Kinetics of the Acid-Catalyzed Decomposition of Trimeric Acetone Peroxide

By Yoshiaki FURUYA and Yoshiro OGATA

(Received November 24, 1962)

Both dimeric and trimeric acetone peroxides explode violently on shock, but they are considerably stable in a solution of organic solvents. In the presence of strong acids, however, these peroxides decompose comparatively fast. Thus far the kinetics of the decomposition of acetone peroxide in solutions have not yet been studied. The present report summarizes our investigation on the kinetics of the sulfuric acid-catalyzed decomposition of trimeric acetone peroxide in acetic acid.

Experimental

Materials. — Trimeric acetone peroxide (abbreviated as TAPO) was prepared by Wolffenstein's method(1) by the reaction of acetone with aqueous hydrogen peroxide containing a small amount of phosphoric acid as catalyst for two or three weeks, and the obtained product was recrystallized from methanol and then from ether, m. p. 97°C, the yield was 80.4%.

---

1) K. Wolffenstein, *Ber.*, **28**, 2265 (1895).

The Criterion of the Reaction Products.—Trimeric acetone peroxide was dissolved in acetic acid containing a known amount of sulfuric acid. The solution was kept standing at 30°C for 30 min.; the solution of the reaction mixture was developed with a mixture of diethyl ether and ethyl acetate (1 : 4 $^{v}/_{v}$) on Toyo Filter Paper No. 54 which was preliminarily treated with a mixture of acetic acid (300 g.), acetic anhydride (80 g.) and zinc chloride (20 g.)[2]. A pink spot was observed by spraying with methanolic solution of 3% *p*-dimethylaminoaniline dihydrochloride. The value of R_f was found to be 0.77, which corresponded to that of peroxyacetic acid.

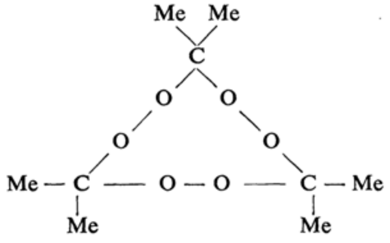
Produced peroxyacetic acid liberated iodine from potassium iodide instantaneously, while the acetone peroxide and acetyl peroxide reacted with aqueous potassium iodide very slowly as shown in Table I; hence peroxyacetic acid could be estimated by iodometry. Aliquots (each 5 ml.) of the reaction solution were poured into 100 ml. of an ice-cooled aqueous solution containing ca. 0.1% potassium iodide, iodine liberated by the reaction with peroxyacetic acid being titrated with 0.01 N sodium thiosulfate.

A solution of 0.005 M TAPO in acetic acid containing 0.18 N sulfuric acid was kept standing for one hour and it was confirmed that the reaction was complete after one hour. Acetone formed by decomposition of TAPO was detected and estimated by gas chromatography. The blank test showed that the concentration of acetone in acetic acid was proportional to the corresponding chromatogram area.

TABLE I. THE RATE OF REACTION OF TAPO (5 ml. OF 0.005 M SOLUTION) WITH AQUEOUS POTASSIUM IODIDE EXPRESSED AS THE CONSUMPTION OF 0.01 N SODIUM THIOSULFATE SOLUTION

Time, min.	2	3	7	13	∞
Consumed 0.01 N $Na_2S_2O_3$, ml.	0.03	0.03	0.13	0.20	14.96

The concentrations of peroxyacetic acid and acetone in two samples taken out from a reaction solution at the same time were found to be 0.0138 and 0.0132 M, respectively; hence it is reasonable that the decomposition of TAPO gives the same molar concentrations of peroxyacetic acid and acetone. Therefore, the stoichiometric equation of this acid-catalyzed decomposition may be written as follows:



$$+3CH_3CO_2H \xrightarrow{H_2SO_4} 3CH_3COCH_3+3CH_3CO_3H$$

A Typical Run for the Rate Measurements.—After a solution of 49 ml. of 0.0051 M TAPO in acetic acid in a stoppered flask had attained the temperature equilibrium at 20°C, the reaction was started by the addition of 1 ml. of 9 N sulfuric acid in acetic acid. Aliquots (each 5 ml.) were taken out at appropriate time intervals and each aliquot was poured into an ice-cooled 100 ml. solution of ca. 0.1% potassium iodide. Iodine liberated by peroxyacetic acid was quickly titrated with 0.01 N sodium thiosulfate solution to estimate the concentration of peroxyacetic acid.

