et al.,[12] and had bp 106–110° (20 mm). It was further purified by redistillation, fractional freezing keeping only material which was solid at 9°, followed by preparative vpc (silicone 710, 150°). trans-p-Chlorocinnamic acid was prepared by mixing 70 g (0.5 mole) of p-chlorobenzaldehyde with 52 g (0.5 mole) of malonic acid and 2 ml of pyridine. The mixture was heated on a steam bath for 24 hr. The solid was collected and washed twice with methanol, giving 84 g (92%) of almost pure acid. Before use it was recrystallized three times from methanol (mp 243–245°). trans-p-Methylcinnamic acid was prepared in the same way starting with p-tolualdehyde. After three recrystallizations from methanol it had mp 197–198°. trans-p-Methoxycinnamic acid was prepared (73% yield) in the same way starting with anisaldehyde. After three recrystallizations from methanol it had mp 171–173°. trans-Cinnamic acid (Eastman) was recrystallized three times from a chloroform–hexane mixture and had mp 132–133°. 4-Pentenoic acid (K & K laboratories) was shown to be pure by vpc and was used without further purification. trans-4-Bromocrotonic acid was prepared by treating 86 g (1.0 mole) of recrystallized crotonic acid with 110 ml (1.5 moles) of purified thionyl chloride on a steam bath for 2 hr. Distillation gave 79 g (76%) of crotonyl chloride, bp 33–37° (18 mm). To a mixture of 23.5 g (0.12 mole) of N-bromosuccinimide in 200 ml of carbon tetrachloride was added 13 g (0.12 mole) of crotonyl chloride. The mixture was heated until all the N-bromosuccinimide had gone into solution (about 3 hr) and was then filtered. To the filtrate was added 100 ml of water, and the mixture was heated until all the carbon tetrachloride

had boiled off. The aqueous layer was heated an additional 15 min and then cooled. The precipitate was filtered and recrystallized twice from hexane, giving 2 g (10%) of 4-bromocrotonic acid, mp 72–74°. Oleic acid (Fisher Scientific Co., free from linoleic acid) had mp 3–4° and was used without further purification.

Potassium phosphate buffer solutions of pH 6.5 were prepared as stock solutions with an ionic strength of 0.8 M by dissolving 38.8 g (0.140 mole) of monobasic potassium phosphate (analytical grade) and 38.7 g (0.087 mole) of dibasic potassium phosphate trihydrate (analytical grade) in water and diluting to 1 l. total volume. Potassium permanganate stock solutions, 2.00×10^{-2} M, were prepared from Acculute volumetric standard solutions. These stock solutions were standardized against arsenous oxide and were found to remain unchanged for 4 or 5 months when kept in the dark.

Kinetic Method. The rate of oxidation by permanganate was determined by following spectrophotometrically the disappearance of permanganate. The stopped-flow reactor which was used employed a conventional design and both the storage and reacting solutions could be well thermostated. The reactor employed a 10-cm cell with a total volume of 3 ml. Approximately 0.2 sec was required to half-fill the cell. A Beckman DU spectrometer and associated electronics was employed, and the output of the energy recording adapter was recorded using a Honeywell–Brown strip-chart recorder having a 0.25-sec full-scale response and chart speeds up to 120 in./min. The photomultiplier was used instead of the regular photocell, and the usual load resistor–capacitor combination was replaced with a 1-megohm resistor in order to decrease the time constant of the detector circuit. The zero level was set using the shutter and dark current control; 100% transmission was set using distilled water in the cell.

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Kinetics of the Nitric Acid Oxidation of Benzyl Ethers to Benzaldehydes

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Abstract: The nitric acid oxidation of benzyl ethers has been studied kinetically in aqueous dioxane. The oxidation is initiated by a small amount of nitrous acid and follows first-order kinetics with respect to the ether. The rate of oxidation is in most cases independent of either nitric acid (over 0.5 M) or nitrous acid, while the oxidation with more dilute (below 0.5 M) nitric acid contains a term of nitric acid in the rate equation. The oxidation is accelerated by increasing the acidity of media; the plot of log k_1 vs. $-H_0$ gives a straight line with a slope of 1.0. The rate constant also increases with increasing dioxane content in the solvent. The apparent energy and entropy of activation are 31–34 kcal/mole and 10–13 eu, respectively. The substituent effect in the benzyl ring satisfies Hammett's equation, giving a ρ value of -1.9. A polar effect is also observed with the substituents in alkyl group, the order of reactivity being i-Pr > Et > Me > C_6H_5. A mechanism which involves the benzyl hydrogen abstraction by the conjugate acid of nitrogen dioxide is postulated and discussed.

