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KINETICS OF THE NITRIC ACID OXIDATION OF BENZALDEHYDES TO BENZOIC ACID[1]

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Abstract—The rates for the nitric acid oxidation of benzaldehydes to benzoic acids have been measured in aqueous dioxan mainly at 90°. The rates are independent of the nitric acid concentration and expressed as: $v = k[\text{ArCHO}]$. Nitrous acid is an effective initiator for the reaction, but it has no influence on the rate expression. The plot of log k vs acidity function (H_0) gives a straight line with a slope of $-0{\cdot}99$. The rate constants for benzaldehyde and *p*-methoxybenzaldehyde increase with increasing content of dioxan in the solvent, while the rate constant for *p*-nitrobenzaldehyde shows the reverse solvent effect. Substituent effect showed no definite trend; the order of reactivities of substituted benzaldehydes in 60 vol % dioxan is $p\text{-MeO} > \text{H} > p\text{-NO}_2$, while the reverse order is observed in 20 vol % dioxan. These data suggest a mechanism which involves a rate-determining hydrogen abstraction from both hydrated and free forms of benzaldehyde by protonated nitrogen dioxide, followed by the rapid hydrolysis of formed benzoyl nitrites.

BENZYL alcohol is easily oxidized to benzaldehyde by the action of nitric acid of relatively low concentration, e.g., below 1·5 M,[2] while benzaldehyde can be converted to benzoic acid with more concentrated nitric acid. Since the kinetics of the oxidation of benzaldehyde is little known, the present study was undertaken to get more information on the mechanism of the oxidation which yielded benzoic acid quantitatively.

Benzaldehyde cannot be oxidized with nitric acid of the concentration below 1·5 M, a higher acidity of the medium then being necessary. In this experiment described, 3–4 M nitric acid in aqueous dioxan (mostly dioxan:water = 4:6 in vol) was used, and the rates measured by means of UV spectrophotometry.

Nitrous acid was an effective initiator. The effect of solvent, substituent and acidity of the media as well as the effect of addition of nitrous acid were studied.

RESULTS AND DISCUSSION

The rate equation. The reaction of benzaldehyde with excess nitric acid followed the expression: $v = k[\text{ArCHO}]$, hence the plot of $\log([\text{ArCHO}]_0/[\text{ArCHO}])$ vs. time gave a straight line (Fig. 1). The analogous straight line was observed with 5·0 M nitric acid up to 54% conversion. The pseudo-first-order rate constants at various initial concentrations were constant as shown in Table 1. The effect of various initial concentrations of nitric acid on the pseudo-first-order rate constant k was studied in the presence of 2·67 M sulfuric acid which was added to maintain acidity for the oxidation. Since the oxidation is accelerated by increasing the acidity, the rate constants were corrected for acidity in order for comparison at the constant acidity ($H_0 = 0$), the results being shown in the last column in Table 2. The corrected rate

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[1] Contribution No. 92.

[2] Y. Ogata, Y. Sawaki, F. Matsunaga and H. Tezuka, *Tetrahedron* **22**, 2655 (1966).

