hydrogen ion, the decomposition follows the over-all course



and is thus, as with diacyl peroxides, a reaction between the peroxidic substance and the solvent. However, in contrast to the decomposition of diacyl peroxides in organic solvents, the reaction is strictly of the first order,^{7-9,11} and it has not been observed to be retarded by any inhibitor. Although two of the three marks of chain decomposition are thus lacking, the effect of organic substances on the rate of persulfate decomposition is striking. Saturation of the buffered aqueous solution of potassium persulfate with ethyl acetate¹¹ caused an eightfold increase in the rate of its decomposition. Methanol was observed by Marie and Bunel¹² to have a similar accelerating

(1) H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925), and later papers.

(2) M. S. Kharasch, S. S. Kane and H. C. Brown, THIS JOURNAL, **63**, 526 (1941).

(3) M. S. Kharasch and M. T. Gladstone, *ibid.*, **65**, 15 (1943).

(4) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

(5) W. E. Cass, *ibid.*, **68**, 1976 (1946).

(6) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(7) M. G. Levi and E. Migliarini, *Gazz. chim. ital.*, **36B**, 599 (1906).

(8) L. Green and O. Masson, *J. Chem. Soc.*, **97**, 2083 (1910).

(9) A. Kailan and E. Leisek, *Monatsh.*, **50**, 403 (1928).

(10) H. Palme, *Z. anorg. Chem.*, **112**, 97 (1920).

(11) P. D. Bartlett and K. Nozaki, *J. Pol. Sci.*, **3**, 216 (1948).

(12) C. Marie and L. J. Bunel, *Bull. soc. chim.*, (3) **29**, 930 (1903).