On treatment of benzyl halide with dilute nitric acid, the halide is hydrolyzed to benzyl alcohol and the alcohol is oxidized to benzaldehyde.[1,2] The nitric acid oxidation of benzyl alcohol to benzaldehyde may be explained by a radical mechanism involving the abstraction of a benzyl hydrogen atom with nitrogen dioxide.[3] Only a few investigators have reported on the heterogeneous reaction of benzyl ethers with nitric acid.[4,5]

It was found that the oxidation of benzyl ether is difficult with pure nitric acid, but it may readily be started by addition of a small amount of sodium

$$ArCH_2OR \xrightarrow{HNO_3} ArCHO \qquad (1)$$
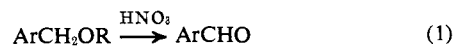
nitrite, resulting in a high yield (over 95%) of benzaldehyde. The present paper describes the kinetic study dealing with the effects of nitrous acid, the acidity of media, temperature, and substituent on the rate of

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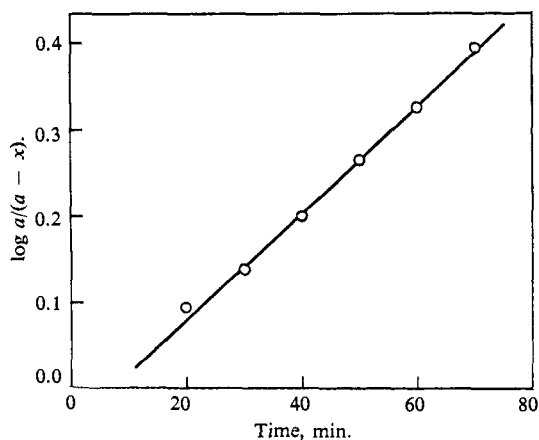(5) B. Reichert and W. Hoss, Arch. Pharm., 280, 157 (1942); Chem. Abstr., 37, 2001 (1943).

Figure 1. Typical first-order plot for the nitric acid oxidation of benzyl methyl ether in 40 vol. % dioxane at 90°. Initial concentration: $[HNO_3]$ = 2.43 M; $[C_6H_5CH_2OCH_3]$ = 0.0488 M; $[NaNO_2]$ = 0.002 M.

Figure 2. Correlation between log $[HNO_3]$ and log k_1(cor). The dotted line is of unit slope. Experimental conditions are shown in Table II.

oxidation. A probable mechanism is discussed on the basis of these data. Most runs were carried out in 40 vol. % dioxane at 90°.

Results

Induction Periods. The oxidation of benzyl methyl ether does not take place with pure nitric acid at 90°, while the addition of a small amount of sodium nitrite started the reaction smoothly (Table I). The rate of oxidation, which follows first-order kinetics with respect to the ethers, is independent of the amount of sodium nitrite added. The reaction is immediately stopped by the addition of urea, a scavenger of nitrous acid.

Benzoyl peroxide or azobisisobutyronitrile can initiate the reaction only after some period of induction. Radical inhibitors such as hydroquinone or p-cresol are also capable of initiating the oxidation. These materials are rapidly oxidized by nitric acid, producing nitrogen oxides which can initiate the reaction. The behavior has also been observed in the case of benzyl alcohol.[3] Sodium nitrite is shown to be the most favorable initiator and is used as a starter in all following oxidations.

Rate Law. The conversion of benzyl methyl ether to benzaldehyde is nearly quantitative. The rate was measured by following the produced aldehyde, which is virtually not oxidized to benzoic acid under these conditions. The oxidation in a large excess of nitric acid fits the first-order kinetics with respect to the ether (Table I and Figure 1).

$$v = k_1[ArCH_2OR] \qquad (2)$$

The first-order rate constant holds constancy up to 60–70% conversion. The rate is not affected by the initial concentration of sodium nitrite, as shown in the last column in Table I.

