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KINETICS OF THE NITRIC ACID OXIDATION OF BENZYL ALCOHOLS TO BENZALDEHYDES*

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Abstract—The oxidation of benzyl alcohols to benzaldehydes by dilute nitric acid (~10%) was studied kinetically in 40 vol% aqueous dioxan. The oxidation is initiated most effectively by nitrous acid, and the rate is proportional to the product of the concentrations of benzyl alcohol and nitric acid, being independent of that of nitrous acid. The rate of oxidation increases with increasing acidity of the media, the plot of logarithm of the rate constant *vs.* acidity function H_0 being a line with a slope of ca. -2. The apparent energy and entropy of activation were 28·3 kcal mole^{-1} and $+1{\cdot}85$ eu, respectively. The substituent effect satisfied Hammett's equation, affording a ρ-value of $-2{\cdot}25$. A probable mechanism is discussed, which involves a rapid and reversible coupling of α-hydroxybenzyl radical with nitrogen dioxide followed by the hydrolysis of α-hydroxybenzyl nitrite (I).

BENZYL chlorides are oxidized by dilute nitric acid to benzaldehydes; e.g., the oxidation of α,α′-dichloro-*p*-xylene to terephthalaldehyde,[1] is an important procedure for the preparation of terephthalic acid. On treatment of benzyl chloride with dilute nitric acid, the halide is hydrolysed to benzyl alcohol and the alcohol gradually oxidized to benzaldehyde.[2] Although this oxidation with pure nitric acid occurs only

$$\mathrm{ArCH_2Cl} \xrightarrow{\mathrm{H_2O}} \mathrm{ArCH_2OH} \xrightarrow{\mathrm{HNO_3}} \mathrm{ArCHO} \qquad (1)$$

after a long period of induction, it proceeds readily on addition of a small amount of sodium nitrite. The present paper describes the kinetic study including the effect of the concentration of nitrous acid, catalysing acid, temperature and substituents and on the basis of these data a probable mechanism is discussed.

EXPERIMENTAL

Materials. Commercial benzyl alcohol was fractionated, b.p. 102·8–103·2°/18 mm and dioxan was purified by rectification with suitable treatment with Na metal, b.p. 101·0–101·2°. HNO_3 and perchloric acid were both of guaranteed grade, and $NaNO_2$ was recrystallized twice from water, m.p. 270°. All substituted benzyl alcohols except the *p*-methoxy compound were synthesized from the corresponding toluenes by photochemical monobromination of the Me group followed by its acetolysis and then alkaline hydrolysis: *p*-methylbenzyl alcohol, b.p. 115–116°/22 mm, m.p. 60° (lit.[3] 61°); *m*-methylbenzyl alcohol, b.p. 113–114°/20 mm; *p*-chlorobenzyl alcohol, m.p. 73° (lit.[4] 73°); *m*-chlorobenzyl alcohol, b.p. 135–136°/34 mm (lit.[4] 234°); *p*-nitrobenzyl alcohol, m.p. 92° (lit.[5] 93°). *p*-Methoxybenzyl alcohol was obtained from the reaction with formaldehyde in the presence of KOH, b.p. 144–145°/25 mm (lit.[6] 134°/12 mm).

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* Contribution No. 82.

[1] I. S. Bengelsdorf, *J. Org. Chem.* **23**, 242 (1958).

[2] Y. Ogata, Y. Sawaki, H. Tezuka and F. Matsunaga, *Kogyo Kagaku Zasshi*, in press.

[3] D. Davidson and M. Weiss, *Organic Syntheses* Coll. Voll. II, p. 590. Wiley, New York (1948).

[4] C. Mettler, *Ber. Dtsh. Chem. Ges.* **38**, 1749 (1905).

[5] W. W. Hartman and E. J. Rahrs, *Organic Syntheses* Coll. Voll. III, p. 652. Wiley, New York (1955).

[6] G. Vavon, *C.R. Acad Sci., Paris* **154**, 360 (1912).

