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DECOMPOSITION OF PERACETIC ACID IN A MIXTURE OF ACETIC ANHYDRIDE, ACETIC AND NITRIC ACIDS*

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Abstract—It was found that peracetic acid is easily decomposed in a mixture of nitric acid, acetic anhydride and acetic acid at 50°. The mechanism of this decomposition was postulated to involve the unimolecular and induced decomposition of peroxyacetyl nitrate. The kinetics of the decomposition was undertaken and the reaction products were investigated.

THE conversion of peracetic acid to acetyl peroxide in acetic acid in the presence of sulphuric acid has been reported, where the total concentration of peroxides is approximately constant,[1] since both peracetic acid and acetyl peroxide in equilibrium are slowly decomposed in acetic acid at 50°. The authors observed that peracetic acid in acetic acid is easily decomposed at 50° in the presence of nitric acid and a small amount of acetic anhydride, only a small amount of the peracid being converted to acetyl peroxide.

The purpose of the present study is to disclose the behaviour of the decomposition of peracetic acid in this mixture by a kinetic method together with the identification of reaction products in the presence or absence of substrates.

RESULTS AND DISCUSSION

Rate law. The decomposition rate of peracetic acid in the presence of nitric acid and acetic anhydride was followed by measuring iodometrically the residual amount of peracetic acid and acetyl peroxide. The amount of acetyl peroxide increased slightly but was below 3%. The rate of the disappearance of the peracid satisfied the pseudo-first-order kinetics (Fig. 1), and the rate constants at various initial concentrations of peracetic acid held good constancy as shown in Table 1. The effect of various initial concentrations of nitric acid and acetic anhydride on the first-order rate constant were estimated and are shown in Figs 2 and 3. The rate was first-order with peracetic acid and with nitric acid except at high concentration of nitric acid. The data in Fig. 3 show that acetic anhydride satisfies first-order kinetics at low concentration of acetic anhydride, but not at higher concentration. This may be due to the equilibrium.

$$Ac_2O + HNO_3 \rightleftarrows AcONO_2 + AcOH \qquad (1)$$

At higher concentration of acetic anhydride, the nitric acid was nearly all converted to acetyl nitrate in the above equilibrium and the concentration of free nitric acid may become lower. Therefore, the observed rate constants do not increase

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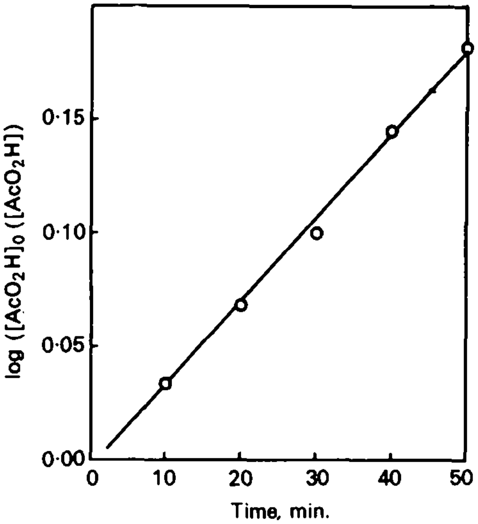


FIG. 1. A typical first-order plot for the decomposition of peracetic acid in acetic acid at 50°
Initial conc.: $(HNO_3) = 0{\cdot}288M, (Ac_2O) = 0{\cdot}133M$.

TABLE 1. RATE CONSTANTS FOR THE DECOMPOSITION OF PERACETIC ACID AT VARIOUS INITIAL CONCENTRATION IN ACETIC ACID AT 50°. INITIAL CONCN.: $(HNO_3) = 0{\cdot}288$ M, $(Ac_2O) = 0{\cdot}133$ M

(AcO_2H) M	First-order rate constants $k_1 \times 10^5$
0·016	5·8
0·029	6·3
0·064	6·2

linearly with increasing amount of acetic anhydride at its higher concentration. A similar deviation from first-order plot was observed at lower concentration of nitric acid in Fig. 2.