The effect of the concentration of nitric acid was examined by determining the oxidation rate at lower concentration of nitric acid in the presence of perchloric acid. Perchloric acid was necessary to raise the acidity of the solution effective for the oxidation to proceed. Since this reaction is acid catalyzed as stated below, rate constants are corrected to those at the standard acidity of H_0 = 0 (Table II). The cor-
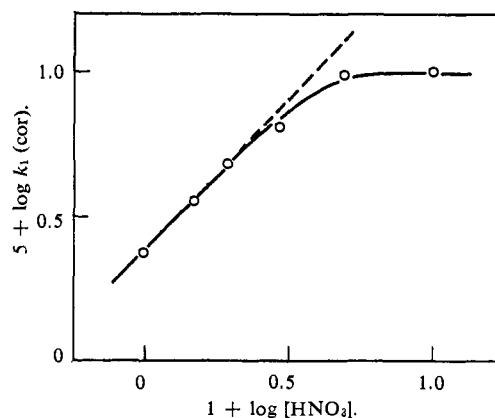
relation between log $[HNO_3]$ and log k_1(cor) exhibits an interesting feature (Figure 2); the rate increases with increasing concentration of nitric acid in the range of $[HNO_3]$ below 0.3 M, while the rate remains con-

Table I. Induction Periods and First-Order Rate Constants in the Presence of Various Added Compounds in 40 Vol. % Dioxane at 90°; Initial Concentration: $[HNO_3]$ = 1.457 M; $[C_6H_5CH_2OCH_3]$ = 0.0492 M

Added compd	Concn, $M \times 10^3$	Induction period, min	First-order rate constant, $k_1 \times 10^5$ sec^{-1}
None	. . .	>480	. . .
NaNO$_2$	2.0	0 ~ 5	6.49
NaNO$_2^a$	2.0	0	6.56
NaNO$_2^b$	2.0	4	5.97
NaNO$_2$	20.0	0	6.30
NaNO$_2$ + urea	2 + 3	>480	. . .
NaNO$_2$ + H$_2$Q^c	2 + 4	0	7.33
BPO^d	2.1	23	5.90
AIBN^e	3.0	58	6.30
H$_2$Q^c	9.1	0	6.54
p-Cresol	9.2	0	7.43

^{a} $[C_6H_5CH_2OCH_3]$ = 0.0984 M. ^{b} $[C_6H_5CH_2OCH_3]$ = 0.0246 M. ^{c} Hydroquinone. ^{d} Benzoyl peroxide. ^{e} Azobisisobutyronitrile.

stant with changing concentration of nitric acid at the range over 0.5 M. Hence the rate is independent of the nitric acid concentration at above 0.5 M and the rate may be expressed as eq 2.

Table II. Effect of the Various Initial Concentrations of Nitric Acid in the Presence of Perchloric Acid in 40 Vol. % Dioxane at 90°; Initial Concentration: $[HClO_4]$ = 1.51 M; $[C_6H_5CH_2OCH_3]$ = 0.0488 M; $[NaNO_2]$ = 0.002 M

$[HNO_3]$, M	$-H_0{}^a$	$k_1 \times 10^5$ sec^{-1}	5 + log k_1	5 + log k_1(cor)^b
0.971	0.460	29.4	1.468	1.00
0.486	0.346	20.7	1.316	0.990
0.291	0.244	11.4	1.057	0.813
0.194	0.194	7.60	0.881	0.687
0.146	0.168	5.17	0.713	0.553
0.097	0.110	3.07	0.487	0.377

^{a} p-Nitroaniline was used as an indicator. ^{b} Log k_1 was corrected to the same acidity (H_0 = 0) according to the equation, log k_1(cor) = H_0 + log k_1, since the plots of log k_1 vs. H_0 gave a straight line with a slope of -1.0 (see Figure 3).
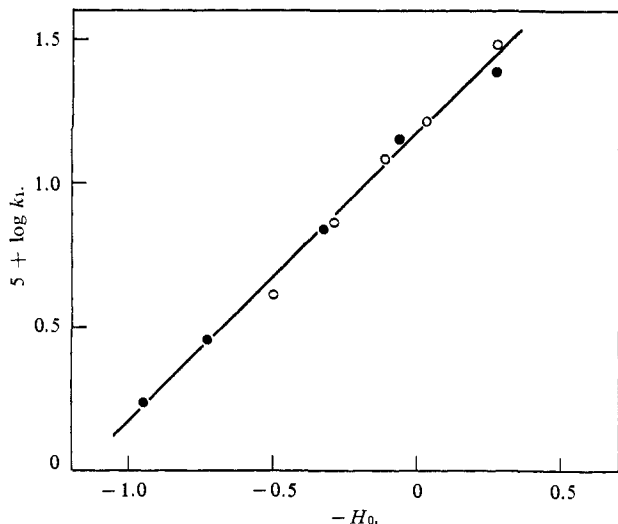
Figure 3. Plot of log k_1 vs. $-H_0$ for the nitric acid oxidation of benzyl methyl ether in 40 vol. % dioxane at 90°. Initial concentration: $[C_6H_5CH_2OCH_3]$ = 0.0537 M; $[NaNO_2]$ = 0.002 M. ●, $[HNO_3]$ = 0.7–2.5 M; ○, $[HNO_3]$ = 0.985 M, $[HClO_4]$ = 0–1.5 M.

