The nmr spectrum of **13** has principal bands at τ 4.40 and 4.57 (multiplet, vinyl, 2 H),[17] τ 6.73 (singlet, $\mathrm{OC}H_3$, 3 H), τ 6.86 (multiplet, W_H = 4.5 cps, $\mathrm{C}H\mathrm{O}$, 1 H), and τ 8.40–9.05 (multiplet, 4 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 74.00; H, 10.40.

Dichlorocarbene Adducts of Mixed 1,3-Pentadienes.[7] The mixture of adducts was prepared (43%) in the usual way[7,11] and separated by preparative glpc. There was obtained **14** (14%), **15** (6%), and **16** (20%) as well as 3% of what is presumed to be a bis adduct.[7] The nmr spectrum of **14** exhibits signals at τ 4.07–5.06 (multiplet, vinyl, 3 H) and τ 8.03–8.90 (multiplet containing a sharp peak at τ 8.64, 5 H).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 48.29; H, 5.57; Cl, 46.80; parent mass peaks 151, 152.

The nmr spectrum of **15** shows signals at τ 4.44–4.83 (multiplet, vinyl, 3 H) and τ 7.59–8.93 (multiplet, 5 H containing a doublet at τ 8.78, J = 5.9 cps).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 48.11; H, 5.33; Cl, 47.10.

The nmr spectrum of **16** ($n^{25}\mathrm{D}$ 1.4783) shows signals at τ 3.93 and 5.09 (multiplet, vinyl, 2 H) and τ 7.50–8.90 (series of multiplets, 6 H).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 48.03; H, 5.42; Cl, 47.00; parent mass peaks, 150, 152.

Reaction of *cis*- and *trans*-2,2-Dichloro-3-methylvinylcyclopropanes (14 and 15) with Potassium Methoxide. In a three-necked flask equipped with a rubber septum, pressure-equilibrated dropping funnel, and nitrogen purge system, 20 g of potassium *t*-butoxide[10] was mixed with 12 ml of methanol and stirred magnetically for 20 min. After removal of alcohols by heating under aspirator vacuum, 78 ml of DMSO[10] was introduced and stirring was continued for another 20 min. A 95% pure mixture of **14** and **15** (2:1) was introduced and the mixture was stirred at room temperature for 25 hr. The usual work-up procedure followed by preparative glpc afforded **17** (31%, $n^{25}\mathrm{D}$ 1.4332) and **18** (23%, $n^{25}\mathrm{D}$ 1.4351).

The nmr spectrum of **17** shows signals at τ 4.18–5.25 (multiplet, vinyl, 3 H), τ 6.69 and 6.73 (singlets, $\mathrm{OC}H_3$, 6 H), and τ 8.53–9.00 (multiplet containing a sharp spike at τ 8.89, 5 H). This spectrum is very similar to that of **14**.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.50; H, 9.89; parent mass peak, 142.

The nmr spectrum of **18** has signals at τ 4.16–5.17 (multiplet, vinyl, 3 H), τ 6.69 and 6.76 (singlets, $\mathrm{OC}H_3$, 6 H), τ 8.26 (poorly resolved quartet appearing as a triplet, J = 8 cps, allylic cyclopropyl, 1 H), and τ 8.50–9.12 (multiplet, 4 H). The τ 8.26 signal indicates a rather large coupling with the other cyclopropyl hydrogen which is consistent with a *cis* geometry between them. The separation of methoxy singlets in **18** is 4.0 cps while that in **17** is 2.4 cps, as predicted for *cis* and *trans* isomers of this type.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.35; H, 9.78; parent mass peak, 142.

Reaction of 1,1-Dichloro-2-(1-propenyl)cyclopropane (16) with Potassium Methoxide. Using the procedure described in the preceding experiment, the reaction of 2.9 g (95% pure) of **16** with potassium methoxide derived from 22.4 g of potassium *t*-butoxide gave **19** (57%, $n^{25}\mathrm{D}$ 1.4434), **20** (*ca.* 5%, $n^{25}\mathrm{D}$ 1.4422), and **21** (*ca.* 5%). The nmr spectrum of **19** has signals at τ 4.00–5.00 (multiplet, vinyl, 2 H), τ 6.75 and 6.88 (singlets, $\mathrm{OC}H_3$, 6 H) superimposed on a multiplet ($\mathrm{C}H\mathrm{O}$, 1 H), τ 8.23 (J = 5.8 cps, doublet, allylic methyl, 3 H), and τ 8.70–9.50 (multiplet, cyclopropyl, 2 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 76.57; H, 9.92. Found: C, 76.58; H, 9.91; parent mass peak, 142.