Results and Discussion

The rate followed the first-order equation with TAPO, although a short induction period was observed, especially when the reaction was slow. The first-order rate constants were shown in Table II. The plot of log *k* vs. acidity function H_0 gave a straight line with a slope of -1.12 as shown in Fig. 1. The energy of activation was calculated to be 19.14

TABLE II. THE RATE CONSTANTS FOR THE DECOMPOSITION OF TAPO TO PEROXYACETIC ACID IN ACETIC ACID WITH VARYING INITIAL CONCN. OF TAPO AT 20°C WITH ACIDITY FUNCTION OF -1.55

Initial concn. of TAPO, M	3×10^{-3}	5×10^{-3}	7×10^{-3}	10×10^{-3}
$k\times10^4$ sec^{-1}	3.99	3.93	4.05	4.07

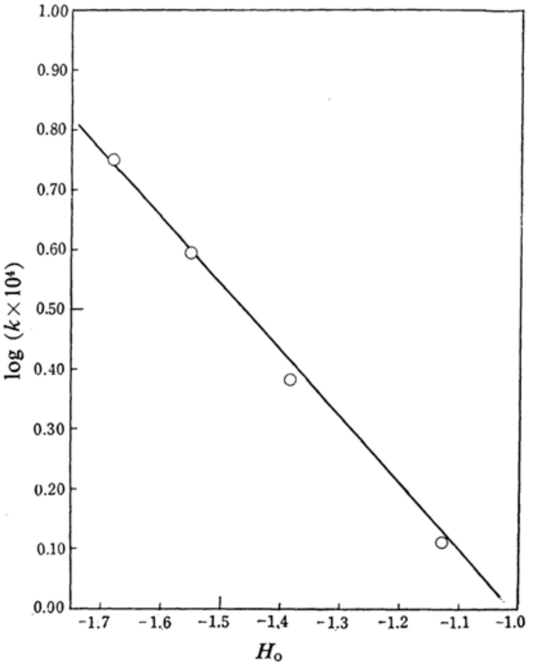


Fig. 1. The plots of log *k* *vs* H_0 for the decomposition of TAPO in acetic acid at 20°C.
Initial concn. of TAPO: 5×10^{-3} M

---

[2] J. Janoušek, *Faserforsch. u. Textiltech.*, **8**, 339 (1957).

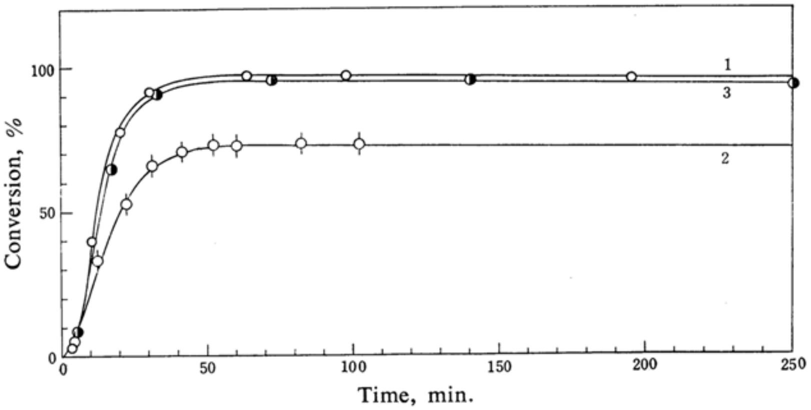


Fig. 2. A typical run for the reaction of TAPO in acetic acid at 30°C.

