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PARTICIPATION OF BOTH HNO_2^+ AND NO_2 IN NITRIC ACID OXIDATION. II BENZOIN IN 40% DIOXAN[1]

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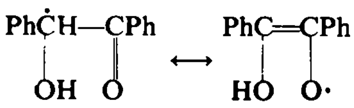
Abstract—The nitric acid oxidation of benzoin has kinetically been studied in 40% dioxan at 90°. The rate is independent of both concentrations of nitric and nitrous acids, and is expressed as $v = k$ [benzoin]. The reaction is acid-catalyzed and the plot of log k *vs* H_0 gives a straight line ($k = k_a h_0 + k_b$) with a slope of *ca* $-0{\cdot}6$, implying participation of both HNO_2^+ and NO_2 as attacking species. The Arrhenius plot gives the values of 10 and 30 kcal/mol as apparent activation energies for k_a and k_b, respectively. The oxidation mechanism is discussed.

THE kinetic study on the nitric acid oxidation of diphenylmethane and triphenylmethane[2] suggested the participation of free nitrogen dioxide, $NO_2^{\cdot}$ besides protonated nitrogen dioxide, $HNO_2^{+\cdot}$ as attacking species in view of the effect of acidity. This behaviour is different from that of benzyl ether[3] and benzaldehyde.[4] The attack of NO_2 which is less effective than $HNO_2^{+\cdot}$ as a H atom abstractor may be caused by the higher stability of intermediate radical due to the presence of phenyl groups.

Therefore, it is expected that benzoin may also give a more stable radical intermediate because of the delocalizability of odd electrons by the benzoyl group as follows:



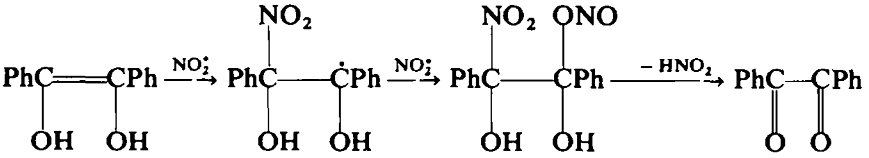
$$\underset{\displaystyle OH}{Ph\dot{C}H}-\underset{\displaystyle \| \atop O}{CPh} \longleftrightarrow \underset{\displaystyle HO}{PhC}=\underset{\displaystyle O\cdot}{CPh}$$

It has been known that nitric acid oxidation of benzoin gives benzil. But the mechanism was uncertain and several pathways were conceivable, e.g., α-H atom abstraction or enolization of benzoin. It was also unknown whether the enol of benzoin was directly attacked by HNO_3 itself as observed in tetracyclone,[5] or whether it undergoes addition of NO_2 as in olefins with NO_2.[6]

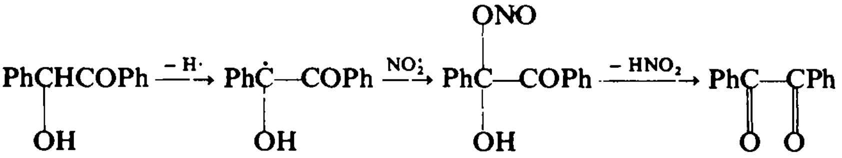
The present paper is a mechanistic study on the nitric acid oxidation of benzoin, which may involve H atom abstraction with both HNO_2^+ and NO_2 as has been observed in the oxidation of diphenylmethane and triphenylmethane.[2]

RESULTS AND DISCUSSION

The reaction of benzoin with N_2O_4. If benzoin is converted into benzil via enolization, the following pathways may be considered: (a) a direct attack of nitric acid itself as Yates *et al.* have suggested,[5] (b) addition of nitrogen dioxide to the enol double bond. The former path is improbable in view of the presence of an inducation period in the oxidation of benzoin with pure nitric acid as shown later. However, the rate equation alone cannot discriminate between pathways (1b) and (1c).



