

Kinetics of the Nitric Acid Oxidation of Nitrosophenol to Nitrophenol<sup>1</sup>

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The oxidation of nitrosophenol to nitrophenol with dilute nitric acid (0.40 *M*) in 20% dioxane–80% water has been studied kinetically by following the rate by ultraviolet spectrophotometry. The rate was much faster than that of nitrosobenzenes<sup>2</sup> and, hence, the enhancement of the rate could not be explained by means of the ordinary substituent effect by a hydroxyl group. The rate is expressed as  $v = k'[\text{nitrosophenol}][\text{HNO}_3]$ , the rate being increased with acidity of the solution. The rate is independent of nitrous acid concentration. A possible mechanism is discussed on the basis of these observations, and it is suggested that the rate-determining step for oxidation of nitrosophenol is different from that for other nitrosobenzenes.

In our previous report<sup>2</sup> on the nitric acid oxidation of nitrosobenzenes to nitrobenzenes, *p*-nitrosoanisole was eliminated from the measurement of substituent effect because of its susceptibility to hydrolysis giving *p*-nitrosophenol. Afterward, *p*-nitrosoanisole was found to yield *p*-nitrophenol. Since *p*-nitroanisole was not hydrolyzed under these conditions, the main reaction should go by way of *p*-nitrosophenol (eq 1).



Nitrosophenol is more rapidly oxidized than nitrosobenzene by nitric acid; the oxidation is rapid and quantitative even in 20% dioxane at 40°, whereas nitrosobenzene is hardly oxidized under these conditions. Hence, the rate of nitrosophenol is difficult to compare with those of other nitrosobenzenes.

In the present paper, nitrosophenol was oxidized by 0.4 *M* nitric acid in 20% dioxane at 40°, and the rate was followed by means of ultraviolet spectrophotometry to elucidate the mechanism.

## Results and Discussion

## Effect of Nitrous Acid and Other Added Compounds.

—The removal of nitrous acid by the addition of urea results in the appearance of a long induction period (Table I), and, hence, the remarkable enhancement of

TABLE I  
EFFECT OF VARIOUS ADDED COMPOUNDS IN THE NITRIC ACID  
OXIDATION OF NITROSOPHENOL IN 20% DIOXANE AT 40°  
(INITIAL CONCENTRATION: [NITROSOPHENOL] =  
0.0535 *M*, [HNO<sub>3</sub>] = 0.40 *M*)

Compd added	<i>M</i>	Induction period, min	First-order rate constant, 10 <sup>4</sup> <i>k</i> , sec <sup>-1</sup>
None	...	>100	...
CO(NH <sub>2</sub> ) <sub>2</sub>	0.1	>100	...
NaNO <sub>2</sub>	0.005	...	2.40
NaNO <sub>2</sub>	0.007	...	2.22
NaNO <sub>2</sub>	0.01	...	2.62
NaNO <sub>2</sub>	0.005 <sup>a</sup>	...	3.72
NaNO <sub>2</sub> + BPO <sup>b</sup>	0.005 + 0.005 <sup>a</sup>	...	3.49
BPO <sup>b</sup>	0.005 <sup>a</sup>	>65	...
AIBN <sup>c</sup>	0.005 <sup>a</sup>	>65	...

<sup>a</sup> Experiments in 40% dioxane. <sup>b</sup> Benzoyl peroxide. <sup>c</sup> Azobisisobutyronitrile.

the oxidation by introducing hydroxyl group into nitrosobenzene could not be explained by assuming nitric acid or nitrate ion as attacking species, in addition

to nitrogen dioxide proposed for the nitric acid oxidation of nitrosobenzene. Nitrous acid is an effective initiator of the present reaction. It is of interest to note that the rate constant is independent of the concentration of added nitrous acid (Table I); this behavior was not observed with the other nitrosobenzenes.

Ordinary initiators in radical reactions such as benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) neither initiate the reaction nor affect the oxidation rate, probably because such initiators decompose hardly at their low temperature such as 40° (Table I).

**The Rate Equation.**—A typical first-order rate equation with respect to nitrosophenol was obtained in excess nitric acid. The rate constants do not vary with changing initial concentration of nitrosophenol (Table II). Hence, the rate, with an excess of nitric acid, is expressed as  $v = k[\text{nitrosophenol}]$ .