Kinetic measurements. A 40 vol% dioxan solution containing benzyl alcohol and HNO_3 of a known concentration was thermostatted at 90° in a flask and the oxidation started by adding $NaNO_2$aq. Aliquots were taken at appropriate intervals of time and the benzaldehyde was estimated as described. Most reactions were carried out to 30–60% conversion, and the constancy of rate constants was confirmed up to 60–80% conversion.

Analytical method. A mixture of the aliquot (5 ml) and water (30 ml) was extracted with 10 and then 5 ml $CHCl_3$. The extract was washed with 1N NaOH to prevent the formation of hemiacetal and diluted with MeOH to the appropriate concentration. The content of aldehyde in the diluted solution was measured by UV spectrophotometry. The molar absorbances together with wavelength in mμ of substituted benzaldehydes in MeOH are indicated below. Benzaldehyde, 11,100 (245 mμ); *p*-chlorobenzaldehyde, 14,700 (254 mμ); *m*-chlorobenzaldehyde, 10,000 (244 mμ); *p*-nitrobenzaldehyde, 11,300 (264 mμ); *p*-tolualdehyde, 12,500 (255 mμ); *m*-tolualdehyde, 12,000 (249 mμ); *p*-anisaldehyde, 15,400 (275 mμ).

The content of HNO_2 was estimated by the absorbance at 535 mμ after its reaction with sulphanilic acid and then with α-naphthylamine. The Hammett's acidity function was determined using *p*-nitroaniline as an indicator.[7]

Stoichiometry. To examine the molar ratio of benzaldehyde produced and HNO_3 consumed, the oxidation of benzyl alcohol in 40 vol% dioxan was done in the presence of perchloric acid. The oxidation was started by the addition of a small amount of $NaNO_2$ and the amount of benzaldehyde determined after 6–8 hr when the oxidation of benzaldehyde by HNO_3 or atmospheric O_2 is negligible under these conditions. The molar ratio $[C_6H_5CHO]/[HNO_3]$ increased as the concentration of benzyl alcohol increased, and it may be concluded that one mole of aldehyde is produced per mole of HNO_3 added (Table 1). The observed lower ratio (<1) of $[C_6H_5CHO]/[HNO_3]$ in the presence of lower concentration of the alcohol may be attributed to the removal of the effective oxidizing species, probably NO_2, from the system.

TABLE 1. STOICHIOMETRY OF THE NITRIC ACID OXIDATION OF BENZYL ALCOHOL IN 40 VOL% DIOXAN AT 90° FOR 6–8 HR; $[HClO_4] = 1{\cdot}01$M

$[C_6H_5CH_2OH]$ M	+	$[HNO_3]$ M	→	$[C_6H_5CHO]$ M	$\frac{[C_6H_5CHO]}{[HNO_3]}$
0·398		0·0985		0·102	1·03
0·299		0·0985		0·101	1·02
0·199		0·0985		0·0905	0·920
0·0995		0·0985		0·0538	0·547
0·0498		0·0493		0·0127	0·258

RESULT AND DISCUSSION

Induction periods. The oxidation of benzyl alcohol with pure nitric acid at 90°, shows a very long induction period (>8 hr). A small amount of sodium nitrite is an effective initiator, but the rate of oxidation is independent of its concentration. This initiation is not observed in the presence of urea, i.e., a scavenger of nitrous acid.

The effect of radical initiators or inhibitors examined is listed in Table 2. Benzoyl peroxide and azo-bis-isobutyronitrile initate the oxidation but to a lesser extent than sodium nitrite. Inhibitors such as β-naphthol or *o*-cresol also initiate the oxidation, no doubt on account of their oxidation with formation of appreciable amounts of nitrogen dioxide or nitrous acid which then act as initiators. No observation of induction period with nitric acid contaminated with nitrogen dioxide confirms this assumption. Sodium nitrite was used as an initiator in all the experiments, and its role in the oxidation is discussed later.

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[7] M. A. Paul and F. A. Long, *Chem. Revs.* **57**, 1 (1957).

