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Kinetic Studies of the Oxidation of Benzils with Peroxyacetic Acid in Acetic Acid

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The oxidation of benzils with peroxyacetic acid in the presence of sulfuric acid in acetic acid has been studied kinetically. The rate of the consumption of peroxyacetic acid has been found to be the sum of the four terms shown in the following equation:

$$-\mathrm{d}[\mathrm{AcO_2H}]/\mathrm{d}t = \{k_d + k_t[\mathrm{H_2SO_4}]\}[\mathrm{AcO_2H}] + \{k_2+k_2'[\mathrm{H_2SO_4}]\}[\mathrm{Bz_2}][\mathrm{AcO_2H}]$$

It is considered that the first and second terms correspond to the decomposition of peroxyacetic acid itself and to the acid-catalyzed reversible transformation of peroxyacetic acid to acetyl peroxide, while the third and fourth terms represent, respectively, the non- and the acid-catalyzed oxidations of benzils with peroxyacetic acid. In both non- and acid-catalyzed oxidations, a probable mechanism passing through benzoic anhydride is postulated.

When the α-diketones are treated with oxidizing agents, such as hydrogen peroxide,(1) potassium periodate(2) and peroxyacetic acid,(3) the corresponding carboxylic acids are obtained. One mechanism of the reaction has already been discussed(1) briefly on the basis of the synthetic results. The present authors have now followed the reaction of benzils with peroxyacetic acid by iodometry and will here discuss a probable mechanism.

Experimental

Materials. Peroxyacetic acid was prepared by the reaction of acetic anhydride with hydrogen peroxide in the presence of sulfuric acid.(4) The benzils were prepared by means of the benzoins(5) obtained from the

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1) J. E. Leffler, *J. Org. Chem.*, **16**, 1785 (1951).

2) V. J. Shiner and C. R. Wasmuth, *J. Am. Chem. Soc.*, **81**, 37 (1959).

3) J. Böeseken and G. Slooff, *Rec. trav. chim.*, **49**, 91 (1930).

4) T. W. Findley, D. Swern and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 413 (1945).

5) R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, p. 94 (1956).

corresponding aldehydes, and were then recrystallized from methanol; benzil,[6] mp 95.5—96°C (lit., 94—95°C); *p*-tolil,[7] mp 103—104°C (lit., 104—105°C); *p*-anisil,[8] mp 133.5—134°C (lit., 133°C). Benzoic anhydride was recrystallized from a mixture of benzene and petroleum ether; mp 43—43.5°C. Benzoic acid was recrystallized from water; mp 122.5—123°C.

Reaction Products Criterion. A mixture (20 m*l*) of benzil (0.1 M), peroxyacetic acid (0.5 M), and sulfuric acid (0.2 N) in acetic acid was heated at 70°C for 10 hr, and then allowed to stand 2 days at room temperature. The reaction mixture was poured into water (100 m*l*). The product extracted with chloroform (30 m*l*) was identified as benzoic acid by the mixed-melting-point method; yield 90%, mp and mmp 122—122.5°C. The evolution of oxygen gas during the reaction was found by means of gas chromatography employing a Hitachi gas chromatograph, model KGL-2A, operated with a 3-m column packed with molecular sieve 13X and using helium with a flow rate of 25 m*l*/min at 38°C. The retention time was 2.5 min for oxygen and 3.2 min for nitrogen. The formation of acetyl peroxide was observed by paper chromatography under the same conditions as have been previously reported.[9]

Typical Run for the Rate Measurements. A solution of 1 m*l* of *ca.* 1 M peroxyacetic acid in acetic acid was poured into a solution of 9 m*l* of 0.11 M benzil in acetic acid to start the reaction after the two solutions had attained a temperature equilibrium at 70°C. Aliquots (each 1 m*l*) were taken out at appropriate time intervals and introduced to 100 m*l* of an ice-cooled aqueous solution of *ca.* 0.06% potassium iodide. The iodine liberated by peroxyacetic acid was quickly titrated with 0.01 N sodium thiosulfate in order to estimate the concentration of the remaining peroxyacetic acid.

Results and Discussion

The initial rate of the reaction satisfied the first-order equation in the concentration of the remaining peroxyacetic acid, as is illustrated in Table 1.