The above results suggest the saturation of an attacking agent produced from nitric acid and nitrous acids. The saturation phenomenon was confirmed by the comparison of rates at different pressure of nitrogen dioxide with $[HNO_3]$ = 1.97 M and $[C_6H_5CH_2OCH_3]$ = 0.1015 M at 90° as follows. The oxidation was found to be faster in a flask with an air-tight stopper ($k_1 \times 10^5$ = 17.0 sec^{-1}) than in that with a loosely held glass stopper ($k_1 \times 10^5$ = 12.9 sec^{-1}). The oxidation rate constant (k_1) decreased to 9.6 × 10^{-5} sec^{-1} when nitrogen dioxide gas was swept out by a passing air stream. These facts strongly suggest that an attacking agent, probably nitrogen dioxide, is rapidly saturated in the reaction system, maintaining a stationary concentration, and that the apparent rate constant, k_1, depends upon the nitrogen dioxide concentration.

Acidity Dependence. The oxidation is accelerated by increasing the acidity of media and the plot of log k_1 vs. $-H_0$ gives a straight line with a slope of 1.0 (Figure 3). The rate is identical at the same acidity irrespective of the kind of added acids, i.e., nitric or perchloric acids. This fact coincides with the observation that the rate equation contains no term of nitric acid except at its low concentration.

Effect of Nitrous Acid. The oxidation is difficult in the absence of nitrous acid, while the rate is independent of the initial concentration of nitrous acid. Moreover, the concentration of nitrous acid in the reaction mixture increases as the oxidation proceeds only with poor reproducibility, and the rate is independent of the concentration of nitrous acid, satisfying first-order kinetics with benzyl ether. The concentrations of nitrous acid in two runs of different acidity, hence with different rate constant, are approximately the same. Thus, it is confirmed that the oxidation rate is not controlled by the concentration of nitrous acid.

Substituent Effect. The rates for the oxidation of substituted benzyl alkyl ethers are listed in Table III. The substituent effect in the benzyl ring fits the Hammett's equation with σ^+, giving a comparatively large ρ value of -1.9 (Figure 4). The substantial departure of the point for p-methoxy group (Figure 4) has been
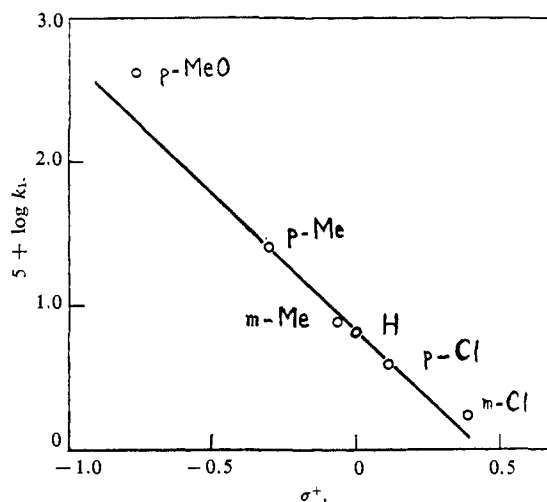
observed with several electrophilic reactions. The polar effect is also observed for the substituents in alkoxyl group. The order of reactivity by these substituents is i-Pr > n-Pr > Et > Me > C_6H_5; benzyl isopropyl ether is about 6-fold more reactive than benzyl methyl ether. Benzyl alcohol is highly reactive.

Figure 4. Plot of log k_1 vs. σ^+ for the nitric acid oxidation of substituted benzyl methyl ethers in 40 vol. % dioxane at 90°.

Table III. Substituent Effect on the Nitric Acid Oxidation of Benzyl Alkyl Ethers, $XC_6H_4CH_2OR$, in 40 Vol. % Dioxane at 90°; Initial Concentration: $[HNO_3]$ = 1.46 M; $[XC_6H_4CH_2OR]$ = 0.04–0.06 M; $[NaNO_2]$ = 0.002 M

Substituent		$k_1 \times$
X	R	10^5 sec^{-1}
p-MeO	Me	422[a]
p-Me	Me	25.1
m-Me	Me	7.76
H	Me	6.49
p-Cl	Me	3.90
m-Cl	Me	1.70
H	i-Pr	40.2
H	n-Pr	13.5
H	Et	13.1
H	Me	6.49
H	Ph	2.15
H	H	87.5

[a] Estimated from the rate ratios (56.7:3.28) with p-methylbenzyl methyl ether at $[HNO_3]_0$ = 0.728 M.