	Initial concn. of TAPO, M	Concn. of H_2SO_4, N	Concn. of added acetone, M
1	0.005	0.18	—
2	0.05	0.18	—
3	0.005	0.18	0.015

kcal./mol. from the average values of $k\times10^4$ sec^{-1} at 20°C, 1.29; at 25°C, 2.53; at 30°C, 3.88 and at 35°C, 6.99 in a solution with acidity function of -1.13.

Since the reaction has an induction period, it may be autocatalytic or consecutive. If the reaction were autocatalytic, the reaction would be accelerated on addition of the decomposition products or reaction mixture, but this was not observed; i. e., peroxyacetic acid, acetone or reaction mixture did not promote the reaction. Furthermore, the induction period was not affected by the addition of either trinitrobenzene, *p*-benzoquinone or Fenton's reagent. Therefore, these radical sources or radical-trapping agents do not seem to play an important role at least in the early stages of this decomposition reaction, but it is propable that the reaction is consecutive and it may go by way of any metastable intermediate.

It is of interest to note that an increase of the initial concentration of TAPO resulted in a decrease of the ultimate yield of peroxyacetic acid. For example, two solutions with initial concentrations of 0.005 M and 0.05 M TAPO, each containing 0.18 N sulfuric acid, were kept standing for 60~100 min. at 30°C until no production of peroxyacetic acid was observed. The amount of acetone in this resulting solution was estimated by gas chromatography, which showed that the reaction, irrespective of the concentration of TAPO, was 100% complete. But the amount of peroxyacetic acid measured iodometrically was only 74.0% of the theoretical with a solution of 0.05 M TAPO, while a solution of 0.005 M TAPO gave 97.0%. This phenomenon is not due to the reversibility of the reaction, since the "apparent equilibrium constants" calculated varied considerably with the change of the concentration of TAPO and added acetone, as shown in Table III, and the addition of acetone had no effect on the rate as obvious in Fig. 2.

TABLE III. THE VARIATION OF "APPARENT EQUILIBRIUM CONSTANTS" WITH THE CHANGE OF INITIAL CONCENTRATION OF TAPO IN ACETIC ACID SOLUTION WITH 0.18 N H_2SO_4

Concn. of TAPO, M	Concn. of acetone added, M	Equilibrium const.
0.005	None	6.32×10^{-8}
0.05	None	1.43×10^{-9}
0.005	0.015	2.58×10^{-5}

As reported previously[3], the phenomenon may be explained by the transformation of the produced peroxyacetic acid into acetyl peroxide, the extent of the transformation being increased with increasing concentration of peroxyacetic acid.

$$CH_3CO_3H+CH_3CO_2H$$
$$\rightleftharpoons CH_3CO\text{-}O_2\text{-}COCH_3+H_2O$$

As shown in Fig. 2, the plot of conversion vs. time gives a slight maximum which suggests the transformation of peroxyacetic acid. Moreover, the paper chromatography of the reaction mixture afforded a spot corresponding to peroxyacetic acid $R_f=0.77$, at 30 min. as stated above, while it gave spots with the R_f values of 0.75 and 0.85, corresponding to peroxyacetic

---

[3] Y. Ogata, Y. Furuya, J. Maekawa and K. Okano, *J. Am. Chem. Soc.*, in press.

acid and acetyl peroxide, respectively[3] at 300 min. The spot corresponding to acetyl peroxide was more remarkable as the concentration of peroxyacetic acid was increased.

Summary

It was confirmed by the iodometry and gas chromatography that one mole of TAPO in acetic acid was decomposed to three moles of acetone and peroxyacetic acid in the presence of sulfuric acid. The rate of the reaction satisfied the first-order equation with a short induction period. The plot of $\log k$ vs. H_0 gave a straight line with a slope of -1.12. When the concentration of TAPO was high, the amount of peroxyacetic acid was not quantitative, probably because of the transformation of peroxyacetic acid into acetyl peroxide.

Department of Applied Chemistry
Faculty of Engineering
Nagoya University
Chikusa-ku, Nagoya