20 [λ_max 232 mμ (ϵ 13,300)] gave an nmr spectrum having signals at τ 3.80–4.30 (multiplet, conjugated vinyl, 2 H), τ 5.13 (multiplet, terminal vinyl, 2 H), τ 7.33–8.26 (multiplet, cyclopropyl, 2 H), and τ 8.79 (singlet, O-*t*-Bu, 9 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.40; H, 10.40; parent mass peak + 1, 153.

The nmr spectrum of **21** shows signals at τ 4.17–5.00 (multiplet, vinyl, 2 H), τ 6.72 (J = 8.0, 4.6 cps, quartet, $\mathrm{C}H\mathrm{O}$, 1 H), τ 6.87 (singlet, $\mathrm{OC}H_3$, 3 H), τ 8.23 (J = 6.0 cps, doublet with secondary splitting, allylic methyl, 3 H), τ 8.83 (singlet, O-*t*-Bu, 9 H), τ 8.98 (J = 8.0, 6.3 cps, quartet, cyclopropyl, 1 H), and τ 9.37 (J = 6.3, 4.6 cps, quartet, cyclopropyl, 1 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 72.12; H, 10.48.

Reaction of 1,1-Dichloro-2-(1-propenyl)cyclopropane (16) with Potassium *t*-Butoxide. A 9.5-g sample of **16** was stirred with a solution of 10 g of potassium *t*-butoxide in 830 ml of DMSO[10] (nitrogen) for 45 min and then quenched with water. The mixture was worked up by pentane extraction; the extract was filtered through glass wool to remove polymer. Fractional distillation afforded 3.8 g of **20**, bp 31° (20 mm), which was found to be essentially pure by glpc. The product was identical in all respects with material obtained as described in the preceding experiment.

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Kinetics of the Nitric Acid Oxidation of Nitrosobenzene to Nitrobenzene in Aqueous Dioxane

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Contribution No. 102 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan. *Received May 2, 1967*

Abstract: The oxidation of nitrosobenzene to nitrobenzene in aqueous dioxane with dilute (≤ 1 *M*) nitric acid containing a small amount of nitrous acid has been studied kinetically by means of ultraviolet spectrophotometry. The yield of nitrobenzenes increases with increasing nitric acid concentration and with increasing dioxane content in the solvent. The concentration of nitrous acid in the system increases as the reaction proceeds, and the reaction is autocatalytic. The rate is expressed as $v = kh_0^{0.5}(1 + 0.5h_0)[\mathrm{NO_3^-}]^{0.5}[\mathrm{HNO_2}]^{0.5}[\mathrm{PhNO}]$. The rate increases with increasing content of dioxane in the solvent in spite of decreasing acidity. The reaction is facilitated by electron-releasing groups and retarded by electron-attracting groups. A probable mechanism is discussed which involves an attack of nitrogen dioxide and/or its conjugate acid on the double bond of nitrosobenzene.

Aromatic nitrations are generally retarded by the addition of nitrous acid because of the removal of nitronium ion. However, in more dilute nitric acid, nitrous acid accelerates nitration, and reactive aromatics such as phenol and mesitylene, etc., are subject to nitrosation by nitrous acid. The resulting nitroso compounds

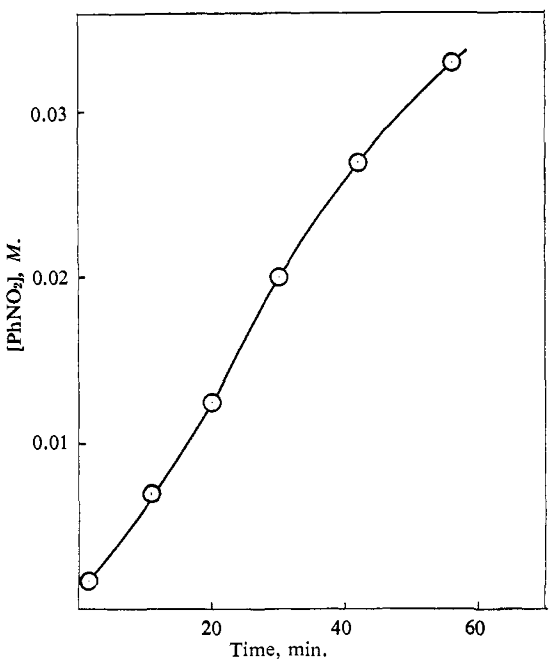

Figure 1. Plot of formed nitrobenzene *vs.* time in the nitric acid oxidation of nitrosobenzene in 40% dioxane at 70°. Initial concentration: $[HNO_3] = 1.0$ *M*, $[NaNO_2] = 0.001$ *M*, $[PhNO] = 0.095$ *M*.