TABLE II  
FIRST-ORDER RATE CONSTANTS FOR THE NITRIC ACID  
OXIDATION OF NITROSOPHENOL AT VARIOUS INITIAL  
CONCENTRATIONS OF REACTANTS IN 20% DIOXANE AT 40°

[Nitrosophenol], <i>M</i>	[HNO <sub>3</sub> ], <i>M</i>	10 <sup>4</sup> <i>k</i> , sec <sup>-1</sup>
0.0527	0.40	2.46
0.0436	0.40	2.69
0.0316	0.40	2.38
0.0202	0.40	2.46
0.0538	0.10	4.72 <sup>a</sup>
0.0538	0.20	12.3 <sup>a</sup>
0.0546	0.30	14.8 <sup>a</sup>
0.0546	0.40	21.4 <sup>a</sup>
0.0573	0.50	26.9 <sup>a</sup>

<sup>a</sup> Values obtained in the presence of 0.20 *M* sulfuric acid. These values were corrected to those at  $H_0 = 0$ .

The rate increased with nitric acid concentration, the plot of  $\log k$  vs.  $\log [\text{HNO}_3]$  giving a straight line with a slope of *ca.* unity, if the *k* values are corrected to those at  $H_0 = 0$  to eliminate the acidity effect (Table II). Hence, the rate is expressed as  $v = k'[\text{nitrosophenol}][\text{HNO}_3]$ . The rate is independent of the concentration of nitrous acid, and this behavior was not observed with other nitrosobenzenes.

**Effect of Acidity of Solution.**—On addition of sulfuric acid, the reaction was accelerated. The plot of  $\log k$  vs.  $H_0$  gave a straight line with a slope of  $-1.2$  (Figure 1). It was confirmed spectrophotometrically that the tautomerism between nitrosophenol and benzoquinone oxime, or their dimerization (see later), was not affected by the acidity of media; *i.e.*, absorption spectra at *ca.* 700  $\mu$  varied little by changing acidity in the present reaction.

(1) Contribution No. 109.

(2) Y. Ogata and H. Tezuka, *J. Amer. Chem. Soc.*, **89**, 5428 (1967).

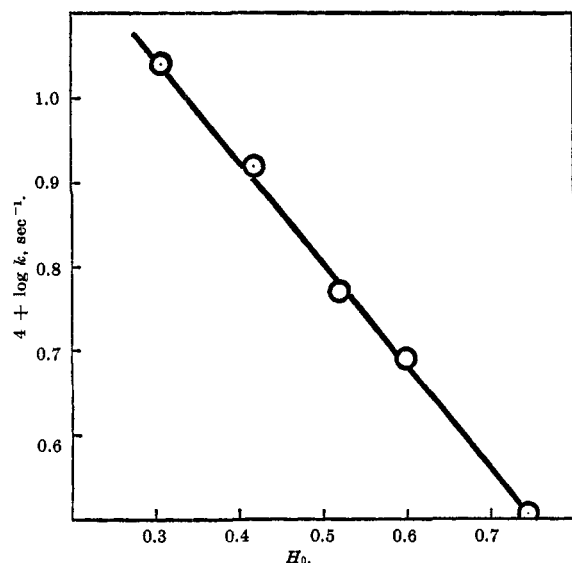


Figure 1.—Plots of  $\log k$  vs. acidity function for the nitric acid oxidation of nitrosophenol in the presence of sulfuric acid in 20% dioxane at 40°.

**The Solvent Effect.**—The rate constant  $k$  increases with an increase of the dioxane content in the solvent in spite of decreasing acidity. This phenomenon has been observed in nitric acid oxidations of some organic compounds,<sup>2-4</sup> and it has been explained in terms of the increasing concentration of attacking species, probably nitrogen dioxide, with the rise of dioxane content.<sup>2-4</sup> This solvent effect is much larger than that for nitrosobenzene, and this fact suggests that the effect is due not only to changes in nitrogen dioxide concentration but also to other factors.

TABLE III

EFFECT OF SOLVENT COMPOSITION ON THE FIRST-ORDER RATE CONSTANTS FOR THE NITRIC ACID OXIDATION OF NITROSOPHENOL AT 40°  
(INITIAL CONCENTRATION:  $[\text{HNO}_3] = 0.40 \text{ M}$ ,  $[\text{NaNO}_2] = 0.005 \text{ M}$ ,  $[\text{NITROSOPHENOL}] = 0.0560 \text{ M}$ )

Dioxane, %	$\epsilon$	$10^4 k$ , $\text{sec}^{-1}$	$H_0$
20	2.0 <sup>a</sup> (—) <sup>b</sup>	2.40 (0.15) <sup>c</sup>	0.76
40	3.7 <sup>a</sup> (38) <sup>b</sup>	3.72 (1) <sup>c</sup>	1.29
60	6.6 <sup>a</sup> (44) <sup>b</sup>	12.5 (19) <sup>c</sup>	1.91

<sup>a</sup> Molar extinction coefficient of nitrosophenol at ca. 700  $m\mu$ .