TABLE 2. INDUCTION PERIODS IN THE PRESENCE OF ADDED COMPOUNDS AT 90°: $[C_6H_5CH_2OH] = 0{\cdot}0506M$, $[HNO_3] = 0{\cdot}739M$

Added compd.	(M)	Induction period (min)	First-order rate const. $k_1 \times 10^5$ sec^{-1}
None	—	>480	—
$NaNO_2$	(0·0001)	10	15·0
$NaNO_2$	(0·0004)	8	15·7
$NaNO_2$	(0·0040)	0	15·2
$NaNO_2$ + Urea	(0·004 + 0·033)	>240	—
$NaNO_2$ + H_2Q^a	(0·004 + 0·040)	0	15·4
$(PhCOO)_2$	(0·00082)	60	18
$(PhCOO)_2$	(0·0082)	40	24
AIBN[b]	(0·0012)	>240	—
AIBN[b]	(0·0061)	80	16
β-Naphthol	(0·0007)	>240	—
β-Naphthol	(0·0035)	8	16
o-Cresol	(0·0046)	>240	—
o-Cresol	(0·0185)	170	15
$C_6H_5CH_2ONO_2$	(0·062)	>240	—
$C_6H_5CH_2ONO_2$[c]	(0·62)	>240	—

[a] Hydroquinone.
[b] Azobisisobutyronitrile.
[c] Benzyl nitrate alone was used in place of benzyl alcohol.

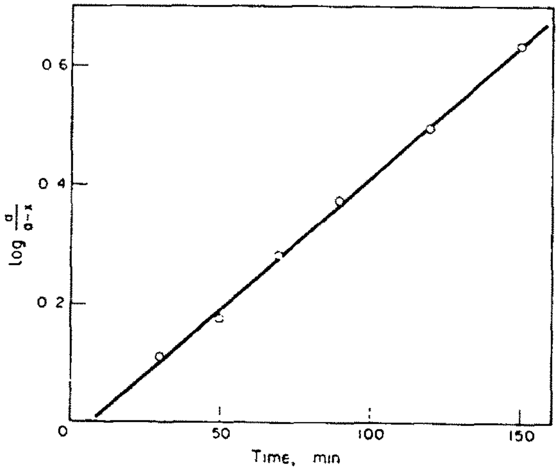

FIG. 1. A typical first-order plot for the oxidation of benzyl alcohol with excess nitric acid: Initial concn., $[C_6H_5CH_2OH] = 0{\cdot}0534M$; $[HNO_3] = 0{\cdot}739M$; $[NaNO_2] = 0{\cdot}002M$.

Rate law. The oxidation rate of benzyl alcohol using sodium nitrite as an initiator was followed by measuring the amount of benzaldehyde produced. The initial concentration of sodium nitrite was independent of the rate (Table 2).

The oxidation of benzyl alcohol by excess nitric acid was found to satisfy first-order kinetics with benzyl alcohol (Fig. 1 and Table 3A). Whereas the oxidation rate of excess benzyl alcohol in the presence of perchloric acid was first-order with nitric acid

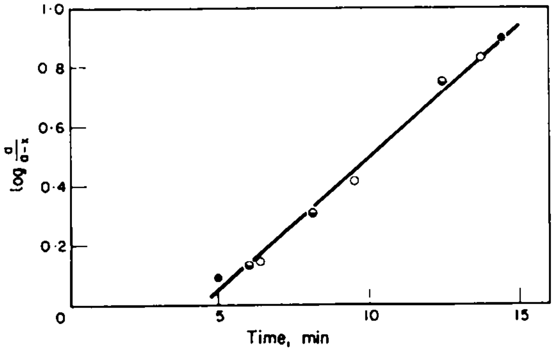

Fig. 2. First-order plot for the oxidation of excess benzyl alcohol by nitric acid: Initial concn., $[C_6H_5CH_2OH] = 0{\cdot}750M$; $[NaNO_2] = 0{\cdot}002M$; $[HClO_4] = 1{\cdot}01M$; $[HNO_3]$: -○- 0·0690M, -◒- 0·0985M, -●- 0·1478M.