are then rapidly oxidized by nitric acid to the corresponding nitro compounds.[1-3]

$$\mathrm{ArH} \xrightarrow{\mathrm{HNO_2}} \mathrm{ArNO} \xrightarrow{\mathrm{HNO_3}} \mathrm{ArNO_2}$$

The oxidation mechanism of the nitroso compounds by nitric acid has been little studied. Nitrosobenzene is oxidized with dilute nitric acid containing a small amount of nitrous acid to nitrobenzene, but the reaction is suppressed with pure nitric acid or nitric acid containing urea, and nitrosobenzene is consumed by other reactions. One of the side reactions may be the formation of *p*-nitrosodiphenylhydroxylamine, $p\text{-}ONC_6H_4N(OH)\text{-}C_6H_5$, which has been observed on treatment of nitrosobenzene with sulfuric acid[4] or nitric acid containing urea.[3]

The present paper deals with the kinetics of oxidation of nitrosobenzene or substituted nitrosobenzenes with dilute (≤ 1 *M*) nitric acid in aqueous dioxane to give nitrobenzenes. The yield of nitrobenzene under the kinetic conditions is *ca.* 70%. The effects of acidity of the reaction media, the concentration of nitric and nitrous acids and reactants, and the substituent and solvent effects are discussed, and a probable mechanism for the reaction is suggested.

Results and Discussion

The Rate Equation. The plot of concentration of nitrobenzene *vs.* reaction time gives an S-shaped curve which implies autocatalysis. The rate constants were estimated graphically by means of the tangent method[5] (Figure 1). The figure is different from an ordinary first-order curve. As reported previously,[6] if the system is saturated with nitrogen dioxide, the rate should be independent of the concentrations of nitric and nitrous acids, but if it is not, the rate should depend on concentrations both of nitric and nitrous acids. Since excess nitric acid is used, the nitric acid concentration is practically constant during the reaction. Hence the autocatalysis may be due to nitrous acid formed as the reaction proceeds (Table I).

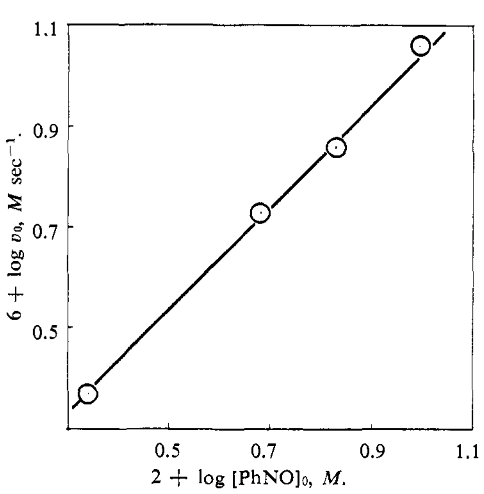

Figure 2. The relation of initial concentrations of nitrosobenzene to the initial reaction rates in 40% dioxane at 70°. Initial concentration: $[HNO_3] = 1.0$ *M*, $[NaNO_2] = 0.001$ *M*.

Table I. The Change of Nitrous Acid Concentration with Time in a Reaction Mixture in the Nitric Acid Oxidation of Nitrosobenzene[a]

Time, min	Nitrous acid concn, *M*	Time, min	Nitrous acid concn, *M*
2	0.0011	32	0.012
10	0.0031	44	0.017
20	0.0059	70	0.019

[a] In 40% dioxane at 70°. Initial concentration: $[HNO_3] = 1.0$ *M*, $[NaNO_2] = 0.001$ *M*, $[PhNO] = 0.048$ *M*.

