TABLE V

COMPARISON OF KINETIC CONSTANTS OF SOME β-CHLOROETHYLAMINES $ClCH_2CH_2NRR'$ 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[e]	.02	1.35[f]	0.4	0.0012
$ClCH_2CH_2$	C_2H_5	−4.87	H[d]	.085	1.5[c]	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. [f] 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.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

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

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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

$$2\,{}^-OSO_2O{-}OSO_2O^- + 2H_2O \longrightarrow 4HSO_4^- + O_2$$

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 acetate[11] caused an eightfold increase in the rate of its decomposition. Methanol was observed by Marie and Bunel[12] to have a similar accelerating

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(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).

effect upon the decomposition of persulfate. Instances of the oxidation of organic compounds by persulfate suggest rather general attack of persulfate or radicals from persulfate[13] upon the C–H link. Because of these facts it was of interest to us to investigate the mechanism of the accelerating effect of an organic compound in aqueous solution upon the decomposition of persulfate. We chose methanol because of its unlimited solubility in water, its availability in high purity, and the hope of an easy quantitative determination of its fate in the reaction.

Experimental Procedure

The potassium persulfate and methanol used were reagent grade.

Persulfate was titrated by a modification of the method recommended by Rosin.[14] The solution to be analyzed was made 1 *M* in potassium iodide and one gram of sodium bicarbonate was dissolved in it. To this sample was added 20–25 cc. of 10% sulfuric acid. During and after the liberation of the carbon dioxide, which provided a convenient means of sweeping out the oxygen, the solution stood in a glass-stoppered flask. After standing for thirty minutes in the dark at room temperature, the liberated iodine was titrated with standard thiosulfate. Five test samples titrated by this method showed persulfate amounting to 99.4, 100.2, 99.0, 100.2 and 99.6% of the theoretical. In the absence of methanol satisfactory results were had by the titration method of Müller,[15] which consists of boiling an aliquot for three minutes with potassium iodide and 2 *M* sodium hydroxide. The resulting mixture of iodide and iodate is acidified and the iodine titrated. Methanol interferes with this method.

A stock buffer solution was prepared which was 0.003 *M* in monopotassium phosphate, 0.097 *M* in the ion $HPO_4^=$ (by adding sodium hydroxide), and 0.1 *M* in potassium sulfate. The *p*H and ionic strength were thus maintained at the same value in all the runs.

To minimize the decomposition of persulfate during heating before the addition of the methanol, about 200 cc. of the buffered solvent was first brought to 80° in the thermostat. This hot solvent was then added to the freshly prepared solution of weighed solid potassium persulfate dissolved at room temperature in about 50 cc. of the solvent the system made up to volume in a volumetric flask and reimmersed in the thermostat for about twenty minutes, when it had reached the temperature of the bath. Then 20 cc. of methanol, preheated in a bulb to 80°, was forced through a tube under its own vapor pressure into the reaction vessel. This rapid addition resulted in efficient mixing. There was some 15% decomposition of the persulfate prior to the admission of the methanol. Aliquot portions of the reacting solution were taken with a pipet at successive times and titrated by the procedure described.

The presence of formaldehyde in a solution in which the persulfate had decomposed in the presence of methanol was demonstrated by the formation of a silver mirror with Tollens reagent and by the isolation of the 2,4-dinitrophenylhydrazone of formaldehyde, fluffy yellow needles, m. p. 161–163°. Thereafter formaldehyde was titrated in the product solutions by the method of Romijn,[16] with which methanol and formic acid are said not to interfere.[17]

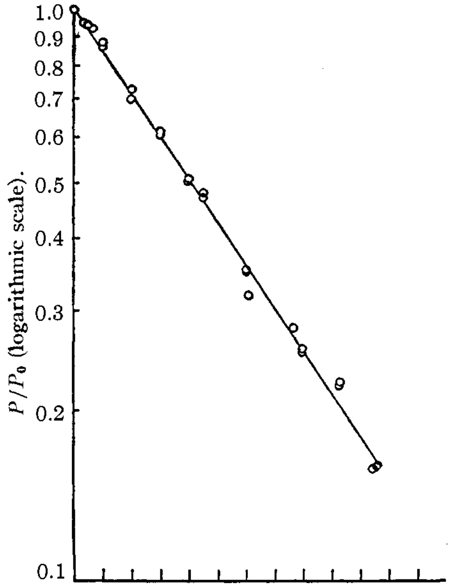

Fig. 1.—Decomposition of potassium persulfate at concentration from 0.00240 to 0.0134 *M* in water at *p*H 8 at 79.8 ± 0.05° (four runs).