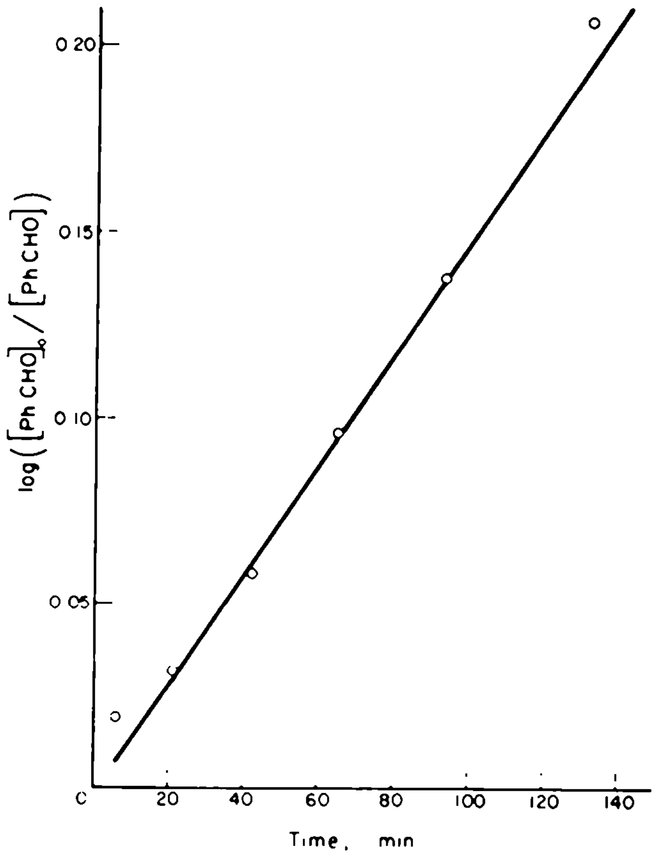

Fig. 1. A typical first-order plot for the nitric acid oxidation of benzaldehyde in 40 vol % dioxan at 90°
Initial concn.: $[HNO_3] = 4{\cdot}0$ M, $[C_6H_5CHO] = 0{\cdot}10$ M, $[HNO_2] = 0{\cdot}02$ M.

constants are independent of initial concentration of nitric acid. The rate equation for the nitric acid oxidation of benzyl ethers is also independent of the concentration of nitric acid above 1 M.[3]

Effect of acidity. The oxidation of benzaldehyde was too slow to measure with nitric acid of the concentration below 1·5 M, which implied the acid-catalysed nature of the reaction. The effect of acidity of the media was measured by adding various

TABLE 1. PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE NITRIC ACID OXIDATION OF BENZALDEHYDE IN 40% DIOXAN AT 90°
Initial concn.: $[HNO_3] = 4{\cdot}0$ M, $[HNO_2] = 0{\cdot}02$ M.

[PhCHO](M)	$10^5 k$, sec^{-1}
0·050	5·18
0·100	5·61
0·200	5·66

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[3] Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.* in press.

TABLE 2. THE EFFECT OF INITIAL CONCN. OF NITRIC ACID ON THE FIRST-ORDER RATE CONSTANT IN 40% DIOXAN AT 90°.
Initial concn.: $[H_2SO_4] = 2·67$ M; $[C_6H_5CHO] = 0·050$ M; $[NaNO_2] = 0·01$ M

Init. concn. HNO_3, M	$-H_0$	$10^4 k$, sec^{-1}	$\log k_{corr.}$*
0·2	0·52	3·68	−4·95
0·5	0·67	5·50	−4·93
0·8	0·82	7·68	−4·93
1·0	0·91	10·0	−4·91
1·5	1·12	18·4	−4·86
1·7	1·19	20·3	−4·88
2·0	1·29	26·6	−4·87

* Rate constants were corrected to those at $H_0 = 0$ according to the equation: $\log k_{corr.} = \log k + 0·99 H_0$

amounts of sulfuric acid to the reaction mixture. The Hammett's acidity function (H_0) was estimated by means of spectrophotometry using o-nitroaniline as an indicator; the plot of log k vs. H_0 gave a straight line with a slope of −0·99.

Effect of nitrous acid. When colourless pure nitric acid was used as an oxidizing agent, an induction period of 90–110 min was generally observed. When a small amount of sodium nitrite was added, the induction period was reduced to less than 10 min, but the rate was independent of the amount of sodium nitrite added. This finding was confirmed by the determination of the amount of nitrous acid in the reaction system. As the oxidation proceeded, the concentration of nitrous acid increased but with poor reproducibility. The oxidation rate, however, always satisfied the first-order kinetics. Hence it is apparent that nitrous acid serves as an initiator

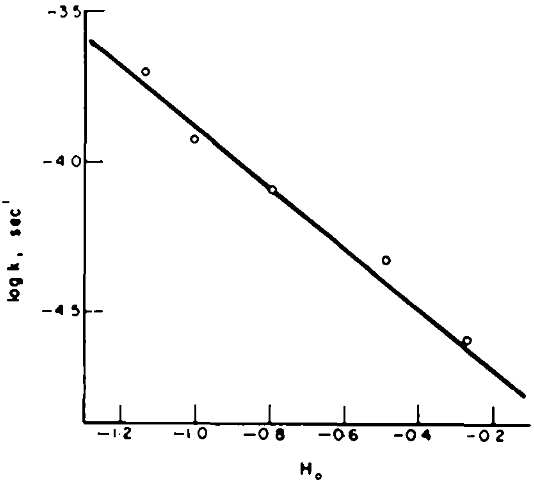

FIG. 2. The correlation between the acidity function H_0 and the pseudo first-order rate constant for the nitric acid oxidation of benzaldehyde in 40 vol % dioxan at 90°
Initial concn.: $[HNO_3] = 3·0$ M, $[C_6H_5CHO] = 0·10$ M, $[NaNO_2] = 0·02$ M, $[H_2SO_4] = 0 \sim 1·78$ M.