Table 3. Rate constants for the oxidation of $C_6H_5CH_2OH$ with HNO_3 at various initial concentration in 40 vol% dioxan at 90°

$[C_6H_5CH_2OH]$ M	$[HNO_3]$ M	First-order rate constants $k_1 \times 10^5\ sec^{-1}$
A. Oxidation by excess nitric acid[a]		
0·0304	0·739	16·4
0·0709	0·739	15·5
0·1069	0·739	14·5
0·1520	0·739	15·6
B. Oxidation of excess benzyl alcohol[b]		
0·750	0·0496	2·80
0·750	0·0690	3·18
0·750	0·0985	3·17
0·750	0·1478	2·77
C. Oxidation at comparable initial concns.[c]		
0·0314	0·134	2·60[d]
0·1176	0·134	2·97[d]
0·0784	0·0670	2·20[d]
0·0784	0·1072	2·36[d]

[a] $[NaNO_2] = 0{\cdot}002M$; $v = k_1[C_6H_5CH_2OH] = (k'[HNO_3])[C_6H_5CH_2OH]$.

[b] $[HClO_4] = 1{\cdot}01M$, $[NaNO_2] = 0{\cdot}002M$; $v = k_1[HNO_3] = (k'[C_6H_5CH_2OH])[HNO_3]$.

[c] $[HClO_4] = 1{\cdot}09M$, $[NaNO_2] = 0{\cdot}004M$.

[d] Second-order rate constant, $k' \times 10^3\ M^{-1}\ sec^{-1}$, $v = K'[C_6H_5CH_2OH][HNO_3]$.

(Fig. 2 and Table 3B). Perchloric acid was necessary for the required acidity of the media. Therefore, the oxidation was found to follow the kinetics first-order with benzyl alcohol and first-order with nitric acid. These results were also confirmed in the perchloric acid-catalysed oxidation of benzyl alcohol by nitric acid with the comparable concentrations of both reagents (Table 3C).

Effect of acidity and temperature. Although the oxidation of benzyl alcohol is difficult with nitric acid below 0·1M, it proceeds smoothly on addition of perchloric acid; i.e., the oxidation is accelerated by increasing the acidty of the solution. Plots of logarithm of first-order constant with benzyl alcohol and second-order rate constant vs. Hammett's acidity function resulted in a slope of +2·11 and +2·18, respectively (Fig. 3). The slope (ca. +2) implies that two protons are concerned in the transition state.

The effect of temperature was measured with initial concentrations of 0·0507M benzyl alcohol, 0·739M nitric acid and 0·002M sodium nitrite at 70, 80, 85, 90 and 95°, giving first-order rate constants of 1·54, 5·70, 8·78, 15·4 and 26·2 sec^{-1}, respectively. The Arrhenius plot of these data gave a straight line. The calculated activation energy (28·30 kcal. $mole^{-1}$) is large, and the activation entropy (+1·85 eu) is of a small positive value.

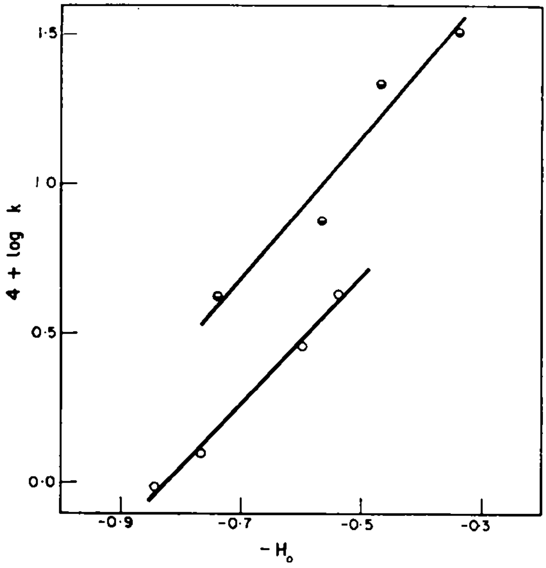

FIG. 3. Plots of log *k* vs. acidity function for the oxidation of benzyl alcohol with nitric acid in the presence of perchloric acid in 40 vol% dioxan at 90°: –○–, first-order rate constant (k_1); –●–, second-order rate constant (k').