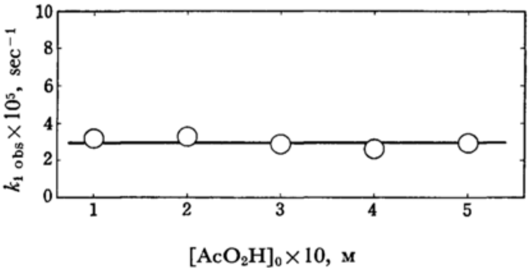

Fig. 1. Plots of $k_{1\,\mathrm{obs}}$ *vs.* initial concentration of peroxyacetic acid in acetic acid at 70°C.
Initial concn. of benzil: 0.1 M
Concn. of H_2SO_4: 0.12 N

The $k_{1\,\mathrm{obs}}$ rate constant with a varying initial concentration of peroxyacetic acid kept a settled

$$-\mathrm{d}[\mathrm{AcO_2H}]/\mathrm{d}t = k_{1\,\mathrm{obs}}[\mathrm{AcO_2H}]$$

value, as is shown in Fig. 1. As is illustrated in

TABLE 1. TYPICAL RATE DATA FOR THE CONSUMPTION OF PEROXYACETIC ACID IN THE OXIDATION OF BENZIL WITH PEROXYACETIC ACID IN ACETIC ACID AT 70°C
Nominal initial concn. of CH_3CO_3H: 1×10^{-1} M
Concn. of $(C_6H_5CO)_2$: 1×10^{-1} M
Concn. of H_2SO_4: 3.0×10^{-2} N

Time min	$(a-x)\times10^2$ M	$\frac{a}{a-x}$	$k_{1\,\mathrm{obs}}\times10^5$ sec^{-1}
0	10.06	1.000	
60	9.28	1.084	2.25
120	8.59	1.170	2.18
180	7.90	1.273	2.23
240	7.23	1.391	2.29
300	6.67	1.508	2.28
360	6.10	1.648	2.31
420	5.59	1.799	2.33
480	5.13	1.960	2.34
			Av. 2.28

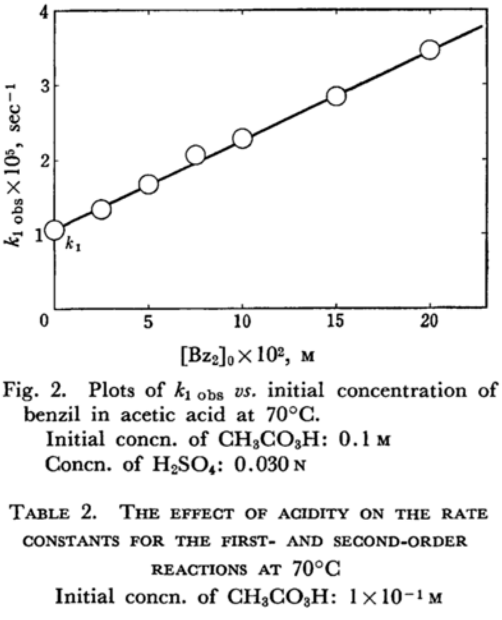

Fig. 2. Plots of $k_{1\,\mathrm{obs}}$ *vs.* initial concentration of benzil in acetic acid at 70°C.
Initial concn. of CH_3CO_3H: 0.1 M
Concn. of H_2SO_4: 0.030 N

TABLE 2. THE EFFECT OF ACIDITY ON THE RATE CONSTANTS FOR THE FIRST- AND SECOND-ORDER REACTIONS AT 70°C
Initial concn. of CH_3CO_3H: 1×10^{-1} M

$[H_2SO_4]$ M	$-H_0$[10]	$k_1\times10^5$ sec^{-1}	$k_{2\,\mathrm{obs}}\times10^4$ M^{-1}sec^{-1}
0	—	0.74 $(=k_d)$[a]	1.00 $(=k_2)$[a]
0.015	0.72	1.07	1.19
0.04	1.18	1.74	1.48
0.06	1.37	1.94	1.83
0.08	1.50	2.51	2.09
0.10	1.60	2.96	2.23

a) The values of k_d and k_2 were estimated by extrapolation in Fig. 3.