but has no effect on the rate. When a scavenger of nitrous acid such as urea was added to the system, a long induction period resulted. Even if nitrous acid together with urea was added the induction period was long (Table 3).

TABLE 3. THE EFFECT OF ADDITION OF SODIUM NITRITE OR UREA ON THE NITRIC ACID OXIDATION OF BENZALDEHYDE IN 40% DIOXAN AT 90°

Initial concn.; $[HNO_3] = 4\cdot0$ M; $[PhCHO] = 0\cdot100$ M

Added compds	(M)	$10^5 k$, sec^{-1}	Induction period, min
None		—	90–110
$NaNO_2$	(0·0004)	5·26	0
$NaNO_2$	(0·002)	5·23	0
$NaNO_2$	(0·02)	5·61	≤ 10
$CO(NH_2)_2$	(0·5)	—	>180
$CO(NH_2)_2 + NaNO_2$	(0·5 + 0·02)	—	>180

Effect of temperature. The first-order rate constants ($10^6 k$, sec^{-1}) were 5·75 at 70°, 9·44 at 75°, 18·4 at 80°, 35·4 at 85° and 56·1 at 90°. The Arrhenius plot afforded a good straight line, which gave the values of 28·6 kcal/mole and −1·37 e.u. for the apparent energy and entropy of activation, respectively.

Effects of solvent and substituent. The effect of substituents in the benzene ring and the effect of dioxan content of the solvent on the oxidation rate of unsubstituted, *p*-methoxy- and *p*-nitrobenzaldehydes were measured. It was found that the solvent effect was influenced by the substituent. Therefore, both effects will be discussed in this section. The solvent effect is given in Table 4. As obvious from the Table, the rates for *p*-methoxy- and unsubstituted benzaldehydes increase as the content of dioxan in the solvent increases.

TABLE 4. THE EFFECT OF SOLVENT COMPOSITION ON THE RATE CONSTANT FOR THE NITRIC ACID OXIDATION OF BENZALDEHYDES AT 90°

Initial concn.: $[HNO_3] = 3\cdot0$ M, $[ArCHO] = 0\cdot050$ M, $[NaNO_2] = 0\cdot01$ M

Vol. % dioxan	$-H_0$	$k \times 10^5$, sec^{-1} substituent		
		p-CH_3O	H	*p*-NO_2
60	−0·22	6·65	3·62	1·51
40	+0·28	3·11	1·92	3·00
20	+0·69	0·812	1·61	2·45

This increase in rate cannot be explained in terms of acidity of the media, since the acidity falls with increasing content of dioxan (Table 4). This solvent effect may be related to the concentration of attacking species, e.g., nitrogen dioxide. Nitrogen dioxide is in equilibrium with nitrosonium and nitrate ions.[4] In polar solvents such

$$2NO_2 \overset{K_1}{\rightleftarrows} NO^+ + NO_3^- \qquad (1)$$

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[4] J. D. S. Goulden and D. J. Millen, *J. Chem. Soc.* 2620 (1950).

as pure nitric or sulfuric acid, the equilibrium constant of Eq. 1, K_1, is extremely large, while in nonpolar organic solvents, it is nearly equal to zero.[4] Nitrosonium ion in Eq. 1 reacts with water giving nitrous acid and proton.

$$NO^+ + H_2O \overset{K_2}{\rightleftarrows} HNO_2 + H^+ \tag{2}$$

As the content of dioxan increases, the suppression of the heterolysis of nitrogen dioxide may result in an increase of the nitrogen dioxide concentration, i.e., the acceleration of the oxidation.