Substituent effect. The rate of the oxidation of substituted benzyl alcohols is summarized in Table 4. The substituent effect satisfied the Hammett's equation, resulting in the negative ρ-value of −2·25 (Fig. 4). Electron-releasing groups in the alcohol accelerate the oxidation, while electron-attracting groups retard the reaction. An attempt to correlate the log *k* with σ^+ was unsuccessful, suggesting the small intervention of resonance effect of the *p*-substituents. These trends are in contrast with

TABLE 4. SUBSTITUENT EFFECT FOR THE OXIDATION OF SUBSTITUTED BENZYL ALCOHOLS IN 40 VOL% DIOXAN AT 90°: $[HNO_3] = 0{\cdot}739M$, $[ArCH_2OH] = 0{\cdot}03–0{\cdot}1M$, $[NaNO_2] = 0{\cdot}002M$

Substituents	$k_1 \times 10^5$, sec^{-1}	Substituents	$k_1 \times 10^5$, sec^{-1}
p-MeO	75·2	*p*-Cl	5·25
p-Me	42·8	*m*-Cl	2·60
m-Me	17·3	*p*-NO_2	0·54
H	16·0		

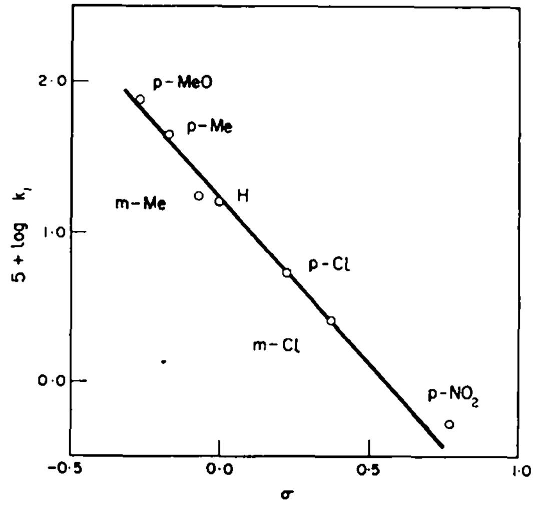

Fig. 4. Hammett's plot for the oxidation of substituted benzyl alcohols with nitric acid in 40 vol% dioxan at 90°.

the autoxidation of benzyl alkyl ethers[8] and the reaction of substituted benzyl methyl ethers with N-bromosuccinimide,[9] which show very small substituent effects. The highly negative ρ-value for the present oxidation indicates that the formation of benzyl radical might not be rate-determining.

Effect of nitrous acid. The rate of oxidation of benzyl alcohol does not increase with increasing concentration of nitrous acid as shown in the last column of Table 2. This was confirmed by estimating the concentration of nitrous acid which increases (Table 5) as the oxidation proceeds, while the rate of oxidation is independent of the increasing amount of the acid, satisfying first-order kinetics with respect to benzyl alcohol. These results suggest that nitrous acid initiates the reaction and its concentration increases as the oxidation proceeds.

Table 5. Variation of the concentration of nitrous acid in the reaction system at 90°: initial concn., $[HNO_3] = 0{\cdot}670M$, $[C_6H_5CH_2OH] = 0{\cdot}118M$

Reaction time min	$[HNO_2]$ M	$[C_6H_5CHO]$ M
0	0·00150	0
17	0·00276	0·016
48	0·00366	0·043
85	0·00585	0·056
154	0·00481	0·079

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[8] G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.* **86**, 2357 (1964).