Solvent Effect. The oxidation of benzyl methyl ether is substantially affected by the medium composition as shown in Table IV. The rate increases with increasing content of dioxane at a constant concentration of nitric acid. In 20, 40, and 60 vol. % dioxane, the relative rates are 0.35, 1, and 2 at their H_0's of -0.26, 0.20, and 0.643, respectively. Hence, this large solvent effect cannot be explained in terms of the acidity of media, because the order of acidities is reversed to those of rates (Table IV). The solvent effect on the oxidation of benzyl alcohol is somewhat different from that of benzyl methyl ether, i.e., the increase of rate is below 20% even if dioxane content is increased 20%.

Temperature Dependence. Table V lists the activation parameters obtained from the Arrhenius plots. Apparent activation energies are considerably high

Table IV. Effect of the Content of Dioxane on the Rate of the Nitric Acid Oxidation of Benzyl Methyl Ether and Benzyl Alcohol at 90°

Substrate	$[HNO_3]$, M	$k_1 \times 10^5$ sec^{-1} 20% DO^a	40% DO^a	60% DO^a
$C_6H_5CH_2OCH_3$	0.728	...	1.33	4.61
$C_6H_5CH_2OCH_3$	0.971	0.79	3.22	6.92
$C_6H_5CH_2OCH_3$	1.457	2.46^b	6.47^c	14.7^d
$C_6H_5CH_2OH$	0.728	11.9^e	12.8^f	15.7^g
$C_6H_5CH_2OH$	1.457	75.0	87.5	116.0

^{a} Vol. % dioxane. ^{b} $H_0 = -0.258$. ^{c} $H_0 = 0.197$. ^{d} $H_0 = 0.643$. ^{e} $H_0 = 0.206$. ^{f} $H_0 = 0.997$. ^{g} $H_0 = 1.25$.

(28–34 kcal mole^{-1}) and activation entropies are positive (2–13 eu). No significant difference was observed between activation energies for benzyl alkyl ether and benzyl alcohol in spite of the large difference in their reactivities.
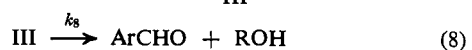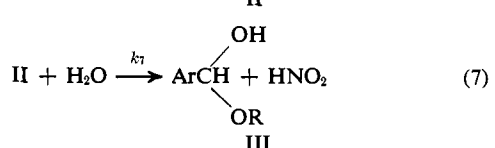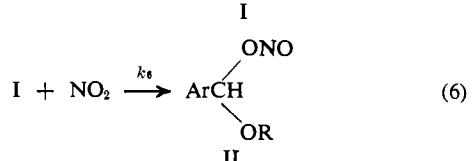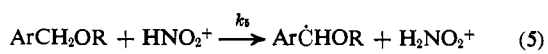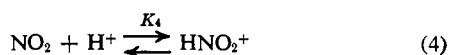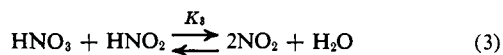
Table V. Activation Parameters for the Nitric Acid Oxidation of Benzyl Alkyl Ethers ($XC_6H_4CH_2OR$) in 40% Dioxane^a

Substrate X	R	$[HNO_3]$, M	$k_1 \times 10^5$ (90°) sec^{-1}	E_a, kcal mole^{-1}	ΔS^*, eu
p-MeO	Me	0.728	56.7	31.6	13.2
H	H	0.728	12.1	28.3	1.9
H	Et	2.43	48.3	31.1	11.4
H	Me	2.43	24.1	34.3	9.7

^{a} Temperature range examined was 70–95°.

Discussion

The Mechanism. The oxidation satisfies the kinetic equation: $v = k_1[ArCH_2OR]$, where k_1 is independent of the concentration of nitric and nitrous acids. The action of nitrous acid as an effective initiator implies that nitrogen dioxide may be the attacking species. Indeed, at the start of the oxidation, the reaction mixture became yellowish red, and the evolution of red fumes of nitrogen dioxide was observed. Furthermore, the acidity dependence (Figure 3) suggests that the more probable attacking agent is protonated nitrogen dioxide. Also, the substituent effect supports similar assumptions as described later. Thence the probable mechanism is as follows.

