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PARTICIPATION OF BOTH HNO_2^+ AND NO_2 IN NITRIC ACID OXIDATION—I

DIPHENYLMETHANES AND TRIPHENYLMETHANE IN 60% DIOXAN[1]

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Abstract—The effect of solution acidity on the rate of the nitric acid oxidation of diphenylmethanes and triphenylmethane in 60% dioxan has been studied. The plot of log k (first-order rate constant for the substrate) *vs* H_0 (acidity function) gave a straight line with a slope of fractional number between − 0·5 and − 0·6. This suggests that the rate constant can be expressed as $k = k_a h_0 + k_b$ and that both nitrogen dioxide and its conjugate acid participate in the reaction as attacking species. It was observed that a polar substituent in the benzene ring mainly affected k_a in the nitric acid oxidation of diphenylmethanes. The mechanism of reaction of these benzyl compounds is discussed.

IN OUR kinetic study[2] of the nitric acid oxidation of diphenylmethane we reported that the kinetic order with respect to h_0 (acidity function) is approx. 1 in 70% acetic acid. Further study[3] revealed that in 60% dioxan, the order of h_0 was between 0·5 and 0·6. We have also attempted to study precisely whether a similar acidity effect is observed in triphenylmethane and benzoin[4] as a basis for the elucidation of the mechanism.

RESULTS AND DISCUSSION

Effect of nitric acid concentration

Nitric acid oxidation of triphenylmethane is said to give triphenylcarbinol quantitatively.[5] In fact, triphenylcarbinol was isolated in a yield of 95%, when triphenylmethane was oxidized with 1·0 M nitric acid in 60% dioxan at 90° for 8 hr. The pseudo-first-order rate constants in excess nitric acid (in the rate equation, $v = k[Ph_3CH]$) are given in Table 1. The k value rises with increase of nitric acid concentra-

TABLE 1. FIRST-ORDER RATE CONSTANTS FOR THE NITRIC ACID OXIDATION OF TRIPHENYLMETHANE IN 60% DIOXAN AT 90°[a]

$[HNO_3]$, M	$[H_2SO_4]$, M	$10^5\,k$ (sec^{-1})	$10^5\,k^b_{corr}$ (sec^{-1})	H_0
1·0	0	7·8	—	—
2·0	0	26·8	—	—
1·0	0·40	12·5	26	0·54
0·80	0·40	9·1	25	0·73
0·60	0·40	7·8	26	0·87
0·40	0·40	6·4	26	1·00

[a] Initial concentration: $[NaNO_2] = 0{\cdot}01$ M, $[Ph_3CH] = 0{\cdot}050$ M

[b] The corrected k value for those at $H_0 = O$

tion owing to the accompanying increase in acidity, but the k value at constant acidity ($H_0 = 0$) is nearly constant (Table 1). Hence, the rate is independent of nitric acid concentration. The initial concentration of triphenylmethane could not be varied greatly because of its poor solubility in aqueous dioxan, but the kinetic order with respect to the substrate should be unity.

Effect of acidity

The oxidation of triphenylmethane was accelerated by increased solution acidity in similar way to diphenylmethane.[2] The plot of log k *vs* H_0 gave a straight line with a slope of fractional number, −0·6, implying that the rate constant can be expressed as summation of first- and zeroth-orders in h_0. Consequently, the plot of log k *vs* h_0 gave a straight line (Fig 1), and hence k can be expressed as follows: $k = k_a h_0 + k_b$. Here, k_b is determined from the intercept of the line at $h_0 = 0$. A plot of log $(k - k_b)$ *vs* H_0 gave a straight line with a slope of approx −1 (Fig 2).

TABLE 2. EFFECT OF ACIDITY ON RATE OF NITRIC ACID OXIDATION OF TRIPHENYLMETHANE IN 60% DIOXAN AT 90°[a]

$10^5\,k$ (sec^{-1})	$10^5\,(k - k_b)^b$ (sec^{-1})	$5 + \log(k - k_b)^b$ (sec^{-1})	H_0
7·9	3·1	0·49	0·84
10·0	5·2	0·71	0·68
12·5	7·7	0·89	0·54
18·4	13·6	1·13	0·26
23·3	18·5	1·27	0·15

[a] Initial concentration: [HNO_3] = 1·0 M, [$NaNO_2$] = 0·01 M, [H_2SO_4] = 0 − 1·0 M, [Ph_3CH] = 0·050 M.

[b] $10^5\,k_b$ = 4·8 as shown in Fig 1

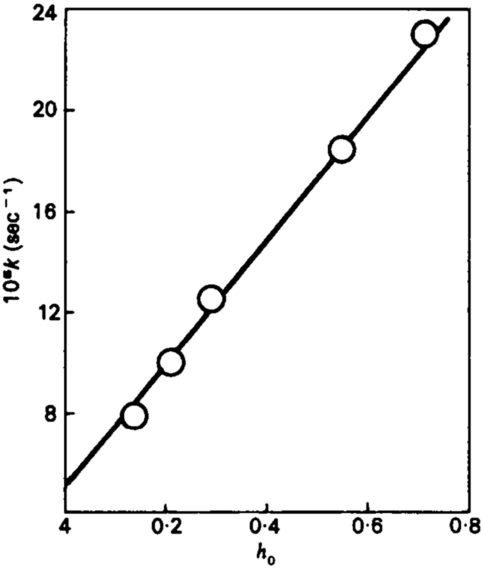


FIG 1. Plot of 10^5 k *vs* h_0 in the nitric acid oxidation of triphenylmethane in 60% dioxan at 90°. Initial concentration: [HNO_3] = 1·0 M, [$NaNO_2$] = 0·01 M, [H_2SO_4] = 0 − 1·0 M, [Ph_3CH] = 0·050 M.

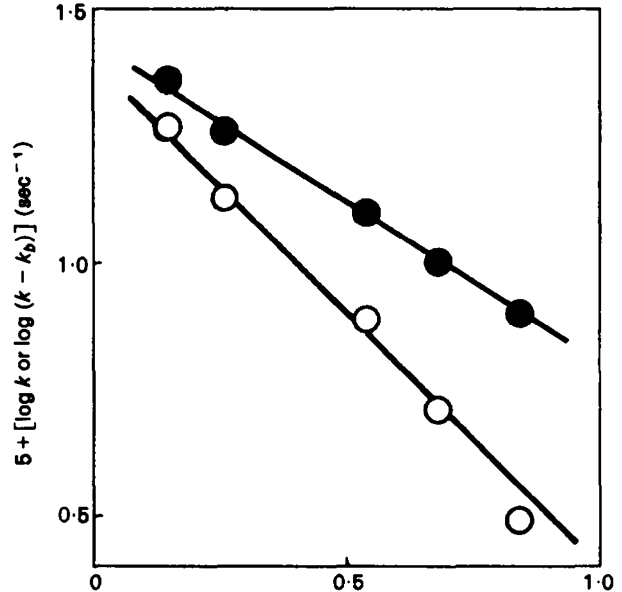


FIG 2. Effect of acidity on rate of the nitric acid oxidation of triphenylmethane in 60% dioxan at 90°. Initial concentration: $[Ph_3CH] = 0{\cdot}050$ M, $[HNO_3] = 1{\cdot}0$ M, $[H_2SO_4] = 0 - 1{\cdot}0$ M, $[NaNO_2] = 0{\cdot}01$ M. ●, Plot of log k vs H_0; ○, Plot of log $(k - k_b)$ vs H_0.

The nitric acid oxidation of diphenylmethane in 70% acetic acid gave an order in h_0 of unity,[2] but this order dropped to 0·5 in 60% dioxan for unsubstituted and some substituted diphenylmethanes. It is more difficult in aqueous acetic acid to keep $[NO_2]$ constant than in 60% dioxan, since stable acetic acid does not reduce nitric acid to nitrous acid. Hence, the observed acidity effect in 60% dioxan may be more reliable than that in 70% acetic acid. When the acidity effect in the nitric acid oxidation of diphenylmethane in 60% dioxan was estimated similarly, the plot of log $(k - k_b)$ vs H_0 gave a straight line with a slope of approx −1 (Fig 3). The values of k_a, *i.e.* the value of log $(k - k_b)$ at zero H_0 in Fig 3, together with the value of k_b are shown in Table 3.

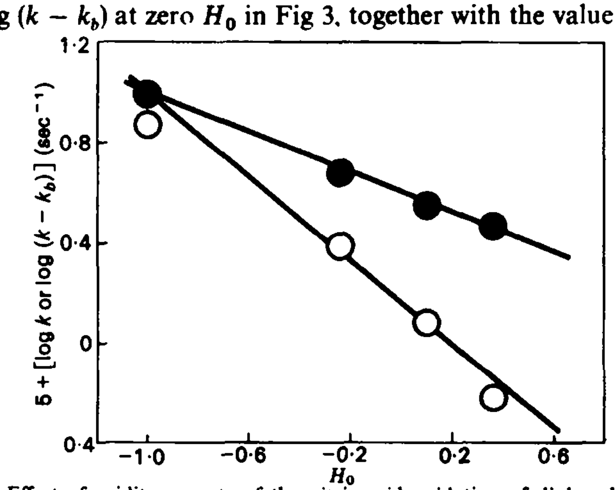
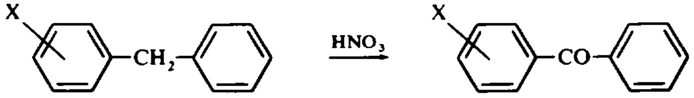


FIG 3. Effect of acidity on rate of the nitric acid oxidation of diphenylmethane in 60% dioxan at 90°. Initial concentration: $[HNO_3] = 1{\cdot}40$ M, $[NaNO_2] = 0{\cdot}02$ M, $[H_2SO_4] = 0 - 2{\cdot}4$ M, $[Ph_2CH_2] = 0{\cdot}050$ M. ●, Plot of log k vs H_0; ○, Plot of log $(k - k_b)$ vs H_0.

TABLE 3. RATE CONSTANTS FOR THE NITRIC ACID OXIDATION OF DIPHENYLMETHANES IN 60% DIOXAN AT 90°[a]



X	(5 + log k_a) (sec^{-1})	(5 + log k_b) (sec^{-1})	10^5 k_b (sec^{-1})
p-Me	1·0	0·32	2·1
m-Me	0·5	0·60	4·0
H	0·2	0·36	2·3
p-Cl	0·2	0·30	2·0

[a] Initial concentration: $[HNO_3] = 1{\cdot}40$ M, $[NaNO_2] = 0{\cdot}01$ M. $[H_2SO_4] = 0-2{\cdot}40$ M, $[ArCH_2Ph] = 0{\cdot}050$ M.

The Hammett plot for k_a is shown in Fig 4, giving a ρ-value of -2, which is fairly large and comparable to the ρ-value for the nitric acid oxidation of benzyl ethers.[6] The values of k_b are nearly constant except for that of *m*-methyldiphenylmethane.

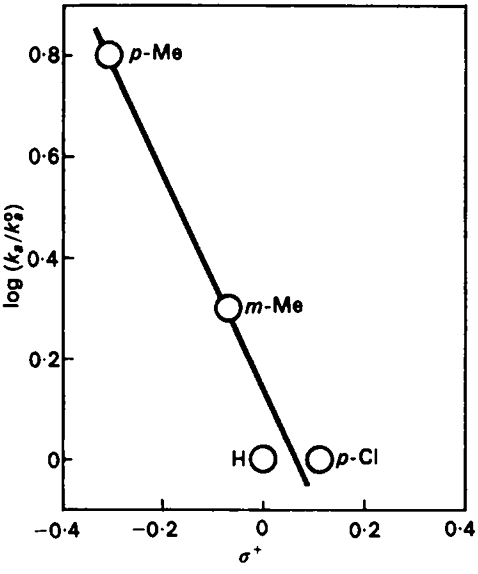


FIG 4. Substituent effect on k_a in the nitric acid oxidation of diphenylmethanes in 60% dioxan at 90°.

These observations suggest an overall mechanism for the reaction:

$$\mathrm{HNO_3 + HNO_2 \overset{K}{\rightleftarrows} 2NO_2 + H_2O} \tag{1}$$

$$\mathrm{H^+ + NO_2 \overset{K_2}{\rightleftarrows} H\dot{N}O_2^{+\cdot}} \tag{2}$$

$$\mathrm{RH + HNO_2^{+\cdot} \xrightarrow{k_3} R\cdot + H_2NO_2^+} \tag{3}$$

$$\mathrm{RH + NO_2^{\cdot} \xrightarrow{k_4} R\cdot + HNO_2} \tag{4}$$

$$\mathrm{R\cdot + NO_2 \rightarrow RONO \xrightarrow{H_2O} ROH + HNO_2}\ \text{etc.} \tag{5}$$

$$\mathrm{R = Ph_2CH\text{-}\ or\ Ph_3C\text{-}}$$

As reported previously,[6, 7] the concentration of NO_2 is determined by the solvent composition and it is nearly constant during a run. The above mechanism leads to a rate law:

$$v = (k_3K_2[H^+] + k_4)[NO_2][RH]$$

In these cases, the observed k, k_a, and k_b correspond to $(k_3K_2[H^+] + k_4)[NO_2]$, $k_3K_2[NO_2]$, and $k_4[NO_2]$ respectively. The oxidation involves a hydrogen atom abstraction, and the selectivity (ρ-value) of the abstraction increases with an increase of electrophilicity of the attacking species.[6, 8] In the hydrogen atom abstraction, the transition-state is said to be as follows:[9]

$$RH + \cdot X \rightarrow [R:H\cdot X \leftrightarrow R^+ H:X^-] \rightarrow R\cdot + HX$$

It is known that substituents on the benzene ring affect the ionization potential of a breaking C—H bond though they have little effect on the bond-dissociation energy.[10] Hence, in the present reaction, a polar substituent seems to affect mainly k_a, *i.e.* k_3K_2, since the transition-state is more polar with protonated species HNO_2^+. NO_2 is said to be electrophilic radical, but its electron affinity is rather small.[11]

It is suggested that NO_2 participates in this oxidation besides HNO_2^+ (conjugate acid of NO_2) as shown in the scheme. In this respect, the present oxidation is different from that of benzyl ethers[6] and benzaldehydes,[7] which involve hydrogen atom abstraction by HNO_2^+ alone. The qualitative order of decreasing reactivity per hydrogen atom on the basis of k values is as follows: $PhCH_2OH > Ph_3CH$[3] $>$ $PhCH_2OCH_3$[4] $>$ Ph_2CH_2[2, 3] $\sim$ PhCHO.[5]

It should be explained here why the less powerful species, NO_2, may participate in the oxidation of diphenylmethane, which is less reactive than benzyl methyl ether. This can be considered as follows. The reactivity of benzyl compounds may be influenced by two factors, *i.e.* (i) the energy of a one electron transfer from the formed radical to the attacking radical and (ii) the stability of the intermediate radical, which is probably related to bond dissociation energy, assuming the resemblance between the activated-complex in the energy-reaction coordinate profile and the intermediate radical. For example, the rates for benzyl methyl ether, *i.e.* α-methoxytoluene, and diphenylmethane, *i.e.* α-phenyltoluene, are much higher than that of toluene:[2, 3, 12] both methoxy and phenyl groups raise the reactivity of substrates. Methoxy group is not so effective for lowering bond energy; the bond dissociation energies of C—H for ethane and ethanol are 98 and 90 kcal/mol, respectively.[13] However, the reactivity of benzyl methyl ether seems to depend mainly on the energy of one electron-transfer. This is generally equated with the ionization potential of the radical formed. An electron-releasing group lowers the ionization potential,[10] and this may account for the enhanced oxidation. Delocalization of the odd electron over the phenyl group of diphenylmethane may stabilize the intermediate radical and lower the bond dissociation energy of α-C—H, resulting in an effective abstraction of hydrogen atom even with NO_2.

The rate for the nitric acid oxidation of benzyl compounds is generally expressed as $v = (k_ah_0 + k_b)[RH]$. In the oxidation of benzyl alcohol, benzyl ether and benzaldehyde, $k_ah_0 \gg k_b$, while in that of diphenylmethane and triphenylmethane, $k_ah_0 \sim k_b$. k_a and k_b may be related to the energy of one electron-transfer and the stability of intermediate radical, respectively.

EXPERIMENTAL

Materials. Triphenylmethane was prepared by Friedel–Crafts reaction of benzene with carbon tetrachloride.[14] Substituted diphenylmethanes were prepared as reported previously.[3] Triphenylmethane had m.p. 93·5–94°, lit[15] 92·5–93°.

Kinetic procedure. The reaction was initiated by the addition of $NaNO_2$ aq to the thermostated reaction mixture. At appropriate time intervals, aliquots were removed, and extracted with chloroform, containing a given amount of benzophenone as an internal standard, and washed with aq NaOH. The extract was dried over anhydrous Na_2SO_4, and the rate of disappearance of triphenylmethane was measured by GLC, using a flame ionization detector operated with a 1 m × 3 mm column packed with PEG 20 M 5% on Chamelite at 200°.

Identification of products. Triphenylmethane (1·17 g) was oxidized with 1 M nitric acid in 60% dioxan at 90° for 8 hr and gave triphenylcarbinol, 1·19 g (95%) which on recrystallization from MeOH gave the pure material, m.p. 163–164°, lit[16] 164°.

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