Results

Figure 1 shows a logarithmic plot of four runs on the decomposition of persulfate at 79.8° without added methanol. The initial persulfate concentrations in these runs were 0.00240, 0.00241, 0.0131 and 0.0134. The agreement of all these runs, as well as the linearity of the plots over 85% decomposition of the persulfate, confirms the first-order character of the decomposition in the absence of added organic compounds.

The qualitative effect of the addition of 0.976 *M* methanol can be observed by making a similar logarithmic plot of the data in this case. The initial apparent first-order rate constant is 0.140 in the presence of methanol. This substance when present in a concentration of about 1 *M* thus accelerates the decomposition of persulfate by a factor of 25.

In addition to its accelerating effect upon the decomposition of persulfate, the presence of methanol changes the order of the reaction so that the logarithmic plots are no longer linear. Straight lines are obtained, however, for all the runs involving methanol if the reciprocal of the square root of persulfate concentration is plotted against time (plot of a 3/2 order reaction) as is done in Fig. 2 for a typical run. Table I summarizes the values of the 3/2 order rate constants so determined, for three different concentrations of methanol. The rate constants are not proportional to the methanol concentration, but appear to vary with its square root. That this change in rate is also as-

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[13] See, for example, C. Moritz and R. Wolfenstein, *Ber.*, **32**, 432, 2531 (1889), on the oxidation of toluene and ethylbenzene, and E. Bekier and S. W. Kijowski, *Rocznicki Chem.*, **15**, 136 (1935) (*Chem. Abst.*, **30**, 3306 (1936)), on the oxidation of acetone catalyzed by silver ion.

[14] Rosin, "Reagent Chemicals and Standards," D. Van Nostrand Co., New York, N. Y., 1946, 2nd edition, p. 349.

[15] E. Müller, *Z. anal. Chem.*, **52**, 299 (1913).

[16] G. Romijn, *Z. anal. Chem.*, **36**, 18 (1897); P. Dobriner, *ibid.*, **39**, 60 (1900).

[17] I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, Vol. 2, p. 444.

sociated with a change in the over-all course of the reaction is shown by a series of titrations for formaldehyde, conducted on the solutions after reaction was complete, and included in Table I.

Of the values of $k_{3/2}$ listed in Table I, the value for 1.464 *M* methanol is the result of a single run; that for 0.976 *M* methanol is the average of five runs yielding constants of 0.807, 0.785, 0.781, 0.813 and 0.780; the constant for 0.488 *M* methanol is the average of three runs yielding constants of 0.610, 0.640 and 0.647.

In a study of the polymerization of allyl alcohol in aqueous solution made in this Laboratory in 1944,[18] the decomposition of the initiating persulfate was observed to deviate from first-order kinetics. Because of the polymerization occurring, the nature, functionality, and concentration of the alcohol was changing during these experiments; however, we have now found that in the one experiment with a high concentration of allyl alcohol (6.30–5.02 *M* during the run) the decomposition of persulfate was clearly of the 3/2 order, while in the other experiments the kinetics more closely approximates this order than it does first order. In the presence of the high concentration of allyl alcohol at 55° the 3/2 order rate constant was 0.33 liters$^{1/2}$ moles$^{-1/2}$ min.$^{-1}$.

TABLE I

RATE CONSTANTS AND FORMALDEHYDE FORMATION IN THE DECOMPOSITION OF 0.015 *M* POTASSIUM PERSULFATE AT 79.8° ± 0.05° AT *p*H 8

Initial methanol concn., moles/l.	$k_{3/2}$ liters$^{1/2}$ moles min.$^{-1}$	$\frac{k_{3/2}}{\sqrt{[CH_3OH]}}$	Per cent. formaldehyde, based on peroxide decomposed
1.952	..	..	100.5
1.464	1.04	0.86	99.1
0.976	0.79	.80	92.9
0.488	0.63	.90	82.8
0.195	..	..	72.9