Effect of temperature. The pseudo-first-order rate constants (10^5 k, sec^{-1}) were 6·8 at 55°, 3·7 at 50°, 2·3 at 45° and 1·3 at 40° (initial conc.: $[HNO_3] = 0{\cdot}288M$, $[Ac_2O] = 0{\cdot}110M$, $[AcO_2H] = 0{\cdot}029M$). The Arrhenius plot afforded a good straight line, which gave the values of 22·3 kcal/mole for the apparent energy of activation.

Analysis of reaction products. The reaction products from an acetic acid solution of nitric acid, acetic anhydride and peracetic acid were carbon dioxide, methane, formic acid, oxalic acid and glycolic acid. The analysis data of gaseous products are summarized in Table 2. Other liquid products were investigated in typical runs 5 and 8 in Table 2. In run 8, no oxalic acid was detected, while formic acid (7–14% on the basis of the decomposed peracetic acid) was observed. In run 5, oxalic acid was identified, the total yield of oxalic and formic acids being 0·3%.

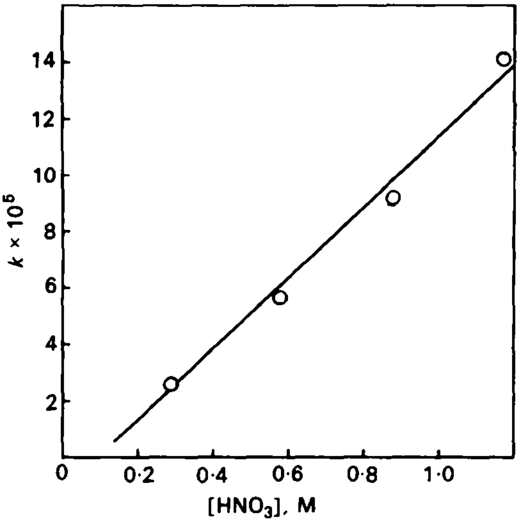


FIG. 2. Effect of nitric acid in acetic acid at 50°
Initial conc.: $(Ac_2O) = 0{\cdot}016M$, $(AcO_2H) = 0{\cdot}029M$, $(H_2SO_4) = 0{\cdot}416M$.

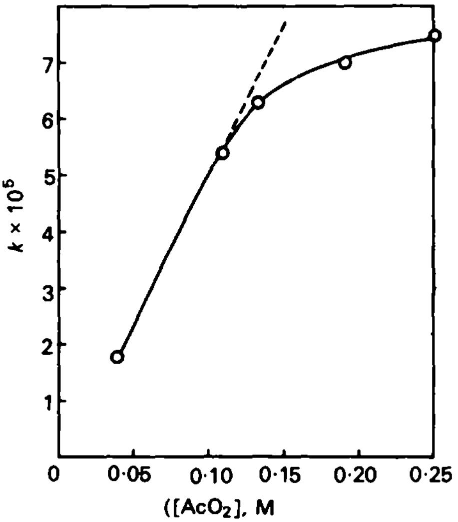


FIG. 3. Effect of acetic anhydride in acetic acid at 50°.
Initial conc.: $(HNO_3) = 0{\cdot}288M$, $(AcO_2H) = 0{\cdot}029M$.

The higher concentration of peracetic acid (runs 6 and 8) and the presence of substrates more susceptible to oxidation (run 9) increase the yield of carbon dioxide, but they had practically no influence on the yield of methane.

Competitive reaction. The competitive abstraction of hydrogen or chlorine from toluene, chloroform, carbon tetrachloride and cyclohexane (Table 3) gave relative abstraction rates of 0·2–0·4, 0·2–0·5, 0·0–0·2 and 1, respectively.

Effect of acetic anhydride and nitric acid in the iodometry of peracetic acid. In this reaction, peracetic acid was analysed by iodometry. The addition of a mixture of

TABLE 2. ANALYSIS OF GAS PRODUCED IN THE DECOMPOSITION OF PERACETIC ACID AT 50°.