$$HNO_3 + HNO_2 \underset{}{\overset{K_3}{\rightleftarrows}} 2NO_2 + H_2O \quad (3)$$

$$NO_2 + H^+ \underset{}{\overset{K_4}{\rightleftarrows}} HNO_2^+ \quad (4)$$

$$ArCH_2OR + HNO_2^+ \overset{k_5}{\longrightarrow} Ar\dot{C}HOR + H_2NO_2^+ \quad (5)$$
$$I$$

$$I + NO_2 \overset{k_6}{\longrightarrow} ArC\overset{ONO}{\underset{OR}{\overset{|}{\diagdown}}}H \quad (6)$$
$$II$$

$$II + H_2O \overset{k_7}{\longrightarrow} ArC\overset{OH}{\underset{OR}{\overset{|}{\diagdown}}}H + HNO_2 \quad (7)$$
$$III$$

$$III \overset{k_8}{\longrightarrow} ArCHO + ROH \quad (8)$$

Our kinetic results suggest that the rate is determined by step 5, i.e., the abstraction of a benzyl hydrogen atom by protonated nitrogen dioxide. If the formation of nitrogen dioxide or the hydrolysis of α-alkoxybenzyl nitrite (II) were a slow step, the rate equation would contain a term of nitric acid or nitrous acid, which is not the case. The radical coupling between nitrogen dioxide and intermediary α-alkoxybenzyl radical I and also the hydrolysis of the resulted nitrite II should be rapid under these conditions.[6] Hemiacetal is likewise an unstable compound[7] and the conversion of II into aldehyde should be fast. The reverse reactions of steps 6, 7, and 8 may be negligible under these conditions in view of the negligible concentration of intermediates.

The above explanation contains an important assumption of the stationary concentration of nitrogen dioxide. Although the direct determination of the amount of nitrogen dioxide present in an aqueous solution has not yet been reported, the above assumption appears to be possible for the reaction in an open vessel on the basis of following reasons. (i) The rate of oxidation increases with increasing concentration of nitric acid at its low concentration (Figure 2). (ii) The evolution of nitrogen dioxide gas is often observed. (iii) The oxidation rate increases with increasing pressure of nitrogen dioxide and is retarded by expelling nitrogen dioxide. (iv) The oxidation rate of benzaldehyde in an ampoule, unlike the case in an open vessel, increases with increasing concentration of nitric acid.[8] The rate equation may thus be expressed as follows.

$$v = k_5[HNO_2^+][ArCH_2OR] =$$
$$k_5K_4[H^+][NO_2][ArCH_2OR]$$

Here, the observed first-order rate constant, k_1, corresponds to $k_5K_4[H^+][NO_2]$, and the observed effect of acidity and nitric acid concentration is comprehensible if $[NO_2]$ is constant at the stationary state.

The observed acidity dependence of the rate leads to the assumption of an attack of the conjugate acid of nitrogen dioxide. Protonated nitrogen dioxide should be more effective for the hydrogen atom abstraction because of its expected high electrophilicity. Positively charged free radicals have already been proposed to be more reactive for hydrogen atom abstraction.[9] Actually, protonated amino radical has been suggested in the decomposition of N-haloammonium ion.[10] Although protonation of nitrogen dioxide has not been reported, it may be possible, since the basicity of nitrogen dioxide seems to be analogous to that of nitrous acid.

It is well known that dinitrogen tetroxide in the media, having a high dielectric constant, is almost completely dissociated, partly homolytically, but chiefly heterolytically, as follows.[11,12]

$$2NO_2 \rightleftarrows N_2O_4 \rightleftarrows NO^+ + NO_3^-$$
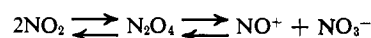
(6) Alkyl nitrites are easily hydrolyzed even at 0°. See, for example, A. D. Allen, *J. Chem. Soc.*, 1968 (1954).

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Table VI. Polar Effect in Hydrogen Abstraction of Ring-Substituted Benzyl Ethers and Alcohols

Attacking radical	Ethers or alcohols	Solvent	Temp, °C	ρ	Reference
$RO_2\cdot$	Benzyl phenyl	Chlorobenzene	60	0	13
$RO_2\cdot$	Benzyl methyl	Chlorobenzene	60	0	13
$RO_2\cdot$	Dibenzyl	Reactants	80–90	-0.65	14
NBS[a]	Benzyl methyl	Reactants	77	$0 \sim -0.3$[b]	15
$HNO_2{}^+$	Benzyl methyl	40% dioxane	90	-1.9	This work
$HNO_2{}^+$	Benzyl alcohol	40% dioxane	90	-2.25	3

[a] N-Bromosuccinimide was used as a radical source. [b] Roughly estimated from relative rates except that of methoxybenzyl methyl ethers.