(1b)



(1c)

In order to distinguish these two pathways, reaction of benzoin with N_2O_4 was attempted in acetic acid at room temperature. The results are shown in Table 1. It is known that enolization of benzoin is too fast to measure in aqueous acetic acid even at 0°.[7] The reaction of olefins with NO_2 is fairly fast.[6] But benzoin was transformed into benzil only with 16% at room temperature for 5 hr. If the reaction goes via addition of NO_2 (Eq. 1b), the reaction will go to completion under our experimental conditions.[6]

A small amount of a strong acid such as sulfuric acid enhances the reaction and the conversion amounts to 51%. This acid catalysis does not agree with path (1b). A similar result was observed with diphenylmethane which is probably oxidized via H-abstraction alone (Table 1). Hence, the acid catalysis is explained by path (1c) where α-hydrogen is abstracted by protonated nitrogen dioxide.

TABLE 1. CONVERSION AND EFFECT OF ACID IN THE OXIDATION OF SUBSTRATES WITH NO_2 IN ACETIC ACID AT ROOM TEMPERATURE (20°)[a]

Substrate	$[H_2SO_4]$, M	Conversion %[b]
PhCH(OH)COPh	0	16
PhCH(OH)COPh	0·035	51
Ph_2CH_2	0	15
Ph_2CH_2	0·035	43

[a] Initial concentration: $[NO_2]$ = *ca* 0·3 M, [PhCH(OH)COPh] = 0·046 M, $[Ph_2CH_2]$ = 0·050 M.

[b] The values after 5 hr.

The oxidation rate of benzoin with some nitrogen oxides, is independent of enolization of benzoin.

Nitric acid oxidation of benzoin in aqueous dioxan. Benzoin was easily oxidized with 2·0 M nitric acid containing a small amount of nitrous acid in 40% dioxan at 90°. In excess nitric acid, a plot of $\log(a/a-x)$ *vs* time gave a straight line (a = initial concentration of benzoin and x = concentration of benzil). First-order rate constants obtained are shown in Table 2. Nitric acid concentration affects the solution acidity with which the first-order rate constant increases. But if the rate constant is corrected to those at $H_0 = 0$ by means of equation: $\log k_{corr} = \log k + 0{\cdot}6\, H_0$, the first-order constants hold nearly constancy and independent of nitric acid concentration as shown in Table 2.

TABLE 2. FIRST-ORDER RATE CONSTANTS AT VARIOUS INITIAL CONCENTRATIONS OF REACTANTS IN THE NITRIC ACID OXIDATION OF BENZOIN IN 40% DIOXAN AT 90°[a]

$[HNO_3]$, M	[PhCH(OH)COPh], M	$10^5\ k$, sec^{-1}
2·0	0·040	7·85
2·0	0·030	7·92
2·0	0·020	8·05
0·20[b]	0·030	7·78[c]
0·40[b]	0·030	7·52[c]
0·60[b]	0·030	7·91[c]
1·0[b]	0·030	7·48[c]

[a] Initial concentration: $[NaNO_2] = 0{\cdot}01$ M.
[b] In the presence of 2·0 M H_2SO_4.
[c] The values compared at $H_0 = 0$.

Effect of nitrous acid and other added compounds is shown in Table 3. The rate is independent of nitrous acid concentration. The induction period without added compounds is short in 2 M nitric acid, and the efficiency of initiation of added compounds is obscure. When benzoin was oxidized with 0·20 M nitric acid in the presence

TABLE 3. EFFECT OF ADDED COMPOUNDS IN THE NITRIC ACID OXIDATION OF BENZOIN IN 40% DIOXAN AT 90°[a]