Initial concn.: (HNO_2) = 1·15 M, (Ac_2O) = 0·28 M, Solvent AcOH

Run No.	(AcO_2H) M	(AcO_2H) Decomposed M	Products (% for decomposed peracetic acid) CO_2	CH_4
1	0	—	0	0
2	0·13	0·07	14	11
3	0·19	0·13	17	17
4	0·25	0·21	17	15
5	0·38	0·23	17	16
6	1·22	0·36	24	15
7	0·32[a]	0·14	17	19
8	0·95[b]	0·78	43	21
9	0·48[c]	0·37	28	21
10	0·47[d]	0·25	20	18
11	0·48[e]	0·25	24	19

[a] (HNO_3) = 0·58 M, (Ac_2O) = 0·28 M.
[b] (HNO_3) = 2·29 M, (Ac_2O) = 0·56 M.
[c] [propionic acid] = 5·60 M.
[d] [oxalic acid] = 0·33 M.
[e] [formic acid] = 1·10 M.

nitric acid, acetic anhydride and acetic acid to aqueous KI liberated iodine. This amount of iodine (y) in the blank test increased with increasing concentration of acetic anhydride or KI, but it was independent of the temperature of the mixture. This y value seems to correspond to the amount of acetyl nitrate formed by a reversible reaction (1). Hence, the addition of peracetic acid which can consume nitric acid should shift the equilibrium (Eq. 1) to the left. If the above mixture of nitric and acetic acids and acetic anhydride was added primarily to water and then to aqueous KI, no iodine was liberated, probably because of the hydrolysis of acetyl nitrate. When peracetic acid was added to the reaction mixture, the y value decreased rapidly until negligible in comparison with the concentration of added peracetic acid, probably because of the consumption of acetyl nitrate. The amount of iodine liberated on addition of a given amount of peracetic acid in the reaction was not affected by the primary addition of water to the mixture before pouring into aqueous KI.

It is known that nitric acid and acetic anhydride form tetranitromethane at low temperature.[2] But tetranitromethane was not detected under these conditions (colour reaction with naphthalene and anthracene was negative).

The mechanism. These observed facts show that this reaction is not one of heterolysis, but homolysis. The observed kinetics and products suggest the following mechanism, which involves an unimolecular and induced decomposition of peroxyacetyl nitrate. Peroxyacetyl nitrate may be decomposed easier than peracetic acid because of the stability of its transition state.

TABLE 3. COMPETITIVE REACTION IN ACETIC ACID AT 50°.
Initial concn.: $(HNO_3) = 1{\cdot}15$ M, $(Ac_2O) = 0{\cdot}28$ M, $(AcO_2H) = 0{\cdot}48$ M

Initial concn. M	Conversion (%)			
	C_6H_{12}	toluene	$CHCl_3$	CCl_4
$(C_6H_{12}) = 0{\cdot}41$ (toluene) = 0·42	45	19	—	—
$(C_6H_{12}) = 0{\cdot}21$ (toluene) = 0·63	5	1	—	—
$(C_6H_{12}) = 0{\cdot}41$ $(CHCl_3) = 0{\cdot}55$	72	—	38	—
$(C_6H_{12}) = 0{\cdot}21$ $(CHCl_3) = 0{\cdot}82$	75	—	13	—
$(CHCl_3) = 0{\cdot}55$ $(CCl_4) = 0{\cdot}70$	—	—	13	ca. 0
$(CHCl_3) = 0{\cdot}28$ $(CCl_4) = 1{\cdot}05$	—	—	27	12

$$AcO_2H + HNO_3 \overset{K_1}{\rightleftharpoons} AcO_2NO_2 + H_2O \tag{2}$$

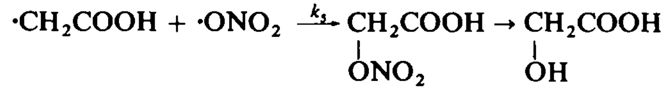
$$H_2O + Ac_2O \overset{K_2}{\rightleftharpoons} 2AcOH \tag{3}$$