In nonpolar solvents, however, the tetroxide dissociates homolytically.[12] These facts explain the observed solvent effect that the oxidation rate increases with increasing content of dioxane in spite of the decreasing acidity. The increase of dioxane content will favor the homolytic dissociation, resulting in an increase of nitrogen dioxide concentration or the acceleration of the oxidation.

Substituent Effect. It has been reported that the rate of abstraction of a α-hydrogen atom from benzyl ether is little affected by the polar substituents.[13–15] The present oxidation was found to be substantially affected by polar substituents both in the benzyl ring and in the alkoxyl group as summarized in Tables VI and VII.

Table VII. Relative Rates for the Hydrogen Abstraction of Benzyl Alkyl Ethers ($C_6H_5CH_2OR$) at Various Conditions

Attacking radical	Solvent	Temp, °C	Me	Et	i-Pr	Reference
$Cl_3C\cdot$	CCl_4	77	1.00	1.3	1.3	17
$RO\cdot$	CCl_4	77	1.00	1.1	1.3	17
$RO_2\cdot$	Chlorobenzene	60	1.0	1.1	...	13
$HNO_2{}^+$	40% dioxane	90	1.00	2.01	3.10	This work

The magnitude of polar effect for hydrogen-abstraction reactions is generally explained in terms of electron affinity of an attacking radical. If nitrogen dioxide itself were an attacking agent for the present oxidation, the resulting large polar effect ($\rho = -1.9$) is not convincing, since the electron affinities (electrophilicity) are in the order $NO_2 \ll RO_2\cdot$.[16] These facts, however, may be explained by assuming $HNO_2{}^+$ as an attacking radical, since positive $HNO_2{}^+$ is presumably more electrophilic than neutral $RO_2\cdot$.

The observed insensitivity of ring substituents in the autoxidation of benzyl ethers has been ascribed to the powerful electron-releasing nature of the ether oxygen;[13] but in some cases, e.g., in the halogenation of benzyl ethers, the effect of alkoxyl group has been said to be considerably small.[17] The present results show a substantially large polar effect both in the benzyl ring and the alkoxyl group; the benzyl hydrogen abstraction is influenced by the substituent in the alkoxyl group as well as in the benzyl ring. These

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trends are apparent at a glance at other investigators' data in Tables VI and VII, although the trends are rather small.

The Oxidation of Benzyl Alcohol. A similar mechanism has been postulated for the nitric acid oxidation of benzyl alcohol.[3] The slow step of this mechanism, however, has been assumed to be the hydrolysis of α-hydroxybenzyl nitrite which corresponds to step 7 ($R = H$). In the course of the present study with benzyl ethers, it seems to be more rational for benzyl alcohol to follow the mechanism similar to that for benzyl ethers, since kinetic results are quite similar to each other and the large polar effect ($\rho = -2.3$) may be understood by assuming the attack of the radical ion, $HNO_2{}^+$. The substituent effect for benzyl alcohols was corrected with a σ value better than with the Brown–Okamoto's σ^+ value as has been reported with the reaction of the t-butoxy radical with toluenes.[18] The observed high value of the slope (1.5–2) in the plots of log k vs. $-H_0{}^3$ is probably due to the fact that the oxidation of the alcohol was carried out in a solvent still unsaturated with nitrogen dioxide, hence resulting in the insertion of some terms of nitric acid in the rate equation.

Experimental Section

Kinetics. The oxidation was started by the addition of an aqueous solution of sodium nitrite to the thermostated mixture of nitric acid and benzyl ethers in a mixed solvent of dioxane–water

Table VIII. Physical Constant of Some Substituted Benzyl Alkyl Ethers ($XC_6H_4CH_2OR$)

X	R	% yield[a]	Bp, °C (mm)	Lit. bp, °C (mm)
H	Me	52	75–77 (31)	17.5 (760)[d]
p-Me	Me	64	86–87 (29)	84 (20)[e]
m-Me	Me	85	85–86 (23)	47 (2)[f]
p-Cl	Me	23[b]	95–96 (21)	60 (2)[f]
m-Cl	Me	38[b]	99–100 (22)	58–60 (1.5)[g]
p-MeO	Me	73[b]	77.2–77.6 (3)	74–75 (1.5)[g]
H	Et	66	81.5–81.8 (23)	185[h]
H	i-Pr	42	89–90 (20)	83.0 (16)[i]
H	n-Pr	51	96–97 (27)	201–205[j]
H	C_6H_5	27	38.2–39.0[c]	39[c]

[a] Yield based on the amount of used benzyl halide. [b] Over-all yield based on the amount of used toluenes or p-methoxybenzyl alcohol. [c] Melting point, °C. [d] W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, J. Am. Chem. Soc., **69**, 2451 (1947). [e] C. D. Gutsche and H. E. Johnson, ibid., **77**, 109 (1955). [f] See ref 13. [g] See ref 15. [h] D. R. Stull, Ind. Eng. Chem., **39**, 517 (197). [i] See ref 19. [j] S. Mitsui, A. Kasahara, and N. Endo, J. Chem. Soc. Japan, Pure Chem. Sect., **75**, 234 (1954).