<sup>b</sup> Molar extinction coefficient of nitrosobenzene at ca. 750  $m\mu$ .

<sup>c</sup> Relative rate constants compared at constant acidity.

Light absorption at about 700–750  $m\mu$  is characteristic of the nitroso group.<sup>5</sup> The molar extinction of nitrosophenol is very small at this wavelength because of the dimerization of nitrosophenol and/or the tautomerism of nitrosophenol to benzoquinone oxime.<sup>5</sup> The absorption of nitrosophenol in dioxane–water at ca. 700  $m\mu$  increases with increasing dioxane content in the solvent in parallel with an increase of the rate constant (Table III). Hence, the rate may depend on the extent of dimerization and/or tautomerization. The observed degree of dimerization of nitrosobenzene also depends on the content of water in water–organic solvent and it is small (Table III). Similarly the

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

(4) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, **88**, 5832 (1966).

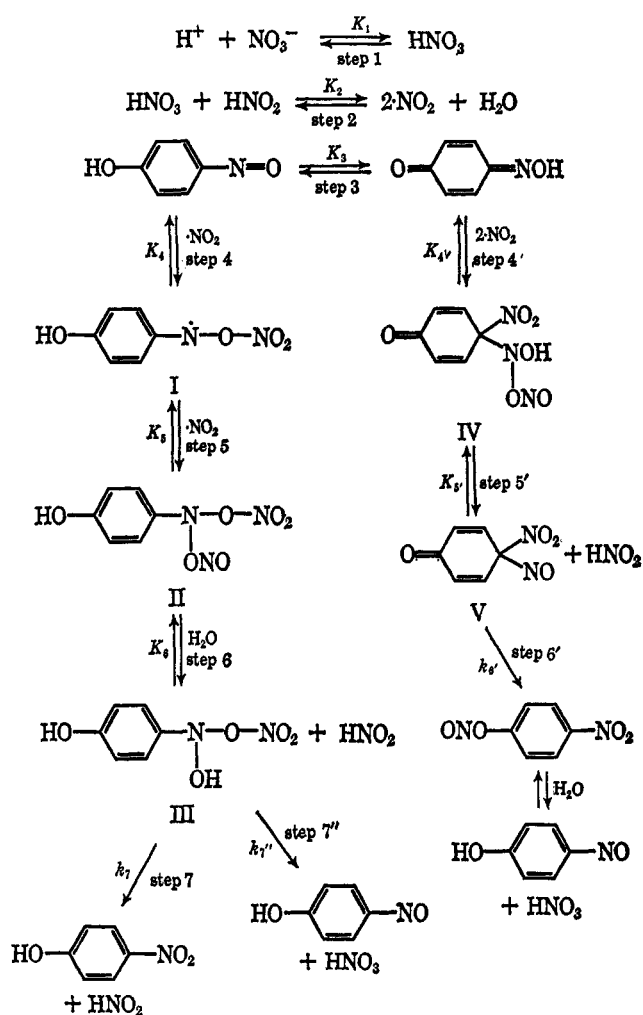
(5) A. Schors, A. Kraaijeveld, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **74**, 1243 (1955).

dimerization of nitrosophenol seems to occur to a fairly small extent. The observed solvent effect on the  $\epsilon$  values probably is not due to the change in the extent of tautomerization but to change in the extent of dimerization because the variation of  $\epsilon$  values with varying solvent composition is nearly comparable with that of nitrosobenzene, which dimerizes but does not tautomerize (Table III). However, the fact that the solvent effect on oxidation of nitrosophenol is larger than that of nitrosobenzene may be explained by assuming a rate-determining homolytic formation of nitrophenol as will be discussed below.

**Effect of Temperature.**—The first-order rate constants ( $10^{-4} \text{ sec}^{-1}$ ) were 0.772, 1.41, 2.40, and 5.68 at 30, 35, 40, and 45°, respectively. An Arrhenius plot afforded a straight line, which gave the values of 25 kcal/mol and 4.6 eu for the apparent energy and entropy of activation, respectively.

**The Mechanism.**—The oxidation of nitrosophenol is much more rapid than that of nitrosobenzene, and its rate is independent of nitrous acid concentration. A possible mechanism is given in Scheme I.