The comparison of benzaldehyde with *p*-methoxybenzaldehyde is of interest. When the solvent is altered from 40 to 20% dioxan, the decrease of the rate for benzaldehyde is ca. 16%, while that for *p*-methoxybenzaldehyde amounts to ca. 75% (Table 4). This fact is explicable by assuming the more facile oxidation of hydrated aldehyde than the free form; i.e., unsubstituted benzaldehyde is hydrated more readily than *p*-methoxybenzaldehyde,[5] which is more nucleophilic, hence the concentration of the hydrated form of benzaldehyde should be higher.

TABLE 5. SUBSTITUENT EFFECT ON THE NITRIC ACID OXIDATION OF SUBSTITUTED BENZALDEHYDES IN 40% DIOXAN AT 90°

Initial concn.: [Aldehyde] = 0·050 M, [$NaNO_2$] = 0·01 M

Substituent	$10^4 k$, sec^{-1} [a]	$10^4 k$, sec^{-1} [b]
p-MeO	7·38	3·11
p-Me	5·31	—
m-Me	5·11	—
H	5·11	1·92
p-Cl	4·45	1·34
m-NO_2	—	1·62
p-NO_2	5·37	3·00

[a] Initial concn.: [HNO_3] = 4·0M

[b] Initial concn.: [HNO_3] = 3·0M

The trend is more remarkable with *p*-nitrobenzaldehyde; its rate in 60% dioxan is smaller than that in 40% dioxan. It is probable that the extremely electrophilic *p*-nitrobenzaldehyde is more strongly hydrated. Therefore, in spite of the lower concentration of nitrogen dioxide, the rate in 40% dioxan is higher than that in 60% dioxan on account of the higher hydration. The order of reactivities in 60% dioxan is *p*-MeO > H > *p*-NO_2, while the order is reversed in 20% dioxan (Fig. 3).

The substituent effect depends on the solvent composition. In 60% dioxan, the substituent effect may affect the rate of hydrogen abstraction of free aldehyde, while in 20% dioxan the effect may influence the equilibrium of hydration more; in 40% dioxan the substituent effect may affect both steps, and hence no straight line or no definite ρ-value is obtainable in the Hammett's plot with Brown's σ^+ (Fig. 3). The oxidation or hydrogen abstraction is facilitated by the electron-releasing group, while the hydration is suppressed by the same group; hence both effects compete with each other, resulting in the inconsistent and reduced substituent effect.

The mechanism. The facts discussed above are summarized as follows: (i) The rate law is first-order in benzaldehyde, the rate being independent of the concentration

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[5] M. M. Aleksankin and I. P. Gragerov, *Chem. Abstr.* 57, 2125 (1962).

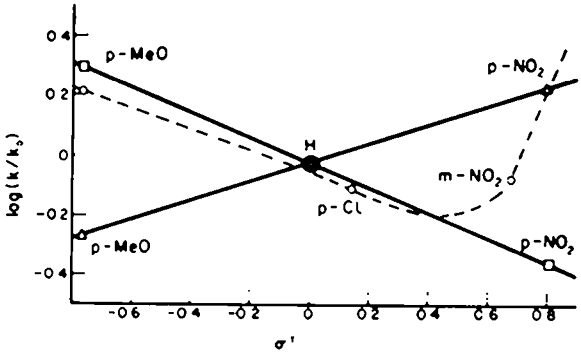


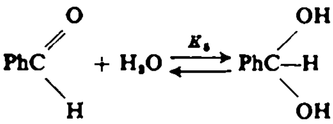
Fig. 3. Hammett's plots for the relative rates of nitric acid oxidation of benzaldehydes in solvents of various dioxan contents at 90°.
Initial concn.: $[HNO_3] = 3{\cdot}0$ M, $[ArCHO] = 0{\cdot}050$ M, $[NaNO_2] = 0{\cdot}01$ M.
△ 20% dioxan, ○ 40% dioxan, □ 60% dioxan

of nitric acid. (ii) The rate is proportional to h_0, where $\log h_0 = -H_0$. (iii) Nitrous acid initiates the reaction but has no influence on the rate. (iv) The effect of substituent shows no definite trend.