[9] R. E. Lovins, L. J. Andrews and R. M. Keefer, *J. Org. Chem.* **30**, 1577 (1965).

The mechanism. Generally, the attacking species in the oxidation are assumed to be nitric acid, nitrous acid, dinitrogen tetroxide, nitrogen dioxide and/or their anhydrides or conjugate acids. For example, molecular nitrous acid and NO^+ were proposed as an oxidizing species for the oxidation of formic acid,[10] and nitrous anhydride for the oxidation of acetophenones to furoxans.[11]

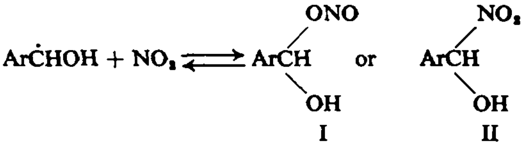
Our results that the rate is expressed as: $v = k'[HNO_3][ArCH_2OH]$ and that nitrous acid initiates the reaction in spite of the independence of the rate on the concentration of the acid eliminate a rate-determining attack of nitric acid, nitrous acid or the analogous species on benzyl alcohol. The conjugate acid such as $N_2O_3^+$, NO_2^+ or NO^+ cannot be an appropriate attacking species, because the oxidation proceeds smoothly in the acidity of 1M nitric acid, when the concentration of these nitogen oxide cations is low.

The mixture becomes yellowish brown even at the start of reaction, suggesting the formation of nitrogen dioxide. Dinitrogen tetroxide, which may be formed from nitric acid and nitrous acid, must dissociate to nitrogen dioxide almost completely on the basis of its dissociation constant.[12] The assumption of nitrogen dioxide, a paramagnetic compound having odd electrons, may also explain the observed radical nature of the reaction. The assumption that nitrous acid is an intermediate is less probable in the presence of nitrogen dioxide which has the stronger electron affinity. Hence, the following mechanism is suggested for the present oxidation, which involves the preliminary abstraction of benzyl hydrogen by nitrogen dioxide.

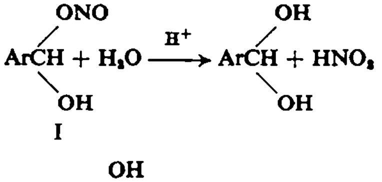
$$NO_2^- + H^+ \rightleftharpoons HNO_2 \tag{2}$$

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

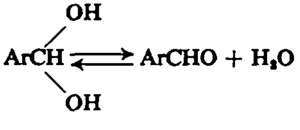
$$ArCH_2OH + NO_2 \rightleftharpoons Ar\dot{C}HOH + HNO_2 \tag{4}$$



$$Ar\dot{C}HOH + NO_2 \rightleftharpoons \underset{\text{I}}{ArCH(ONO)(OH)} \quad \text{or} \quad \underset{\text{II}}{ArCH(NO_2)(OH)} \tag{5}$$



$$\underset{\text{I}}{ArCH(ONO)(OH)} + H_2O \xrightarrow{H^+} ArCH(OH)(OH) + HNO_2 \tag{6}$$



$$ArCH(OH)(OH) \rightleftharpoons ArCHO + H_2O \tag{7}$$

Nitric acid is a strong acid and hence it should dissociate sufficiently under these conditions. If the Eqs 2–5 are rapid and if the hydrolysis of the nitrite I is rate-determining, since the concentration of each component in Eqs 2–5 should be substantially

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[10] J. V. L. Longstaff and K. Singer, *J. Chem. Soc.* 2610 (1954).

[11] H. R. Snyder and N. E. Boyer, *J. Amer. Chem. Soc.* **27**, 4233 (1955).

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

lower than those of nitrate ion and of benzyl alcohol, the rate of oxidation may be written as follows:

$$\begin{aligned} v &= k_6[H^+][I] \\ &= k_6K_2K_3K_4K_5[H^+]^2[NO_3^-][ArCH_2OH]/[H_2O] \end{aligned}$$

Here, k and K's are rate and equilibrium constants of the subscripted steps, respectively. This rate law does not involve the term of nitrous acid or nitrogen dioxide, although these species are present in the reaction mechanism. The rate of oxidation is proportional to the product $[ArCH_2OH][NO_3^-]$ and the plots of $\log k$ vs. $-H_0$ should give a line with a slope of 2 as is the case.