Discussion

At no point in the investigation has any evidence appeared that the decomposition of persulfate ion can be induced by any radicals normally involved in its aqueous decomposition. Therefore the simplest interpretation of the mechanism is by some such scheme as the following

$$S_2O_8^{=} \xrightarrow{k_1} 2SO_4^{\dot{-}} \quad (1a)$$

$$SO_4^{\dot{-}} + H_2O \xrightarrow{k_2} HSO_4^{-} + OH\cdot \quad (2)$$

$$2OH\cdot \xrightarrow{k_3} H_2O + {}^1/_2O_2 \quad (3)$$

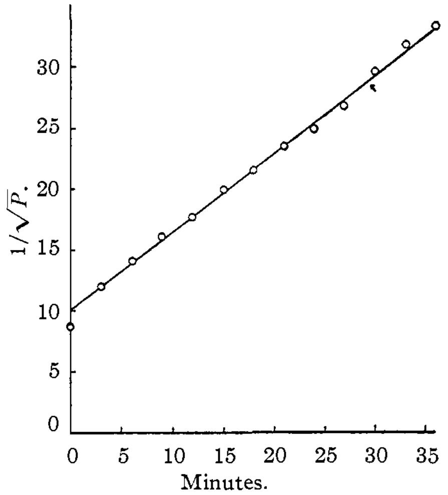

Fig. 2.—Decomposition of persulfate (0.01375 *M*) at 79.8° and *p*H 8 in presence of 0.488 *M* methanol, plotted as a 3/2 order reaction. The arrow marks 90% reaction.

Although there are two kinds of free radicals involved in this chain, admitting of three possible chain-terminating steps, yet the order of the reaction tells us that the sulfate ion radicals $SO_4^{\dot{-}}$ do not recombine with one another appreciably, for if they did so the reaction would be of half order with respect to persulfate ion, and even a small contribution from such a recombination would make the observed first-order rates vary with initial concentration of persulfate. Furthermore, if sulfate ion radicals and hydroxyl radicals combined they would form Caro's acid, which Palme[10] found to be absent under these experimental conditions. The inclusion of Equation 3 in the above scheme does not imply the exclusion of a similar disproportionation between a hydroxyl radical and a sulfate ion radical. It seems, however, that with water as the solvent Equation 2 represents the most probable fate for the sulfate ion radical. It will be noted that although the sequence Equations 1–3 involves free radicals, initiation, termination and transfer, there is no chain propagation reaction in the sense of attack on the starting material by radicals.

By comparison of the over-all rates of decomposition of persulfate with and without methanol present we may conclude that in 1 *M* methanol 96% of the persulfate ions disappear by being attacked by a free radical other than those present in the water reaction. This new free radical must also be one which is present at a steady-state concentration proportional to the square root of the concentration of persulfate ions. These requirements are met by the following scheme.

$$S_2O_8^{=} \xrightarrow{k_{1a}} 2SO_4^{\dot{-}} \quad (1a)$$

$$S_2O_8^{=} + CH_3OH \xrightarrow{k_{1b}} HSO_4^{-} + SO_4^{\dot{-}} + CH_2OH\cdot \quad (1b)$$

$$SO_4^{\dot{-}} + CH_3OH \xrightarrow{k_4} HSO_4^{-} + CH_2OH\cdot \quad (4)$$

$$CH_2OH\cdot + S_2O_8^{=} \xrightarrow{k_5} HSO_4^{-} + SO_4^{\dot{-}} + CH_2O \quad (5)$$

$$2CH_2OH\cdot \xrightarrow{k_6} CH_3OH + CH_2O \quad (6)$$

It would of course be possible that Reaction 2 should occur here as well as in the absence of methanol, and the methanol be attacked by the result-

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[18] M. E. Fleischer, unpublished experiments.

ant hydroxyl radicals instead of directly by sulfate ion radicals. In the related problem of the emulsion polymerization of allyl acetate,[11] although the concentration of the organic compound in the aqueous phase was considerably less than here, it was definitely shown that at least 75% of the polyallyl acetate chains were initiated by sulfate ion radicals rather than by hydroxyl radicals.[19] Allyl acetate, therefore, competes very successfully with water for the sulfate ion radicals, and it seems probable that methanol does likewise.