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6) H. T. Clarke and E. E. Dreger, "Organic Syntheses," Coll. Vol. I, p. 87 (1956).
7) R. Stierlin, *Ber.*, **22**, 376 (1889).
8) M. Bösler, *ibid.*, **14**, 323 (1881); A. T. Mason and L. A. Dryfoos, *J. Chem. Soc.*, **63**, 1300 (1893).
9) Y. Ogata, Y. Furuya, J. Maekawa and K. Okano, *J. Am. Chem. Soc.*, **85**, 961 (1963).

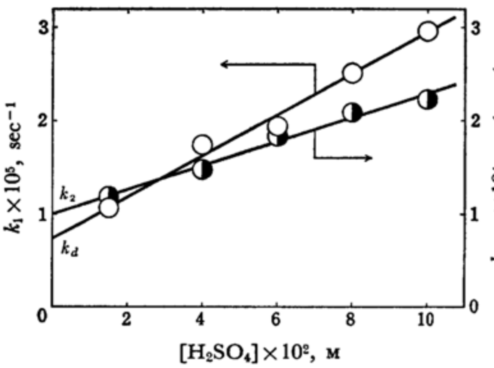

Fig. 3. Effect of the acidity of medium on the rate constants at 70°C.

Initial concn. of CH_3CO_3H: 0.1 M

Fig. 2, however, the plots of $k_{1\,\mathrm{obs}}$ *vs.* the initial concentration of benzil gave a straight line, which satisfied the following equation:

$$k_{1\,\mathrm{obs}} = k_1 + k_{2\,\mathrm{obs}}[Bz_2]$$

The plots of k_1 and $k_{2\,\mathrm{obs}}$ *vs.* the concentration of sulfuric acid gave straight lines, as Table 2 and Fig. 3 show; these lines followed the accompanying equations, respectively:

$$k_1 = k_d + k_t[H_2SO_4]$$

and $$k_{2\,\mathrm{obs}} = k_2 + k_2'[H_2SO_4]$$

The plots of $\log(k_1-k_d)$ and $\log(k_{2\,\mathrm{obs}}-k_2)$ *vs.* H_0[10] gave straight lines with slopes of −0.94 and −0.95 respectively (Fig. 4). From these results, it may be considered that the proton participates once before the rate-determining step in both the acid-catalyzed first-order and second-order reactions.

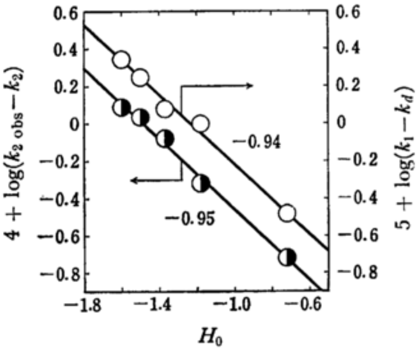

Fig. 4. Plots of $\log(k_1-k_d)$ and/or $\log(k_{2\,\mathrm{obs}}-k_2)$ *vs.* H_0 in acetic acid at 70°C.

Finally, the rate equation is expressed as:

$$-\mathrm{d}[AcO_2H]/\mathrm{d}t = \{k_d + k_t[H_2SO_4]\}[AcO_2H] + \{k_2 + k_2'[H_2SO_4]\}[Bz_2][AcO_2H]$$

TABLE 3. SUBSTITUENT EFFECT FOR THE OXIDATION OF BENZIL WITH PEROXYACETIC ACID IN ACETIC ACID AT 70°C

Initial concn. of CH_3CO_3H: 1×10^{-1} M

Benzils	$k_2\times10^5$ M^{-1}sec^{-1}	$k_2'\times10^3$ M^{-2}sec^{-1}
Benzil	10.0	1.29
p-Tolil	3.2	2.45
p-Anisil	1.5	2.81

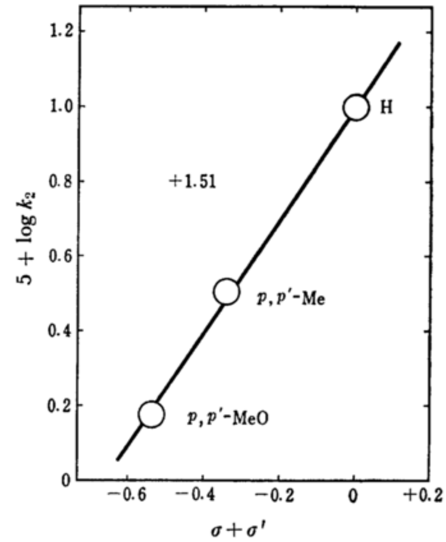

Fig. 5. Hammett plots for the non-catalyzed oxidation of substituted benzil to the corresponding benzoic acid in acetic acid at 70°C.