The substituent effect or the highly negative ρ-value indicates the presence of Eqs. 4 and 5. That is, if the abstraction of benzyl hydrogen is rate-determining, the ρ-value would be small as is the case for similar reactions.[8,9] Hence, nitrite I or nitro compound II, which may be formed by coupling of α-hydroxybenzyl radical with nitrogen dioxide, should be decomposed or hydrolysed to benzaldehyde and nitrous acid in the rate-determining step 6. Intermediate II, however, may be less important because of its lower stability as reported previously.[12] Intermediate I is more probable because of its higher stability.[13] The conversion of nitrite I to benzaldehyde should be acid-catalysed and the α-elimination of I should be less probable in the absence of any effective base.[14] Thus, the protonated nitrite is probably hydrolysed. Although alkyl nitrite is easily hydrolysed at 0°,[15] the reaction of nitrogen dioxide with benzyl alcohol or aliphatic alcohols may occur even more readily at −10°.[16]

Concerning the reaction of benzyl alcohol with nitrogen dioxide, a mixture of equimolar quantities (ca. 0·015M) of the alcohol and dinitrogen tetroxide in carbon tetrachloride was kept at 0–20° and the products analysed by IR spectrometry. Benzaldehyde (ca. 10%) was produced after 5 min at 0°, but the main product was benzyl nitrite, the unchanged benzyl alcohol being less than 2%. The subsequent reaction of benzyl nitrite with nitrogen dioxide was slow, and after 20 hr at 15–20° ca. 80% of the nitrite was oxidized to benzaldehyde together with some benzyl nitrate (below 5%). When anhydrous Na_2SO_4 was added to remove water from the reaction, the rapid formation of the aldehyde (ca. 5% in this case) was observed for 5 min, but the subsequent oxidation was suppressed; i.e., water is neccessary in the nitrogen dioxide oxidation of benzyl nitrite to benzaldehyde. These facts suggest that the reaction of benzyl nitrite with nitrogen dioxide may proceed through the hydrolysis of an intermediate such as benzal nitrite, $ArCH(ONO)_2$, and that the rapid reaction of benzyl alcohol with nitrogen dioxide at an early stage would proceed through α-hydroxybenzyl nitrite (I) which should be more reactive than the benzal nitrite.[17] Therefore, the formation of the intermediate I is supported. A similar intermediate has been postulated in the reaction of benzyl alcohol with dinitrogen tertoxide.[18,19]

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[13] Ethyl nitrite was obtained as a main product in the pyrolysis of ethyl nitrate, J. B. Levy, *J. Amer. Chem. Soc.* **76**, 3254 (1954).

[14] See, for example, J. W. Baker and D. M. Easty, *J. Chem. Soc.* 1193 (1952).

[15] A. D. Allen, *J. Chem. Soc.* 1968 (1954).

[16] W. Langenbeck and M. Richter, *Chem. Ber.* **89**, 202 (1956).

[17] It is well-known that acetals are more stable than hemiacetals on hydrolysis; e.g., M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **77**, 3146 (1955).

[18] B. D. Field and J. Grundy, *J. Chem. Soc.* 1110 (1955).

[19] J. B. Cohen *et al.*, *J. Chem. Soc.* **71**, 1050 (1897).

The conversion of benzyl alcohol to the nitrate or the nitrite was not appreciable under the present conditions of oxidation with nitric acid. The failure to isolate nitrite I may be attributed to its instability and very low concentration; i.e., the present oxidation is conducted via very small amounts of the intermediates, nitrogen dioxide, α-hydroxybenzyl radical, and I. The proposed mechanism requires the reversible homolytic dissociation of I (Eq. 5), which is attained by the stability of the radicals produced.