$[NHO_3]$, M	Added compd	Concn, M	Induction period, min	$10^5\ k$, sec^{-1}
2·0	$NaNO_2$	0·005	2	8·05
2·0	$NaNO_2$	0·010	2	7·92
2·0	$NaNO_2$	0·015	2	7·95
2·0[b]	$NaNO_2$	0·010	2	9·95
2·0	None	—	20	8·05
2·0	B.P.O.[c]	0·005	35	7·95
2·0	Resorcin	0·01	6	7·82
2·0	H_2Q[d]	0·01	16	7·60
0·20[e]	None	—	75	10·4
0·20[e]	$NaNO_2$	0·01	20	10·4
0·20[e]	H_2Q[d]	0·0046	10	11·1
0·20[e]	Resorcin	0·0045	38	10·1
0·20[e]	B.P.O.[c]	0·005	57	10·2

[a] Initial concentration: [PhCH(OH)COPh] = 0·030 M.
[b] The value in 60% dioxan.
[c] Benzoyl peroxide.
[d] Hydroquinone.
[e] In the presence of 2·0 M H_2SO_4.

of 2·0 M sulfuric acid, a long induction period of 75 min appeared (Table 3). Nitrous acid, hydroquinone and resorcin are effective initiators, while benzoyl peroxide is less effective. Hence, nitric acid itself cannot be the attacking species. The initiation effected by hydroquinone and resorcin may be due to their ready oxidation with nitric acid to form nitrous acid.[2]

In general, nitrous acid in the system increases as the oxidation proceeds, but the increase is often irregular.

Effect of acidity of solution. The oxidation of benzoin is enhanced by increased acidity of the solution. Plot of log k *vs* H_0 gave a straight line with a slope of a fractional number, $-0{\cdot}6$ instead of -1. The similar results were obtained in the nitric acid oxidation of diphenylmethanes and triphenylmethane in 60% dioxan.[2] The apparent first-order rate constant is the sum of terms which are dependent and independent of h_0, i.e., $k = k_a h_0 + k_b$. The value of k_b is estimated from an intercept of a plot of k *vs* h_0 as reported previously with triphenylmethane.[2] A plot of log $(k - k_b)$ *vs* H_0 gave a straight line with a slope of *ca* -1. The value of log $(k - k_b)$ at $H_0 = 0$ is that of log k_a.

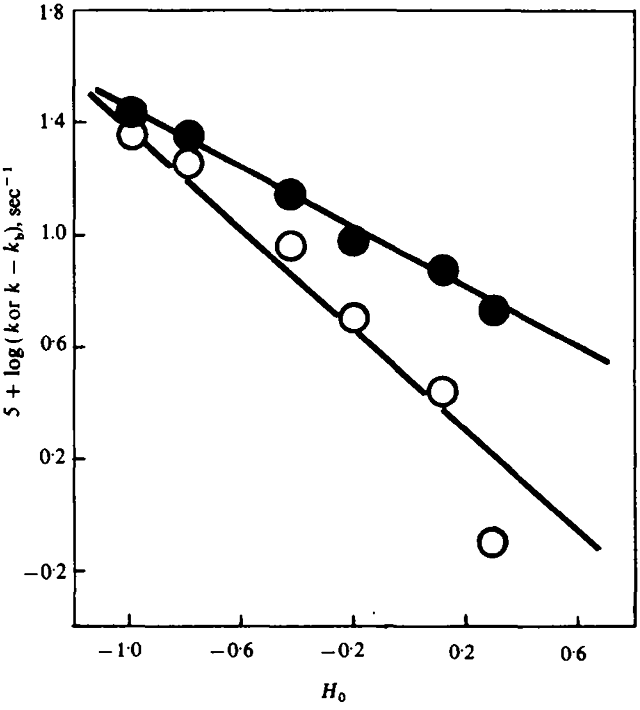


FIG. 1 Effect of acidity in the nitric acid oxidation of benzoin in 40% dioxan at 90°: Initial concentration: [PhCH(OH)COPh] = 0·030 M, [HNO_3] = 1·33 M, [$NaNO_2$] = 0·01 M, [H_2SO_4] = 0 – 2·4M. ● Plot of log k *vs* H_0; ○ Plot of log $(k - k_b)$ *vs* H_0.

Effect of temperature. The rate is expressed as $v = (k_a h_0 + k_b)$ [substrate] as in the case of triphenylmethane etc,[2] where k_a and k_b correspond to the attacks of HNO_2^+ and NO_2, respectively. It is said that a protonated radical species is more powerful than a neutral radical in the H-abstraction,[8] and it has less activation energy.[8] In the present reaction, activation energy of k_a is smaller than that of k_b as shown in Fig 2. The acidity effect of solution was measured at 80°, 85°, 90° and 95°, and k_a and k_b were obtained by means of the same treatment as shown in the previous section. The results are shown in Table 4. Arrhenius plots for k_a, k_b and k (Fig 2) give apparent energies of activation (kal/mol) of 10 for k_a, 30 for k_b and 23·4 for k.

TABLE 4. TEMPERATURE EFFECT ON k, k_a AND k_b IN THE NITRIC ACID OXIDATION OF BENZOIN IN 40% DIOXAN[a]

Temp °C	$5 + \log k_a$, sec^{-1}	$10^5 k_b$, sec^{-1}	$5 + \log k_b$, sec^{-1}
95	0·6	6·6	0·82
90	0·5	4·6	0·66
85	0·5	2·5	0·40
80	0·3	1·4	0·15

[a] Initial concentration: $[HNO_3] = 1{\cdot}33$ M, $[NaNO_2] = 0{\cdot}01$ M, [PhCH(OH)COPh] = 0·030 M, $[H_2SO_4] = 0$–1·4 M.

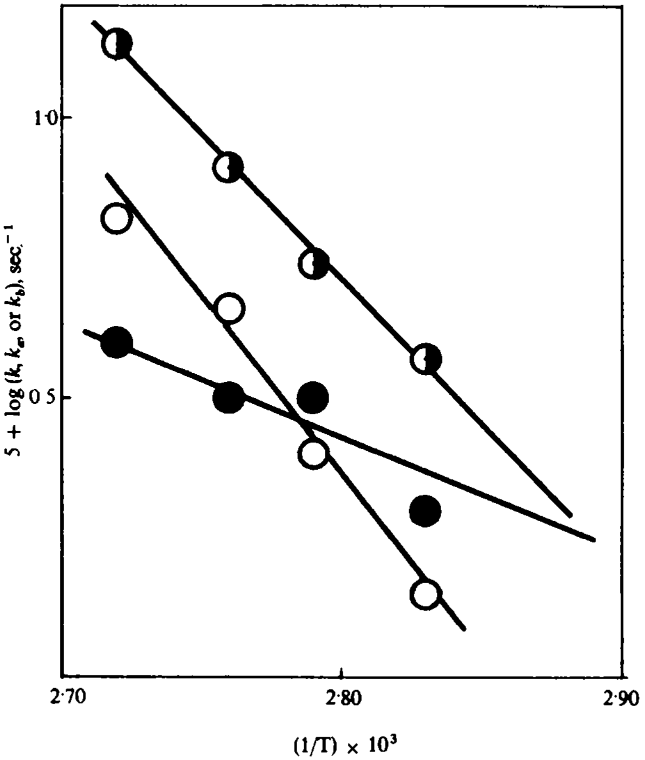


FIG. 2 Arrhenius plot for k, k_a and k_b in the nitric acid oxidation of benzoin in 40% dioxan. ◐, k; ●, k_a; ○, k_a.

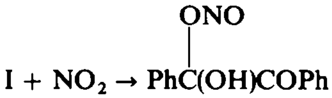
Mechanism. These facts lead to a probable scheme for the nitric acid oxidation of benzoin as follows.

$$HNO_3 + HNO_2 \overset{K_1}{\rightleftarrows} 2\,NO_2^{\cdot} + H_2O \tag{1}$$

$$H^+ + NO_2^{\cdot} \overset{K_2}{\rightleftarrows} HNO_2^{+\cdot} \tag{2}$$

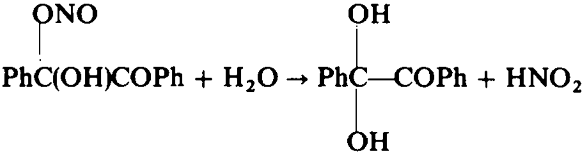
$$\mathrm{PhCH(OH)COPh + HNO_2^{+}} \xrightarrow{k_3} \underset{\mathrm{I}}{\mathrm{PhC(OH)COPh}} + \mathrm{H_2NO_2^{+}} \qquad (3)$$

$$\mathrm{PhCH(OH)COPh + NO_2^{\cdot}} \xrightarrow{k_4} \mathrm{I + HNO_2} \qquad (4)$$



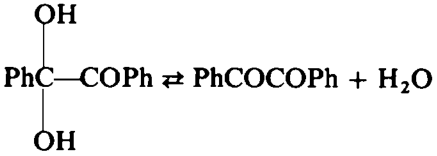
$$\mathrm{I + NO_2 \rightarrow Ph\overset{ONO}{\overset{|}{C}}(OH)COPh}$$

(5)



$$\mathrm{Ph\overset{ONO}{\overset{|}{C}}(OH)COPh + H_2O \rightarrow Ph\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}{-}COPh + HNO_2}$$

(6)



$$\mathrm{Ph\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}{-}COPh \rightleftarrows PhCOCOPh + H_2O}$$

(7)

If steps 3 and 4 are rate-determining, the rate is expressed as $v = (k_3K_2[H^+] + k_4)$ $[\mathrm{NO_2}][\mathrm{PhCH(OH)COPh}]$. The observed first-order rate constant, k, corresponds to $(k_3K_2[H^+] + k_4)[\mathrm{NO_2}]$. Hence, k depends on the concentration of $\mathrm{NO_2}$, but the concentration of $\mathrm{NO_2}$ may be nearly constant at the stationary state, since the increased nitrogen dioxide with the reaction easily vaporizes out of the system.[3, 4] The k value increases in the solvent containing more organic component because of its higher solubility of $\mathrm{NO_2}$;[3, 4] for example, the k value in 60% dioxan is larger than that in 40% dioxan in spite of the higher acidity in 40% dioxan than in 60% dioxan (Table 3). The observed k_a and k_b values correspond to k_3K_2 $[\mathrm{NO_2}]$ and k_4 $[\mathrm{NO_2}]$ respectively. The apparent energy of activation in k_a was smaller than that in k_b as described above. Here, k_a contains equilibrium constant, K_2, and the temperature effect in k_a also contains that in K_2. But the change of K_2 with temperature seems to be small, since the difference between log K^{950} and log K^{809} is considered to be very small in equation, $\ln K = -\Delta H/RT + \text{const.}$

Finally, the delocalizability of the intermediate radical by the benzoyl group will render $\mathrm{NO_2}$, a species less reactive than $\mathrm{HNO_2^{+}}$, to participate in the oxidation.

EXPERIMENTAL

Materials. Benzoin and benzil were purified by recrystallization from MeOH; benzoin, m.p. 136–137°, lit.[9] 137°; benzil, m.p. 96·5°, lit.[9] 96·5°. The absorbances at peak wave lengths in MeOH were as follows: benzoin, $\lambda_{\max}$, 247 mμ (log ε 4·08); benzil, $\lambda_{\max}$, 260 mμ (log ε 4·25).

Kinetic procedure. The rate for the nitric acid oxidation of benzoin to benzil was measured by means of UV spectrophotometry at $\lambda = 249$ and 260 mμ.

Acidity function was measured by using *o*-nitroaniline as an indicator as reported.[2] Nitrous acid was determined as shown previously.[3, 4]

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