The sequence of steps 1a–4–5–6 leads to the kinetic equation

$$\frac{-\mathrm{d}(S_2O_8^=)}{\mathrm{d}t} = k_{1a}\,(S_2O_8^=) + k_5\sqrt{\frac{k_{1a}}{k_6}}(S_2O_8^=)^{3/2} \quad (7)$$

It is reasonable in view of the strong acceleration by methanol that the second term of this expression should be more important than the first, and such a mechanism would therefore predict the observed 3/2 order kinetics. The sequence of steps 1b–4–5–6 leads to the slightly different equation

$$\frac{-\mathrm{d}(S_2O_8^=)}{\mathrm{d}t} = k_{1b}(S_2O_8^=)(CH_3OH) + k_5\sqrt{\frac{k_{1b}}{k_6}}(S_2O_8^=)^{3/2}(CH_3OH)^{1/2} \quad (8)$$

This equation, again with neglect of the first term on the right, predicts not only the 3/2 order of the reaction but also the linear dependence of the rate constant on the square root of methanol concentration (Table I). Equations (7) and (8) are derived on the assumption that every sulfate ion radical reacts with methanol to produce a hydroxymethylene radical. As the concentration of methanol is reduced to the point where this is no longer true, Equations 1–6 predict that an increasing fraction of the sulfate ion radicals will react with water (or possibly with the accumulating formaldehyde), leading to shorter chains and smaller total amounts of formaldehyde, as observed.

It is assumed that the removal of hydrogen from methanol occurs from carbon, leading to a hydroxymethylene radical rather than from oxygen to yield a methoxyl radical, since the relative normal energies of the C–H and O–H bonds (87.3 and 110.2 kcal. mole, respectively)[20] make the former process seem much the more probable.

Reaction 5, as depicted, may well be an over-all process which actually occurs in two steps

$$CH_2OH\cdot + S_2O_8^= \longrightarrow SO_4^{\dot{-}} + HOCH_2OSO_3^- \quad (5a)$$

$$HOCH_2OSO_3^- \longrightarrow CH_2O + HSO_4^- \quad (5b)$$

Very little is known as yet concerning the mode of attack of free radicals upon peroxides in the induced decomposition.

Finally, there is no definite evidence for Equation 6 in preference to a direct union of the two hydroxymethylene radicals to yield ethylene glycol. The high yield of formaldehyde is scarcely conclusive on this point, since the chains are obviously long enough to limit the occurrence of chain-termination products to a few per cent. of the total. Any of these indicated variations could be introduced into the proposed reaction scheme without vitiating its kinetic consequences.

It should be noted that the evidence for the absence of chain decomposition of persulfate in water in the absence of organic compounds is of a negative character and is not altogether complete. In the decomposition of benzoyl peroxide in ether solutions the kinetics, as here, is that of a first order reaction, yet induced decomposition is readily suspected because the reaction is so much faster than in other solvents, and the presence of free radicals other than those of oxygen is shown by the uptake of oxygen during the reaction with the formation of new peroxides. In the case of persulfate decomposing in water solution there can be no free radicals other than those of oxygen, and oxygen-sensitivity is therefore not to be expected even if a long chain reaction were taking place. There is a possible mechanism for this reaction which includes induced decomposition of persulfate ions by hydroxyl radicals, and which still predicts decomposition of the first order. Such a mechanism includes adding to Equations 1a and 2 the following

$$OH\cdot + S_2O_8^= \xrightarrow{k_9} HSO_4^- + SO_4^{\dot{-}} + {}^1/_2O_2 \quad (9)$$

$$OH\cdot + SO_4^{\dot{-}} \xrightarrow{k_{10}} HSO_4^- + {}^1/_2O_2 \quad (10)$$

The induced decomposition of persulfate by hydroxyl radicals will be of the first order now only if Equation 10 represents the mode of chain termination rather than Equation 3. This possibility is mentioned only for completeness; as far as our evidence goes, persulfate decomposition in water may well be an example of the case, unusual to date, in which the spontaneous, unimolecular decomposition is uncomplicated by any induced process involving the free radicals of the chain.

Summary

The decomposition of potassium persulfate at 79.8° in aqueous solution at *p*H 8 is strictly of the first order, with no evidence of induced decomposition by free radicals analogous to that observed in the decomposition of diacyl peroxides in organic solvents. The presence of methanol or allyl alcohol accelerates the reaction (as much as 25-fold in the case of methanol) and the alcohols change the reaction to one of 3/2 order. In the reaction with methanol formaldehyde is produced, its amount being equivalent to the persulfate decomposed when the initial methanol is 1.5 *M*, and becoming less at lower methanol concentrations. Mechanisms are presented to account for these observations.

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[19] Of the polymer molecules, 75% contained sulfate end-groups. The fraction of the kinetic chains initiated by sulfate ion radicals must be at least as high as this and may be higher because of chain transfer leading to some polymer molecules without any end-group from the initiator (ref. 11).

[20] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd edition, 1940, p. 53.