The comparison of the rate of the present oxidation (at 90°) with the rate of acid-catalysed hydrolysis of alkyl nitrite at 0° reported previously[15] is not appropriate, since these two reactions differ in the conditions used and the concentration of the nitrite I cannot be estimated. However, the rate constant k_1 for the present oxidation is calculated to be 2×10^{-9} sec^{-1} with $[NO_3^-] = 0{\cdot}74M$ at 0° by means of the extrapolation of the Arrhenius plot, and the rate is 2×10^{-10} at $[ArCH_2OH] = 0{\cdot}1M$. The rate of hydrolysis of alkyl nitrite is ca. 0·2[nitrite] at the same acidity.[15] The value of K_3 or $[NO_2]^2/[HNO_2][NHO_3]$ and K_4 are immeasurably low;[10] the value of $[HNO_3]$ is about 0·1M, and hence the concentration of I $(= K_3K_4K_5[HNO_3][ArCH_2OH]/[H_2O])$ may be very small. Therefore, it is not strange, if the over-all rate of oxidation, 2×10^{-10}, exceeds the rate of hydrolysis or 0·2 [I]. In other words, the above mechanism requires that the concentration of nitrite I must be less than 10^{-9} M.

The highly negative value of ρ suggests the greater importance of the preliminary protonation of I. It should be remembered that the acid-catalysed hydrolysis of t-butyl nitrite is 2·4 times as fast as that of n-propyl nitrite[15] and that the acidity of anilinium ion gives a highly positive ρ-value ($\sim$3), while the acidic hydrolysis of most carboxylic esters have a small ρ-value ($\sim -0{\cdot}2$).[20] The failure of the correlation with σ^+ may be that the bond fission in the hydrolysis rate is less important than the protonation equilibrium of I; i.e., the rate of hydrolysis of I is controlled by the concentration of the conjugate acid of I rather than by the sensitivity of the acid for hydrolysis.

An alternative mechanism is the rate-determining α-hydrogen elimination of the nitrate III.

$$ArCH_2OH + HNO_2 \rightleftharpoons ArCH_2ONO + H_2O \qquad (8)$$

$$ArCH_2ONO + HNO_3 \rightleftharpoons \underset{(III)}{ArCH_2ONO_2} + HNO_2 \qquad (9)$$

$$\left\{\begin{array}{ll} (III) + H_2O \longrightarrow ArCH_2OH + HNO_3 & (10) \\ \text{or} & \\ (III) \longrightarrow ArCHO + HNO_2 & (11) \end{array}\right.$$

This scheme is attractive, since the rate is independent of the concentration of nitrous acid, but it does not explain the observed slope of ca. 2 in the plots of log k vs. $-H_0$, and it does not account for the α-hydrogen elimination from III producing benzaldehyde and HNO_2 in spite of the easier hydrolysis of III in acidic aqueous dioxan. In fact, benzyl nitrate cannot initiate the oxidation of benzyl alcohol and benzyl nitrate itself gives no appreciable amount of benzaldehyde in these acidic media (Table 1).

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[20] J. F. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions* p. 178. Wiley, New York (1963).

Benzyl nitrate in neutral aqueous dioxan has been reported to give 6–8% benzaldehyde, while the addition of hydroquinone in the reaction mixture gave no aldehyde,[21] but the present oxidation is carried out under quite different conditions. The oxidation of benzyl alcohol can occur even in the presence of hydroquinone (Table 1). Moreover, the observed radical nature, the presence of NO_2 in the system and the easy oxidation of benzyl alcohol with NO_2 also agree with the mechanism proposed (Eqs 2–7).

Another mechanism is the hydrolysis of the nitrate formed by oxidation of nitrite I by nitric acid or nitrogen dioxide. However, the hydrolysis of I is probably faster than its oxidation to nitrate under these conditions.

[21] G. R. Lucas and L. P. Hammett, *J. Amer. Chem. Soc.* **64**, 1928 (1942).