The initial rate was estimated graphically by the tangent method at the end of the induction period. Initial rates were obtained by varying the initial concentrations of nitrosobenzene, and the plot of logarithm of initial rate *vs.* logarithm of nitrosobenzene concentration gives a straight line with a slope of *ca.* 1 (Figure 2). Therefore, the reaction is first order in nitrosobenzene. When over 0.005 *M* sodium nitrite is added, the conversion curve approaches a straight line, since the induction period disappears. It is difficult to measure exactly the effect of nitrous acid by varying the amount of sodium nitrite, since a preliminary introduction of sodium nitrite causes a slight reaction between dioxane and nitric or nitrous acid resulting in an increase of the concentration of nitrous acid.

The pseudo-first-order rate constant increases with increasing concentration of nitrous acid or with time. The pseudo-first-order rate constant at each time was measured; tangents were drawn at various times on

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(1) F. H. Westheimer, E. Segel, and R. Schramm, *J. Am. Chem. Soc.*, **69**, 773 (1947).

(2) R. M. Schramm and F. H. Westheimer, *ibid.*, **70**, 1782 (1948).

(3) A. I. Titov and N. G. Laptev, *Zh. Obshch. Khim.*, **18**, 741(1948); *Chem. Abstr.*, **43**, 5013 (1949).

(4) E. Bamberger, H. Büsdorf, and H. Sand, *Ber.*, **31**, 1513 (1898).

(5) R. Livingston in "Investigation of Rates and Mechanisms of Reactions," S. L. Fries and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p 182.

(6) Y. Ogata, H. Tezuka, and Y. Sawaki, *Tetrahedron*, **23**, 1007 (1967).

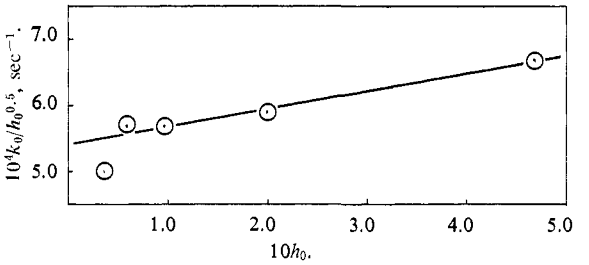

Figure 3. Plot of initial relative rate constants *vs.* acidity function h_0 for the oxidation of nitrosobenzene with nitric acid in the presence of sulfuric acid in 70% dioxane at 70°.

plots like Figure 1 and the slopes were then divided by the concentrations of nitrosobenzene remaining at the various times. The nitrous acid concentration was determined spectrophotometrically at the same time (Table II). The plot of log k *vs.* log $[HNO_2]$ gave a straight line with a slope of *ca.* 0.4, *i.e.*, the reaction is nearly one-half order in nitrous acid.

Table II. The Relation between Log k and Nitrous Acid Concentration in Nitric Acid Oxidation of Nitrosobenzene[a]

3 + log $[HNO_2]$, M	5 + log k, sec^{-1}	3 + log $[HNO_2]$, M	5 + log k, sec^{-1}
0.88	0.95	1.20	1.08
1.01	1.01	1.28	1.13
1.11	1.05	...	...

[a] In 70% dioxane at 70°. Initial concentration: $[HNO_3]$ = 0.40 M, $[NaNO_2]$ = 0.005 M, $[PhNO]$ = 0.051 M.

The effect of initial concentrations of nitric acid, $[HNO_3]_0$, on the initial pseudo-first-order rate constant, k_0, was studied in the presence of 0.5 M sulfuric acid which was added to keep enough acidity for the oxidation. The rate constants were corrected for the acidity to compare at the constant acidity ($H_0 = 0$) (Table III). The plot of log k_0 *vs.* log $[HNO_3]_0$ gave a straight line with a slope of *ca.* 0.5. Hence, the rate of the present reaction is first order in nitrosobenzene and one-half order in nitric and nitrous acids.

Table III. The Effect of Initial Nitric Acid Concentration on the Initial Oxidation Rate[a]

1 + log $[HNO_3]_0$, M	4 + log k_0,[b] sec^{-1}	1 + log $[HNO_3]_0$, M	4 + log k_0,[b] sec^{-1}
−0.30	0.43	0.18	0.70
−0.097	0.52	0.30	0.73
0	0.57	0.38	0.76

[a] In 60% dioxane at 70°. Initial concentration: $[HNO_3]$ = 0.05–0.24 M, $[H_2SO_4]$ = 0.50 M, $[NaNO_2]$ = 0.005 M, $[PhNO]$ = 0.048 M. [b] Rate constants were corrected to those at $H_0 = 0$.