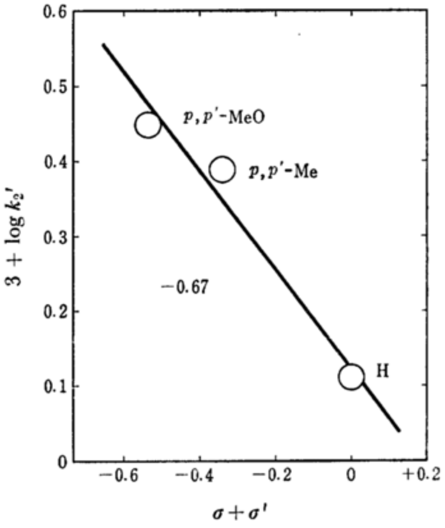

Fig. 6. Hammett plots for the acid-catalyzed oxidation of substituted benzil in acetic acid at 70°C.

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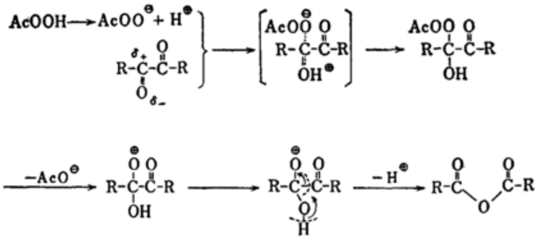
[10] N. F. Hall and W. F. Spengeman, *J. Am. Chem. Soc.*, **62**, 2487 (1940).

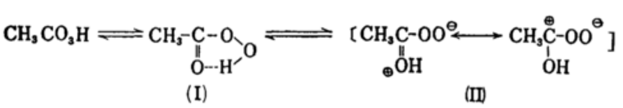
It may be considered from the reaction products that the first, second, third, and fourth terms represent the decomposition of peroxyacetic acid itself,[11] the acid-catalyzed reversible transformation of peroxyacetic acid to acetyl peroxide,[9] and the non-catalyzed and the acid-catalyzed oxidation of benzils with peroxyacetic acid respectively. In this paper, only the third and fourth terms have been dealt with.

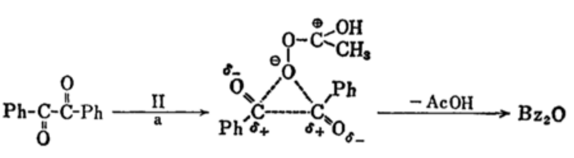
The introduction of an electron-releasing group into the benzil retarded the non-catalyzed oxidation of benzil and accelerated the acid-catalyzed oxidation (Table 3), and Hammett's plot gave positive and negative ρ-values of $+1.51$ and -0.67 respectively, as shown in Fig. 5 and/or 6.

On the oxidation of benzil with hydrogen peroxide in benzene, Leffler obtained an oily matter which gave benzoic acid by hydrolysis.[1] Thus, a reaction mechanism passing through acid anhydride has been suggested. The reaction scheme in Leffler's fashion is described as:



The mechanism consists of three steps, such as the addition of peroxyacetic acid to the carbonyl group of benzil, the elimination of the acetoxy anion from the adduct, and the deprotonation. Neither the step 1 nor 2 is the rate-determining step in this reaction, since the step 1 is the protonation and the step 2 should have a $-\rho$ value. Only the deprotonation could satisfy the experimental results shown in Fig. 5. It has not been confirmed by Leffler that the deprotonation is the rate-determining step. For these reasons, Leffler's scheme is unbelievable. A more probable mechanism is considered to be as follows:



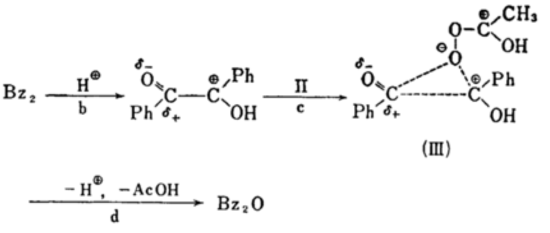


From the results such as the second-order in the concentrations of benzil and peroxyacetic acid and/or the positive ρ-value in the Hammett plots of $\log k_2$ *vs.* $\sigma+\sigma'$, the step a is probably the rate-determining step in the non-catalyzed oxidation of benzil with peroxyacetic acid, and the non-catalyzed oxidation is probably a nucleophilic attack by negative oxygen of peroxyacetic acid, II. If the reaction is an electrophilic attack of peroxyacetic acid, I, the value of ρ must be negative.

On the other hand, it is presumed that protonation to a substrate occurs once before the rate-determining step in the acid-catalyzed oxidation, as has been described above. In fact, the absorption maximum of benzil in acetic acid at 260 mμ decreases with an increase in the acidity. This phenomenon is probably due to the protonation to the carbonyl group of benzil.

Also, the acid-catalyzed reaction is probably a nucleophilic attack of peroxyacetic acid, II, because the k_2'/k_2 ratio is nearly 10. As the positivity on the carbonyl carbon in protonated benzil is much larger than that in free benzil induced by only the polarity of the C–O bond of the carbonyl group, the rate of the acid-catalyzed reaction will be ten times larger than the non-catalyzed one. A nucleophilic attack on the positive carbonyl carbon atom of free or protonated benzil by positive oxygen of peroxyacetic acid can not be considered. The existence of protonated benzil was observed by the ultraviolet spectrophotometry described above.

These results suggest this probable mechanism in the acid-catalyzed oxidation of benzil:



If the deprotonation determines the reaction, Hammett's plot of $\log k_2'$ *vs.* $\sigma+\sigma'$ is expected to give a positive ρ-value. It cannot be supposed that the elimination of acetic acid from the transition state, III, is influenced by a substituted group on the benzene ring. The step c probably determines the reaction rate.

The negativity of a carbonyl oxygen atom in benzil is increased by an electron-releasing group. Thus, the concentration of protonated benzil is enlarged with an increase in the electron-releasing degree. In other words, the equilibrium constant, K, for the protonation to benzil is enlarged with an increase in the electron-releasing force.

$$Bz_2 + H^{\oplus} \overset{K}{\rightleftharpoons} Bz_2H^{\oplus}$$

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[11] T. Suzuki, I. Iwamoto and S. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 1212 (1962).

$$Bz_2H^{\oplus} + AcO_2H \xrightarrow{k}$$

$$[Bz_2H^{\oplus}] = K[H^{\oplus}][Bz_2]$$

$$v_{(acid\ cat)} = k[Bz_2H^{\oplus}][AcO_2H]$$

$$= kK[H^{\oplus}][Bz_2][AcO_2H]$$

$$\therefore\ k_2' = kK$$

On the other hand, the rate constant, k, for the reaction of protonated benzil with peroxyacetic acid may decrease with an increase in the electron-releasing degree, since the positivity of a carbonyl carbon atom in protonated benzil will be decreased by an electron-releasing group. However, the proportion of the diminution in the positivity of carbonyl carbon in protonated benzil caused by an electron-releasing group is not so great as to have a considerable influence upon the reaction rate. Thus, the influence of a substituent on the equilibrium constant, K, may be much larger than that on the k rate constant. Consequently, the acid-catalyzed rate constant, k_2', which is equal to the product of k by K, will be increased by an electron-releasing group with a Hammett ρ-value of -0.67. By means of these hypotheses, the kinetic findings can be explained without difficulty.

The value of $3\times10^{-3}\,\mathrm{sec}^{-1}$ was obtained as the rate constant for the hydrolysis of benzoic anhydride in the presence of 0.027 N sulfuric acid at 70°C. The value divided by the calculated concentration of water in the reaction solvent is about two hundred times larger than the value of $k_{2\,obs}$ obtained under the same reaction conditions. Hence, the step of the hydrolysis of benzoic anhydride is undoubtedly not the rate-determining step.

The oxidation is a sort of Baeyer-Villiger reaction.

The non- and acid-catalyzed oxidations may be summarized as follows: