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KINETICS OF THE NITRIC ACID OXIDATION OF SUBSTITUTED DIPHENYLMETHANES[1]

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Abstract—The nitric acid oxidation of substituted diphenylmethanes has been kinetically studied in 70 vol % aqueous acetic acid and in 60 vol % aqueous dioxan at 90°. The Hammett's plot for the substituent effect correlates to σ^+ rather than σ, giving a negative ρ-value of $-1{\cdot}7$ in 70 vol % aqueous acetic acid and $-1{\cdot}2$ in 60 vol % aqueous dioxan.

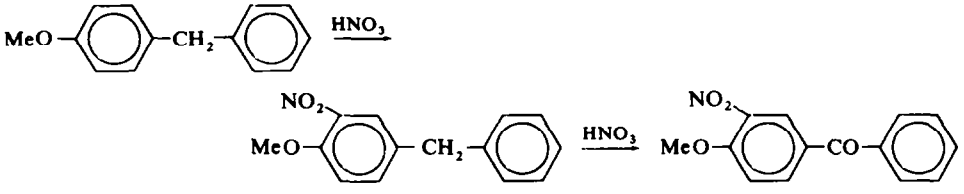
IN a previous paper,[2] a mechanism proposed for the kinetics of the nitric acid oxidation of diphenylmethane involves a rate-determing step of α-hydrogen abstraction from diphenylmethane by protonated nitrogen dioxide (HNO_2^+).

The present paper reports the effect of a substituent on the nitric acid oxidation rate of diphenylmethanes.

RESULTS AND DISCUSSION

Substituent effect. Substituted diphenylmethanes were oxidized to the corresponding substituted benzophenones with dilute (2·5 ~ 3·0 M) nitric acid containing a small amount of nitrous acid. The first-order rate constant k was measured in 70 vol % aqueous acetic acid and 60 vol % aqueous dioxan as shown in Table 1.

In the reaction of *p*-methoxydiphenylmethane, nitration occurred before oxidation to give 3-nitro-4-methoxybenzophenone. Since *p*-methoxybenzophenone was not nitrated under the same conditions, this reaction must proceed via the following steps.



Hence, the rate of oxidation of *p*-methoxydiphenylmethane without nitration could not be measured.

Table 1 shows that electron-releasing groups in the substrate accelerate the oxidation, while electron-attracting groups retard it. The substituent effect satisfies the Hammett equation as illustrated in Fig. 1 (in aqueous acetic acid as solvent) and Fig. 2 (in aqueous dioxan).

In the nitric acid oxidation of aromatic hydrocarbons, a similar substituent effect has been observed,[3] i.e. in the nitric acid oxidation of substituted xylenes, electron-attracting groups retard the rate. Crandall *et al.*[3] have reported that the oxidation

rate was affected only by the inductive effect of the substituents. However, it was found that the rate of oxidation of diphenylmethanes was affected by both inductive and resonance effects, which is obvious in the comparison of the *para* (inductive + resonance) value with the *meta* (inductive alone) value in Figs 1 and 2. The value of $\log(k/k_0)$ is correlated to σ^+ rather than to σ, probably because diphenylmethane, in contrast to substituted xylenes,[3] involves no ortho effect.

The Hammett's plot gives different ρ values (calculated by the least-square method) depending on the solvents used for the oxidation, i.e. $-1{\cdot}7$ in 70 vol % acetic acid and $-1{\cdot}2$ in 60 vol % dioxan. The explanation for this is as follows. A main factor of the polar effect for the H atom abstraction is the electron affinity of an attacking radical, i.e. the selectivity in the H atom abstraction is governed by the electrophilicity of the attacking radical,[4] since the transition state is more polar a more effective substituent effect is expected. In general, an attacking radical is less sensitive to the polar effect on hydrogen abstraction (i.e. smaller absolute value of ρ) in complexing solvents.[5,6] It is known that NO_2^+ is solvated in dioxan and its electrophilicity should decrease;[7] hence the ρ value in dioxan should be lower than the ρ value in acetic acid. On the other hand, this type of solvation would be poor in acetic acid because of its poor basicity. Therefore, a higher electrophilicity of attacking radical is expected in aqueous acetic acid.

TABLE 1. SUBSTITUENT EFFECT ON THE NITRIC ACID OXIDATION OF SUBSTITUTED DIPHENYLMETHANES AT 90°
Initial conc.: [Diphenylmethane] = 0·05 M, [$NaNO_2$] = 0·02 M

Substituent	10^5k, sec^{-1} in AcOH aq.[a]	10^5k, sec^{-1} in dioxan aq.[b]
p-Me	45·5	15·5
m-Me	34·2	9·00
H	13·8	4·79
p-Cl	12·2	4·70
m-Cl	—	1·07
m-NO_2	—	0·891
p-NO_2	0·783	1·11

[a] In 70 vol % acetic acid [HNO_3] = 2·5M
[b] In 60 vol % dioxan [HNO_3] = 3·0M

Effect of acidity. The rate of nitric acid oxidation of diphenylmethane was first-order with respect to h_0 (acidity function) in 70 vol % acetic acid, although in our recent study with unsubstituted diphenylmethane, the plot of log k *vs* $-H_0$ gave a slope of 0·9 by means of least squares. The effect of acidity was further studied with some substituted diphenylmethanes in both 70 vol % acetic acid and 60 vol % dioxan. The plot of log k *vs* $-H_0$ gave straight lines with slopes of 0·5–0·6 with *p*-methyl- and *p*-chlorodiphenylmethane, where k is the rate constant in the rate equation: $v = k$-[diphenylmethane]. It is suggested that not only HNO_2^+ but also NO_2^+ may attack diphenylmethane, but at present, the further discussion is difficult.

The rate constant k_1 is higher in aqueous dioxan than in aqueous acetic acid, when the comparison is made at the same acidity function. This may be due to the high

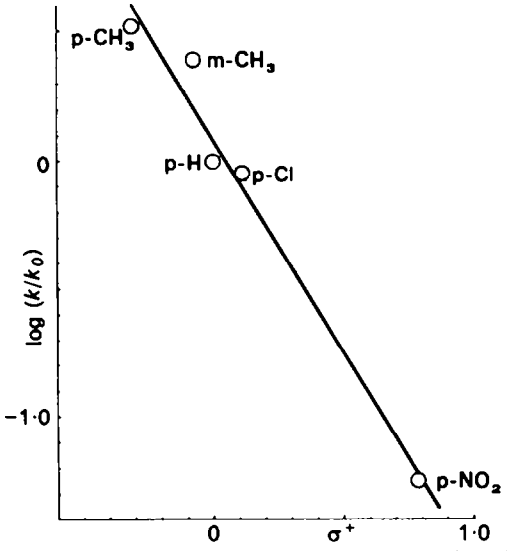


FIG. 1. Hammett's plots for the relative rates of nitric acid oxidation of diphenylmethanes in 70 vol% acetic acid. Initial conc.: $[ArCH_2Ph] = 0{\cdot}050M$, $[HNO_3] = 2{\cdot}5$ M $[NaNO_2] = 0{\cdot}02$ M

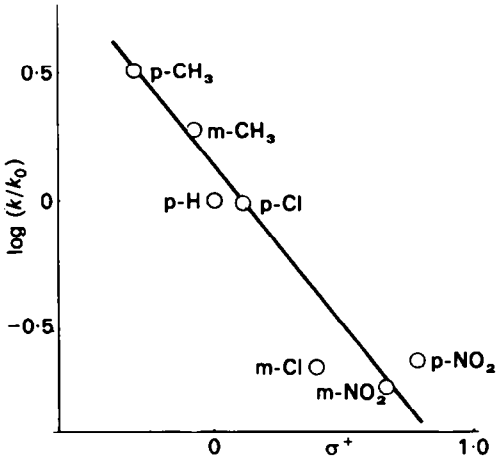


FIG. 2. Hammett's plots for the relative rates of nitric acid oxidation of diphenylmethanes in 60 vol. % dioxan.
Initial conc.: $[ArCH_2Ph] = 0{\cdot}05$ M, $[HNO_3] = 3{\cdot}0$ M, $[NaNO_2] = 0{\cdot}02$ M

solubility of NO_2^+ in aqueous dioxan and the observation that dioxan reacts with nitric acid to give nitrous acid.[2]

The mechanism of the reaction may be expressed as follows:

$$HNO_3 + HNO_2 \overset{K_1}{\rightleftharpoons} 2NO_2^+ + H_2O \quad (1)$$

$$NO_2^+ + H^+ \overset{K_2}{\rightleftharpoons} HNO_2^{2+} \quad (2)$$

$$Ar_2CH_2 + HNO_2^{2+} \overset{k_3}{\rightarrow} Ar_2\dot{C}H + H_2NO_2^+ \quad (3)$$
(I)

$$Ar_2CH_2 + NO_2^{\ddagger} \overset{k_4}{\rightarrow} \underset{(I)}{Ar_2\dot{C}H} + HNO_2 \quad (4)$$

$$Ar_2\dot{C}H + NO_2^{\ddagger} \rightarrow Ar_2CH(ONO) \quad (5)$$

$$Ar_2CH(ONO) + H_2O \rightarrow Ar_2CH(OH) + HNO_2 \quad (6)$$

$$Ar_2CH(OH) + HNO_2^{\ddagger} \text{ (or } NO_2^{\ddagger}) \rightarrow Ar_2\dot{C}OH + H_2NO_2^{+} \text{ (or } HNO_2) \quad (7)$$

$$Ar_2\dot{C}OH + NO_2^{\ddagger} \rightarrow Ar_2COH(ONO) \quad (8)$$

$$Ar_2COH(ONO) \rightarrow Ar_2CO + HNO_2 \quad (9)$$

In this mechanism, the hydrogen abstraction from Ar_2CH_2 (steps 3 and 4) is rate-determining.

EXPERIMENTAL

Materials. Substituted diphenylmethanes were prepared by reduction of the corresponding substituted benzophenones[8] prepared by the Friedel-Crafts reaction of benzene with substituted benzoyl chlorides.[9] The UV spectral data of substituted diphenylmethanes and benzophenones are given in Table 2.

TABLE 2. ULTRAVIOLET SPECTRA OF SUBSTITUTED DIPHENYLMETHANES AND BENZOPHENONES.

Substituent	Diphenylmethane		Benzophenone	
	λ max(mμ)	log ε	λ max(mμ)	log ε
p-OCH_3	278·5	3·24	290	4·25
m-Me	263	2·83	254	4·21
p-Me	265·7	2·82	258	4·22
H	262	2·61	252	4·38
m-Cl	268·5	2·74	252	4·54
p-Cl	269	2·78	260	4·32
m-NO_2	264	3·90	232	4·34
p-NO_2	278	3·91	266	4·29

Kinetic experiments. The rates were measured according to the procedure reported previously.[2] The measurements of acidity function were conducted colourimetrically by using 4-chloro-2-nitroaniline in 70 vol % acetic acid and *o*-nitroaniline in 60 vol % dioxan as indicators.

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