$$AcO_2NO_2 \xrightarrow{k_1} CH_3\cdot + CO_2 + \cdot ONO_2 \tag{4}$$

$$AcOH + CH_3\cdot \xrightarrow{k_2} CH_4 + \cdot CH_2COOH \tag{5}$$

$$AcOH + \cdot ONO_2 \xrightarrow{k_3} HNO_3 + \cdot CH_2COOH \tag{6}$$

$$AcO_2NO_2 + \cdot CH_2COOH \xrightarrow{k_4} AcOCH_2COOH + \cdot ONO_2 \tag{7}$$



$$\cdot CH_2COOH + \cdot ONO_2 \xrightarrow{k_5} \underset{\displaystyle ONO_2}{CH_2COOH} \rightarrow \underset{\displaystyle OH}{CH_2COOH} \tag{8}$$

The rate of peracetyl nitrate decomposition is expressed as:

$$v = k_1[AcO_2NO_2] + k_4[AcO_2NO_2][\cdot CH_2COOH]$$

$$v = K_1K_2\frac{[AcO_2H][HNO_3][Ac_2O]}{[AcOH]^2}\ k_1 + \left(\frac{k_1k_3k_4}{k_5}\right)^{\frac{1}{2}}[AcOH]^{\frac{1}{2}}$$

This rate equation agrees with the above observation, although the latter form corresponding to the induced decomposition is somewhat obscure.

The unimolecular decomposition (Eq 4) should be ca. 17% in the total decomposition of peracetic acid in view of the yield of methane in Table 2, since methane is supposed to be produced only from peracetyl nitrate. Assuming a cage reaction:

$$\mathrm{AcO_2NO_2} \rightarrow (\mathrm{CH_3\cdot \cdot CO_2 \cdot \cdot ONO_2}) \rightarrow \mathrm{CH_3ONO_2} + \mathrm{CO_2}$$

more carbon dioxide should be evolved than methane at a low concentration of peracetic acid, when both methane and carbon dioxide are produced from peracetyl nitrate. However, this is not the case (Table 2). The other 83% decomposition of peracetic acid, i.e., AcO_2NO_2, may be due to the induced decomposition. Induced decompositions other than Eq. 7 are also conceivable:

$$\mathrm{CH_3COO_2NO_2} + \mathrm{\cdot CH_2COOH} \rightarrow \mathrm{CH_3CO_2\cdot} + \mathrm{O_2NOCH_2COOH} \qquad (7')$$

$$\mathrm{CH_3COO_2NO_2} + \mathrm{CH_3\cdot} \rightarrow \mathrm{CH_3CO_2CH_3} + \mathrm{\cdot ONO_2} \qquad (9)$$

If the reaction of Eq. 7′ occurs to a considerable extent, the amount of methane should increase with an increase of the concentration of peracetic acid, because the high concentration of peracetic acid increases the induced decomposition. However, the amount of methane is almost constant and independent of the concentration of peracetic acid, and hence Eq. 7′ is improbable. The possibility of Eq. 9 cannot be excluded, but as the amount of methane is almost equal to that of carbon dioxide at low concentration of peracetic acid (i.e., low concentration of $CH_3COO_2NO_2$), it is considered that the contribution of Eq. 9 is small.

More carbon dioxide is produced than methane at higher concentration of peracetic acid or in the presence of an oxidizable substance. This means that a certain amount of carbon dioxide is formed by a pathway other than the unimolecular decomposition of peracetyl nitrate.[4] If formic acid is added at the start of reaction, slightly more carbon dioxide than methane is evolved. As oxalic acid does not show such a tendency (runs 10 and 11 in Table 2), carbon dioxide may be produced from formic acid. In fact, considerable amounts of formic acid are formed at higher concentration of peracetic acid, while only small amounts are formed at lower concentration. It is not obvious how formic and oxalic acids are formed, but may be assumed that oxalic acid is formed by oxidation of glycolic acid. Formic acid may be formed by the following process:

$$\begin{array}{l} \mathrm{AcO_2NO_2} + \mathrm{CH_3\cdot} \rightarrow \mathrm{AcOCH_3} + \mathrm{\cdot ONO_2} \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad \mathrm{AcOH} + \mathrm{HCO_2H} \end{array} \qquad (10)$$

Such a decomposition induced by $CH_3\cdot$ would produce CO_2 at high concentration of peracetic acid, i.e., at high concentration of AcO_2NO_2.

The presence of radical $CH_3\cdot$ is probable in view of the evolution of methane from the reaction mixture. Since $CH_3\cdot$ is very active and its life is very short, the coupling reaction of $CH_3\cdot$ with other radicals may be negligible.

The existence of radical $\cdot CH_2COOH$ was confirmed by the following method. If the reaction was carried out in the presence of carbon tetrachloride, monochloracetic acid is produced, which is considered to be formed by chlorine abstraction by $\cdot CH_2COOH$ from carbon tetrachloride.

There is no direct evidence for the presence of a nitrogen trioxide radical. Probable attacking species other than the above radicals are nitrogen dioxide or trioxide, but since the properties of $\cdot NO_3$ are little known,[3] there is no simple method to distinguish between $\cdot NO_2$ and $\cdot NO_3$. But as nitrous acid is not detected in the reaction mixture and the abstraction of hydrogen from acetic acid with $\cdot NO_2$ should be slower than that with $\cdot NO_3$, $\cdot NO_2$ is not considered as an attacking species.

The relative rates of H atom abstraction by $CH_3\cdot$ against the abstraction of Cl atom from carbon tetrachloride at 100° are 0·75 for toluene, 4·8 for cyclohexane and 11·1 for chloroform.[4] The results of our competitive reaction suggest the existence of some radical which has a lower selectivity than $CH_3\cdot$. This radical may be $\cdot NO_3$.

EXPERIMENTAL

Materials. Commercial AcOH and Ac_2O were fractionated, b.p. 117·5–118·0° and 139·0°, respectively. HNO_3 was of guaranteed grade. Peracetic acid was prepared from Ac_2O and 60% H_2O_2.[4] The concentration of peracetic acid and acetyl peroxide was 3·70–3·74 N, and acetyl peroxide was less than 3% for total peroxide.

Kinetic measurements. An AcOH soln containing Ac_2O and HNO_3 of a known concentration was thermostated at 50° in a flask and the decomposition was started by adding peracetic acid. Aliquots were taken at appropriate intervals of time and poured into ice-cold KI aq (0·5%, 100 ml). Immediately, peracetic acid was titrated with 1/100N Na_2SO_3. Acetyl peroxide in this mixture was warmed for 20–30 min at 50° in order to convert to peracetic acid and was titrated with 1/100N Na_2SO_3.

Gas analysis. Gas was identified by GLC (column: SiO_2 for CO_2, SiO_2 and MS5A for CH_4 and others). CO_2 was absorbed in 30% KOH aq and was estimated by its weight increase. CH_4 was measured by a gas burette after the absorption of CO_2.

Liquid analysis. Formic acid was identified by the Nessler reagent. Any aldehyde present would be oxidized by peracetic acid and hence, only formic acid would give a positive test with Nessler reagent. Oxalic acid was identified by the colour reaction (red) of manganese sulfate.[6] Glycolic acid in the reaction soln was identified by chromatography (developer: phenol–H_2O–HCOOH, R_f: 0·60).[7] Formic and oxalic acids were estimated by titration with $KMnO_4$ aq. The content of nitrous acid was estimated by the absorbance of its aqueous soln at 535 mμ after its conversion to diazonium salt and coupling with sulphanilic acid and then α-naphthylamine. Virtually no nitrous acid was detected.

Reaction of substrates. The GLC analysis for the identification of products was carried out using a column (column: 12 g of PEG 20M, column length: 2 m, carrier gas: H_2, column temp,: 140°).

Competitive reaction. The competitive reactions of cyclohexane, toluene, chloroform and carbon tetrachloride were carried out at two initial concentrations. Remaining substrates were estimated by GLC (column: Apiezon greese, column length: 2 m, carrier gas: N_2). The results are shown in Table 3.

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