Table IV. The Yields of Nitrobenzene in the Presence of Added Compounds in Nitric Acid Oxidation of Nitrosobenzene[a]

Added compd, M	Yield of nitrobenzene, %	Added compd, M	Yield of nitrobenzene, %
...	0	BPO,[b] 0.005	77
$CO(NH_2)_2$, 0.05	0	AIBN,[c] 0.005	77
$NaNO_2$, 0.005	78		

[a] In 60% dioxane at 70°. Initial concentration: $[HNO_3]$ = 1.0 M, $[NaNO_2]$ = 0.005 M, $[PhNO]$ = 0.048 M. [b] Benzoyl peroxide. [c] Azobisisobutyronitrile.

Effect of Added Compounds. The oxidation is initiated by the addition of a small amount of sodium nitrite and influenced by the concentration of nitrous acid, but ordinary initiators in radical reactions such as benzoyl peroxide (BPO) and azobis(isobutyronitrile) (AIBN) can also initiate the oxidation (Table IV). This may be explained by the formation of appreciable amounts of nitrous acid by the interaction of the reactants with nitric acid and BPO or AIBN.[7] The formation of nitrobenzene was not observed in the presence of urea, *i.e.*, a scavenger of nitrous acid.

Effect of Acidity. The present reaction is catalyzed by acid. The effect of acidity of media was measured by adding various amounts of sulfuric acid to the reaction mixture. The Hammett acidity function (H_0) was estimated by means of spectrophotometry using *p*-nitroaniline as an indicator, but the plot of log k_0 *vs.* H_0 gives a straight line with a slope of fractional number such as −0.6. Then the value of $(10^4k_0/h_0^{0.5})$ was plotted against h_0 ($H_0 = -\log h_0$) as shown in Figure 3. Figure 3 gives the equation $(10^4k_0/h_0^{0.5}) = 5.5(1 + 0.5h_0)$. Therefore, the rate is expressed as $v = kh_0^{0.5}(1 + 0.5h_0)$. $[NO_3^-]^{0.5}[HNO_2]^{0.5}[PhNO]$.

Simultaneous attack of protonated and free nitrogen dioxide which has been suggested previously[6] can explain the above expression. In spite of a very low concentration, protonated nitrogen dioxide should be very reactive.

Effect of Temperature. The effect of temperature on the rate was studied with 0.40 M nitric acid, 0.005 M sodium nitrite, and 0.049 M nitrosobenzene at 50, 60, 70, 75, and 80°, giving initial first-order rate constants, 10^5k_0, of 1.0, 3.3, 8.8, 14, and 22 sec^{-1}, respectively. The Arrhenius plots gave a straight line. The apparent energy and entropy of activation are calculated from these data to be 21 kcal/mole and −18 eu, respectively.

Table V. The Effect of Solvent Composition on the Initial Rate Constant for the Nitric Acid Oxidation of Nitrosobenzene at 70°[a]

Dioxane, vol. %	10^5k_0, sec^{-1}	Yields of nitrobenzene, %	H_0
20	...	37	0.09
40	15	53	0.7
60	23	78	1.16

[a] Initial concentration: $[HNO_3]$ = 1.0 M, $[NaNO_2]$ = 0.005 M, $[PhNO]$ = 0.048 M.

Solvent Effect. The solvent effect is given in Table V. It is obvious from the table that the rate increases as the content of dioxane in the solvent increases, although the acidity of media falls with increasing content of dioxane. The yield of nitrobenzene increases also as the content of dioxane increases. This solvent effect may be explained on the basis of the concentration of

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

the attacking species, nitrogen dioxide. Nitrogen dioxide is in equilibrium with nitrosonium and nitrate ions as shown below.[6]

$$2NO_2 \rightleftharpoons NO^+ + NO_3^-$$

As the content of dioxane increases, the suppression of ionization of nitrogen dioxide may result in an increase of nitrogen dioxide concentration;[6] hence it accelerates the oxidation. Treatment of nitrosobenzene in 20% dioxane with 1 *M* nitric acid containing urea at 70° shows 60% consumption of nitrosobenzene at 50 min, while a similar reaction in 60% dioxane gave only 10% consumption of nitrosobenzene. Since the acidity falls with increasing content of dioxane, the acid-catalyzed side reaction may be suppressed.