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(4:6 vol. %). The homogeneous reaction mixture was allowed to stand in a flask with a loosely held glass stopper without stirring; no difference in rates was observed between reactions with and without stirring. Aliquots were taken out at appropriate intervals of time, and the produced aldehyde was estimated by means of ultraviolet spectrophotometry after extracting with chloroform as reported previously.[8]

Materials. Substituted benzyl methyl ethers except the p-methoxy derivative were prepared by way of the side-chain bromination of corresponding toluenes, followed by treatment with sodium methoxide. p-Methoxybenzyl ether was synthesized by the bromination of p-methoxybenzyl alcohol[3] by the hydrogen bromide method,[19] followed by methanolysis with sodium methoxide. Benzyl alkyl ethers were obtained by the treatment of benzyl chloride with sodium alkoxide at the reflux temperature for 3–4 hr. The ethers were all purified by rectification under vacuum (Table VIII).

The other materials were the same with those described previously.[3]

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Rates of Bromination of Polynuclear Aromatic Hydrocarbons[1]

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Abstract: Rate constants for the bromination of several polynuclear aromatic hydrocarbons by molecular bromine were determined in aqueous acetic acid at 25°. Partial rate factors were obtained from the rates and the major reaction products. The partial rate factors, and some obtained previously, were correlated with MO reactivity parameters and with the rates of other electrophilic substitution reactions. Addition accompanies substitution in the bromination of phenanthrene and anthracene.

Although interest in the reactivities of polynuclear aromatic systems has increased as a result of the availability of various MO reactivity parameters with which the experimental reactivities can be compared, there are only very few reactions series in which these reactivities have been assessed in direct electrophilic substitution reactions. The studies that cover the largest number of compounds are those on nitration,[4] deuterio deprotonation,[5] the basicity toward hydrogen fluoride,[6] and, to a lesser extent, chlorination.[7] To these we now add bromination.

Results

Reactions were carried out in aqueous acetic acid. In acetic acid, as well as in other solvents of low dielectric constant, the kinetics of bromination is complicated by the intervention of terms which are of high order in bromine, and by the complexing of unreacted bromine with bromide ion which is formed as the reaction proceeds.[8] It is for this reason that investigations that did employ bromination for a comparison of relative rates have often relied on a comparison of time intervals required to reach a definite per cent of reaction, and rate constants were not determined. For instance,

in an earlier study of bromination, Mason compared the times for 5 and 10% bromination of hydrocarbons in 80% acetic acid.[9] Under these conditions, the bromination of benzene, naphthalene, and biphenyl was approximately third order over-all, but the reaction of phenanthrene followed second-order kinetics. Its reactivity could therefore not be compared with that of the other compounds. It would seem, then, that the method of comparing reaction times is beset by hazards, particularly if the compounds differ widely in reactivity.

The reasons for the complexity of aromatic bromination are now well understood, and conditions have been worked out under which the high orders in bromine can be reduced and the reaction conducted under conditions such that the total order of reaction is two, first order in both hydrocarbon and stoichiometric bromine. This can be accomplished by increasing the water content, or, more importantly, by conducting the reaction in the presence of a large excess of bromide ion.[10] Under these conditions, much of the bromine is complexed to tribromide ion, which reduces the free bromine concentration to such small amounts that the high-order terms become negligible.[11] Also, since most of the bromine is present as tribromide ion, the small amount of bromide ion that is formed during reaction does not interfere with the second-order kinetics. It has previously been shown that under those conditions the relationship $k_{obsd} = k_2 K/(K + Br^-)$ (eq 1) holds, where k_2 is the rate constant for bromination by free bromine and K the dissociation constant of the tribromide ion. Rate constants are determined at various bromide ion concentrations at a constant ionic strength, and the true rate constant, k_2, is obtained as the slope

(1) Relative Reactivities of Polynuclear Aromatic Systems. IV.

(2) Taken from the Ph.D. thesis of L. Altschuler, Bryn Mawr College, May 1966.

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