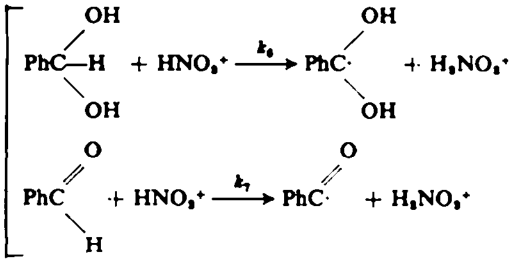
These results suggest a mechanism which assumes protonated nitrogen dioxide acting as an attacking species in the rate-determining step.

$$HNO_2 + HNO_3 \overset{K_3}{\rightleftharpoons} 2NO_2 + H_2O \tag{3}$$

$$H^+ + NO_2 \overset{K_4}{\rightleftharpoons} HNO_2^+ \tag{4}$$

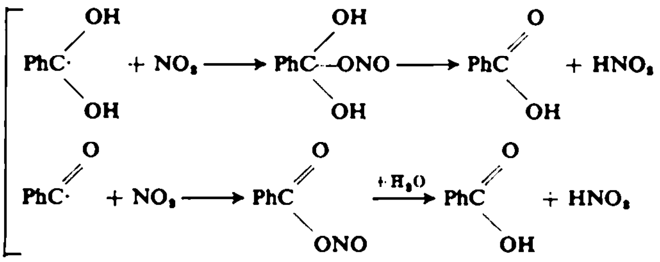


$$PhC(=O)H + H_2O \overset{K_5}{\rightleftharpoons} PhC(OH)_2H \tag{5}$$



$$PhCH(OH)_2 + HNO_2^+ \xrightarrow{k_6} Ph\dot{C}(OH)_2 + H_2NO_2^+ \tag{6}$$

$$PhC(=O)H + HNO_2^+ \xrightarrow{k_7} Ph\dot{C}{=}O + H_2NO_2^+ \tag{7}$$



$$Ph\dot{C}(OH)_2 + NO_2 \longrightarrow PhC(OH)_2ONO \longrightarrow PhC(=O)OH + HNO_2 \tag{8}$$

$$Ph\dot{C}{=}O + NO_2 \longrightarrow PhC(=O)ONO \xrightarrow{+H_2O} PhC(=O)OH + HNO_2 \tag{9}$$

Nitric acid reacts with nitrous acid to produce nitrogen dioxide,[6,7] a small part of which may be protonated. The protonated nitrogen dioxide attacks both hydrated and free benzaldehydes. The hydrogen abstraction from hydrated benzaldehyde should be easier than that from free form. The radicals produced by the hydrogen abstraction may rapidly couple with nitrogen dioxide to form benzoyl nitrite (Eqs. 8 and 9). Benzoyl nitrite or its hydrate should be easily hydrolysed to benzoic acid.

In this scheme, the rate-determining step may be either hydrogen abstraction or hydrolysis of the nitrite on the basis of the observed rate law. The rate-determining hydrolysis (steps 8 and 9) is less probable, because benzoyl nitrite may be very susceptible to hydrolysis under these conditions.[8] Therefore, the hydrogen abstraction should be rate-determining.

The hydrogen abstraction ability of the attacking radical parallels with its electrophilicity,[9] and it has been pointed out that neutral radicals became more powerful hydrogen abstractors by their protonation as exemplified by $\cdot ClH^+$ or $\cdot NH_3^+$ radicals.[10] The present reaction has been carried out in solutions of high acidity and the rate is proportional to the acidity function (h_0). Hence the authors suggest protonated nitrogen dioxide as a principal attacking species. The electrophilicity of attacking radical may also parallel with the sensitivity to polar substituent effect or Hammett's ρ-value.[9] Although the substituent effect on the α-hydrogen abstraction from benzyl alkyl ethers is generally small, a large effect ($\rho = -1{\cdot}6$) was observed[3] in the nitric acid oxidation of benzyl alkyl ethers, implying the same charged attacking species, HNO_2^+.

The hydrogen abstraction from paraffins by free nitrogen dioxide to form alkyl radicals which leads to nitroparaffins has been suggested by several investigators, but no one suggests the protonated nitrogen dioxide as an attacking species, probably because the reaction was carried out in vapour phase or the investigators pay little attention to the acidity effect.[11]

If the hydrogen abstraction (steps 6 and 7) is rate-determining, the rate may be expressed as:

$$v = k_6[HNO_2^+][PhCH(OH)_2] + k_7[HNO_2^+][PhCHO]$$
$$= (k_6K_5[H_2O] + k_7)K_4[NO_2][H^+][PhCHO].$$

Here, k and K are rate and equilibrium constants of subscripted steps.