The increasing yield of nitrobenzene at a high content of dioxane may be explained in terms of both enhancement of oxidation and suppression of the side reaction.

Substituent Effect. The rate of the oxidation of substituted nitrosobenzenes is summarized in Table VI.

Table VI. The Substituent Effect on the Nitric Acid Oxidation of Substituted Nitrosobenzenes[a]

Substituent	10^5k_0, sec^{-1}	Substituent	10^5k_0, sec^{-1}
p-Me	9.5	*p*-Cl	4.8
m-Me	11.7	*m*-Cl	5.1
H	8.8	*m*-NO_2	4.2

[a] In 70% dioxane at 70°. Initial concentration: [ArNO] = 0.048 *M*, [HNO_3] = 0.40 *M*, [$NaNO_2$] = 0.005 *M*.

p-Nitrosoanisole in acidic solution is so reactive even at low temperature that it is easily hydrolyzed to *p*-nitrosophenol,[8] and the *p*-nitrosophenol formed is in equilibrium with *p*-benzoquinone monoxime. Therefore, methoxy and hydroxyl groups are eliminated in the discussion of the substituent effect. The reaction is facilitated by electron-releasing groups and retarded by electron-attracting groups. Although the effect of substituents shows a departure from the Hammett equation, the ρ value approximates to -0.5. *meta* groups have in general a higher enhancement of the rate than *para* groups, *e.g.*, CH_3 and Cl. The same results have been reported for nitrosotoluene by Yoshida, *et al.*,[9] but an accurate discussion of the substituent effect is difficult at present from these data.

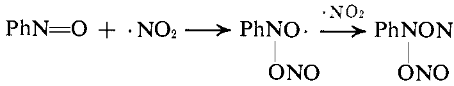
Mechanism. The present reaction can be initiated by nitrous acid. The most probable attacking species may be nitrogen dioxide or its conjugate acid, and nitrosonium ion, nitric oxide, and dinitrogen trioxide are excluded in view of the rate law and solvent effect. The attacking agent proposed for the nitric acid oxidation of benzyl ethers[10] and benzaldehydes[6] was nitrogen dioxide or protonated nitrogen dioxide. Furthermore, the formation of nitrobenzene by treating nitrosobenzene with nitrogen dioxide in chloroform[11] and the oxidation of nitrosotoluene by nitrogen dioxide on the pathway for the nitration of toluene has been reported.[9]

The reaction solution has been assumed to be saturated with nitrogen dioxide in the nitric acid oxidation of benzyl ethers[10] and benzaldehydes;[6] hence the rate law has been independent of nitric and nitrous acid concentrations. The present reaction, however, differs from these reactions in conditions, and the solution is not saturated with nitrogen dioxide, resulting in the dependence of rate on both concentrations of nitric and nitrous acids. Therefore, the nitrous acid concentration increases as the reaction proceeds, autocatalysis being observed.

A number of radical additions on the nitroso group are known which consume two radical species,[12] *e.g.*

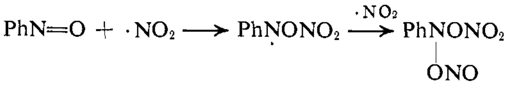
$$t\text{-BuN}{=}O + t\text{-Bu}\cdot \longrightarrow (t\text{-Bu})_2NO\cdot \xrightarrow{t\text{-Bu}\cdot} (t\text{-Bu})_2NO\text{-}t\text{-Bu}^{13}$$

Analogously, the present reaction might be expressed as



$$PhN{=}O + \cdot NO_2 \longrightarrow \underset{ONO}{PhNO\cdot} \xrightarrow{\cdot NO_2} \underset{ONO}{PhNONO_2}$$

However, another scheme is possible, *i.e.*



$$PhN{=}O + \cdot NO_2 \longrightarrow Ph\dot{N}ONO_2 \xrightarrow{\cdot NO_2} \underset{ONO}{PhNONO_2}$$

The radical, $Ph\dot{N}ONO_2$, may be more stable than $PhN(ONO)O\cdot$, because of the delocalization of an odd electron over the benzene ring. Furthermore, the observed substituent effect suggests electrophilic behavior of attacking species; hence the attack on the oxygen atom rather than the nitrogen atom of nitrosobenzene is more probable. The observed rate law and the acidity effect suggest a rate-determining attack of both free and protonated nitrogen dioxides, and lead to the following mechanisms

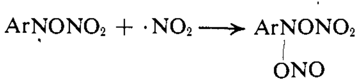
$$H^+ + NO_3^- \overset{K_1}{\rightleftharpoons} HNO_3 \quad (1)$$

$$HNO_3 + HNO_2 \overset{K_2}{\rightleftharpoons} 2\cdot NO_2 + H_2O \quad (2)$$

$$H^+ + \cdot NO_2 \overset{K_3}{\rightleftharpoons} HNO_2\cdot^+ \quad (3)$$

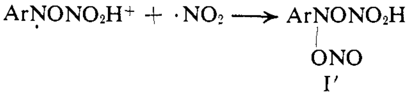
$$ArN{=}O + \cdot NO_2 \xrightarrow{k_4} Ar\dot{N}ONO_2 \quad (4)$$

$$ArN{=}O + HNO_2\cdot^+ \xrightarrow{k_5} Ar\dot{N}ONO_2H^+ \quad (5)$$



$$Ar\dot{N}ONO_2 + \cdot NO_2 \longrightarrow \underset{ONO}{ArNONO_2} \quad (6)$$

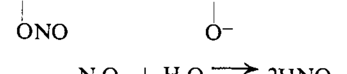
I



$$Ar\dot{N}ONO_2H^+ + \cdot NO_2 \longrightarrow \underset{ONO}{ArNONO_2H^+} \quad (7)$$

I′

$$\underset{ONO}{ArNONO_2} \longrightarrow \underset{O^-}{Ar\overset{+}{N}{=}O} + N_2O_3 \quad (8)$$



$$\underset{ONO}{ArNONO_2H^+} \longrightarrow \underset{O^-}{Ar\overset{+}{N}{=}O} + N_2O_3 + H^+ \quad (9)$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2 \quad (10)$$

Nitric acid reacts with nitrous acid to produce nitrogen dioxide,[6,7,9] a small amount of which may be protonated. The addition of both these species on nitroso-

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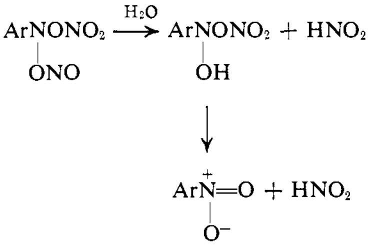
[12] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, p 373.

[13] A. K. Hoffman, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Am. Chem. Soc.*, **86**, 639 (1964).

benzene gives radicals which again couple with nitrogen dioxide to form I or I′. The addition products (I and I′) may decompose rapidly to form dinitrogen trioxide which gives, on hydrolysis, nitrous acid. Assuming that the initial attack on the nitroso group (steps 4 and 5) is rate determining, the rate may be expressed as

$$\begin{aligned} v &= (k_4[\cdot \mathrm{NO_2}] + k_5[\mathrm{HNO_2}\cdot{}^+])[\mathrm{ArNO}] \\ &= \{k_4(K_2K_1)^{0.5}[\mathrm{H^+}]^{0.5}[\mathrm{NO_3^-}]^{0.5}[\mathrm{HNO_2}]^{0.5} + \\ &\qquad k_5K_3(K_2K_1)^{0.5}[\mathrm{H^+}]^{1.5}[\mathrm{NO_3^-}]^{0.5}[\mathrm{HNO_2}]^{0.5}\}[\mathrm{ArNO}] \\ &= k_4(K_2K_1)^{0.5}[\mathrm{H^+}]^{0.5}\left(1 + \frac{k_5}{k_4}K_3[\mathrm{H^+}]\right) \times \\ &\qquad [\mathrm{NO_3^-}]^{0.5}[\mathrm{HNO_2}]^{0.5}[\mathrm{ArNO}] \end{aligned}$$

Here, k and K are rate and equilibrium constants of subscripted steps. The rate expression explains the observation: $v = kh_0^{0.5}(1 + 0.5h_0)[\mathrm{NO_3^-}]^{0.5}[\mathrm{HNO_2}]^{0.5}[\mathrm{PhNO}]$. The observed value of $(k_5/k_4)K_3[\mathrm{H^+}]$ is between 0.01 and 0.25, *i.e.*, $(k_5/k_4)K_3[\mathrm{H^+}] \ll 1$. Therefore, it is apparent that protonated nitrogen dioxide contributes very little to this oxidation probably because the nitroso compound, highly reactive toward the radical,[12] can readily react with free nitrogen dioxide without activation by protonation. Furthermore, the concentration of protonated nitrogen dioxide may be very low, since the reaction was carried out in a solution of low acidity. The mechanism for the decomposition of addition products (steps 8 and 9) is still obscure; the following pathway may also be possible.



$$\underset{\mathrm{ONO}}{\mathrm{ArNONO_2}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{OH}}{\mathrm{ArNONO_2}} + \mathrm{HNO_2} \longrightarrow \underset{\mathrm{O^-}}{\mathrm{Ar\overset{+}{N}{=}O}} + \mathrm{HNO_2}$$

Finally, the oxidation may compete with side reactions. To increase the yield of nitro compounds, our observation shows that the reaction should be carried out in a solvent of high dioxane content and at higher temperature.

Experimental Section

Materials. Substituted nitrobenzenes were purified by rectification when they were liquid, and by recrystallization when they were solid: nitrobenzene, bp 99.5–101° (22 mm); *p*-nitrotoluene, mp 53–53.5°; *m*-nitrotoluene, bp 112.2–115° (21–22 mm); *p*-nitrochlorobenzene, mp 82–82.5°; *m*-nitrochlorobenzene, mp 44–44.5°; *m*-dinitrobenzene, mp 90°.

Nitrosobenzene was prepared by the sodium dichromate oxidation of phenylhydroxylamine which was produced by the reduction of nitrobenzene by zinc powder.[14] Substituted nitrosobenzenes were prepared by the ferric chloride oxidation of correspondingly substituted phenylhydroxylamines in an aqueous alcoholic solution:[15] nitrosobenzene, mp 67.2–67.8° (lit.[16] 68°); *p*-nitrosotoluene, mp 46.5–47° (lit.[17] 47°); *m*-nitrosotoluene, mp 54–54.5° (lit.[18] 53–53.5°); *p*-nitrosochlorobenzene, mp 91–91.3° (lit.[19] 92–93°); *m*-nitrosochlorobenzene, mp 72.5–73.5° (lit.[17] 72°); *m*-nitronitrosobenzene, mp 88° (lit.[20] 89.5–90.5°). *m*-Nitronitrosobenzene was prepared by the oxidation of *m*-nitroaniline by Caro's acid.[20]

Measurement of Acidity. The Hammett acidity function was measured spectrophotometrically according to the method previously reported using *p*-nitroaniline as an indicator.[7]

Measurement of Nitrous Acid Concentration in the Reaction Mixture. Though a method analogous to that used previously[6] was employed for the determination of nitrous acid, α-naphthol was used instead of α-naphthylamine, since the diazotization might occur as a side reaction in this case, and only a small amount of diazonium salt was detected.

Kinetic Procedure. An aqueous dioxane solution of nitric acid was thermostated at 70°. After the addition of sodium nitrite, oxidation was started by adding the solution of nitrosobenzenes to the reaction system. Aliquots were taken out at appropriate intervals of time, and the system was extracted with chloroform. The extract was washed with saturated aqueous sodium bicarbonate and diluted with methanol to the appropriate concentration, and the contents of nitrosobenzenes and nitrobenzenes were measured using ultraviolet spectrophotometry by means of the simultaneous equation. The molar absorbances together with wavelengths (mμ) of substituted nitrosobenzenes and nitrobenzenes in methanol are: nitrosobenzene, 1070 (250), 7420 (305); nitrobenzene, 7160 (250), 650 (305); *p*-nitrosotoluene, 1420 (260), 12,600 (315); *p*-nitrotoluene, 7360 (260), 1130 (315); *m*-nitrosotoluene, 1950 (260), 8310 (307); *m*-nitrotoluene, 7630 (260), 1460 (307); *p*-nitrosochlorobenzene, 1800 (260), 11,900 (315); *p*-nitrochlorobenzene, 9330 (260), 710 (315); *m*-nitrosochlorobenzene, 2290 (258), 5170 (302); *m*-nitrochlorobenzene, 6890 (258), 960 (302); *m*-nitronitrosobenzene, 10,200 (230), 15,600 (250); *m*-dinitrobenzene, 18,000 (230), 14,400 (250).

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