Nitrogen dioxide in the vapor phase is in an equilibrium with nitric and nitrous acids in the solution.[7] Since the reaction was carried out in an open vessel, nitrogen dioxide was evolved from the surface. Hence, it is possible that the solution is saturated with nitrogen dioxide, and the concentration of nitrogen dioxide is kept constant during the reaction. This assumption is further supported by the report that if the reaction was carried out in a sealed tube, the rate depended on the concentration

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[6] P. Gray and A. D. Yoffe, *Chem. Revs.* **55**, 1069 (1955).

[7] H. Prick, *Gmelins Handbuch* **4**, 907 (1936).

[8] Alkyl nitrite is easily hydrolysed even at 0°, A. D. Allen, *J. Chem. Soc.* 1968 (1954).

[9] S. Kato and F. Mashio, *Kagaku no Ryoiki* **12**, 40 (1958).

[10] T. F. Williams, *J. Amer. Chem. Soc.* **84**, 2895 (1962).

[11] T. S. Godfrey, E. D. Hughes and C. Ingold, *J. Chem. Soc.* 1063 (1965); A. I. Titoff *et al.*, *Ber. Akad. USSR* **81**, 1085 (1951); F. Asinger and K. Halcour, *Chem. Ber.* **94**, 83 (1961); H. Schechter and D. K. Brain, *J. Amer. Chem. Soc.* **85**, 1806 (1963).

of nitric acid,[12] and by the fact that the rate for the oxidation of benzyl methyl ether becomes dependent on the concentration of nitric acid at the concentration below 0·2 M, where the solution is supposed to be unsaturated with nitrogen dioxide.[3] The constancy of concentration of nitrogen dioxide leads to a simplified rate equation: $v = k[\mathrm{PhCHO}]$, which is consistent with the observation.

EXPERIMENTAL

Materials. Substituted benzaldehydes were purified by rectifications after washing with $NaHCO_3$aq., when they were liquid, and by recrystallizations when they were solid. Benzaldehyde, b.p. 77·8–78·5°/26 mm; *p*-anisaldehyde, b.p. 143–143·5°/35 mm; *p*-methylbenzaldehyde, b.p. 100–101°/30 mm; *m*-methylbenzaldehyde, b.p. 102–104°/40 mm; *p*-chlorobenzaldehyde, m.p. 47·5–48°; *p*-nitrobenzaldehyde, m.p. 106·2–106·8°; *m*-nitrobenzaldehyde, b.p. 119–122°/7 mm. Absorption coefficients of these aldehydes have been reported previously.[2]

Kinetic procedure. The rates for the oxidation of benzaldehydes were measured by means of UV spectrophotometry as reported in the previous paper.[2] Since the reaction was carried out at higher acidity, chf used for extraction often contained a small amount of acid even after washing with 0·5 N NaOH. Hence 1 ml of 0·2 N NaOH was added to the last extract of chf for the complete elimination of the remaining acid which interfered the spectrophotometry by accelerating the formation of benzaldehyde hemiacetal in MeOH.

The Hammett's acidity function was measured spectrophotometrically according to the method previously reported, but *o*-nitroaniline was used as an indicator instead of *p*-nitroaniline on account of the higher acidity of the reaction soln.[2] The same method as the previous paper was also used for the determination of nitrous acid.

Reaction product. The oxidation of benzaldehyde (3·18 g) with 5·50 M HNO_3 at 90° for 3 hr gave benzoic acid, which was recrystallized from water yielding pure benzoic acid, m.p. 123·2°, m.m.p. 123·2—123·8°, 3·44 g (94%).

Acknowledgments—The authors are grateful to Mr. K. Matsuyama and Mr. M. Mineno for their helpful assistance in performing these experiments.

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[12] K. NAMBA, T. YOSHIDA, T. OZAWA and S. TAMURA, *19th Annual Meeting, Chem. Soc. Japan.* Yokohama (1966).