SCHEME I

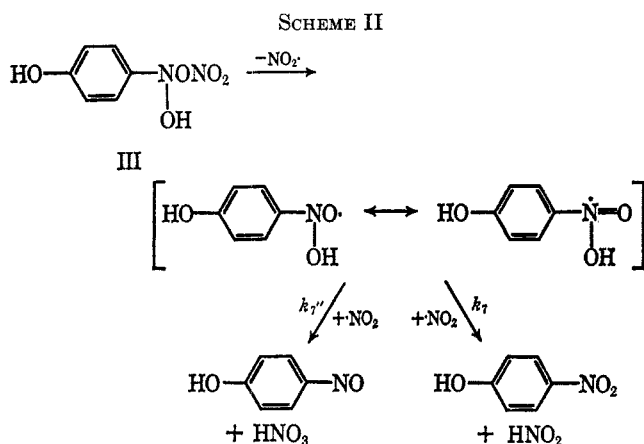


Nitrosophenol is in equilibrium with benzoquinone oxime,<sup>5,6</sup> and both species may be attacked. The most probable pathway involves an attack of nitrogen dioxide on the nitroso group in the same way as on

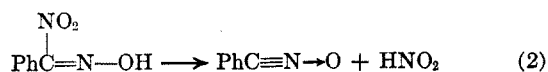
(6) L. C. Anderson and M. B. Geiger, *J. Amer. Chem. Soc.*, **54**, 3064 (1932).

nitrosobenzene. The rate-determining step for nitrosobenzene is step 4,<sup>2</sup> but in the present reaction, the rate should be determined by step 7 instead of step 4 because the rate is independent of nitrous acid concentration. The two nitrogen dioxide radicals in steps 4 and 5 are equivalent to a nitrous acid in step 2 and thus cancel in the rate equation yielding the relation given in eq 4. Since the slow step for nitrosobenzene is not slow in the present reaction, nitrosophenol may be much more rapidly oxidized than nitrosobenzene. In the present reaction, step 4 may probably be rapid because of the stable intermediate of the semiquinone-type radical I.

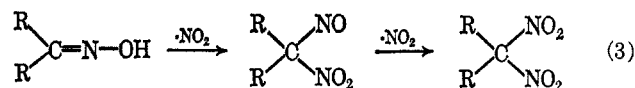
Generally, alkyl nitrites are easily hydrolyzed,<sup>7</sup> but it is obscure whether nitrate II is decomposed *via* hydrolysis or directly as in nitric acid oxidation of nitrosobenzenes. The reversibility of the hydrolysis (6) is required for the explanation of the independence of rate on the nitrous acid concentration. Therefore, the preliminary hydrolysis of the nitrite may occur also with other nitrosobenzenes. According to the ordinary  $\beta$  elimination, nitrosophenol should be formed instead of nitrophenol but  $\gamma$  elimination to form nitrophenol also may occur as in Scheme II.



The elimination of nitrous or nitric acid from intermediate III may occur by a polar mechanism as  $H^+$  plus  $NO_2^-$  or  $NO_3^-$ , but it seems less probable, since the oxidation is more retarded in more polar solvents such as water-rich dioxane (Table III). Therefore, intermediate III probably decomposes homolytically rather than heterolytically in analogy to the dissociation of dinitrogen tetroxide. Even if nitrosophenol and nitric acid may be formed from III, the products are the original reactants. Hence, the rate of the formation of nitrophenol depends on Scheme II; *i.e.*,  $k_7$  is independent of the rate of reproduction of nitrosophenol,  $k_7''$ . The similar homolytic  $\gamma$  elimination is expected for the formation of nitrile oxide from nitrolic acid, *i.e.*, eq 2.<sup>8</sup>



Since oximes can be oxidized by nitrogen dioxide as shown in eq 3,<sup>9</sup> benzoquinone oxime may be oxidized



to intermediate IV and then V. The nitroso group may naturally rearrange homolytically to the oxygen atom of carbonyl group, because of the formation of a stable benzene ring by the elimination of either nitro or nitroso group from V. The rearrangement of nitro group gives rise to the initial state. No further oxidation of the nitroso group in V is likely, since the rearrangement should be faster than the oxidation because of the retarding effect on oxidation exerted by the electron-attracting *gem*-nitro group as in the oxidation of *m*-nitronitrosobenzene.<sup>2</sup>

The mechanism in eq 3 leads to a rate law (eq 4)

$$v = k_7[\text{III}] + k_8'[\text{V}] \\ = \{K_2K_1(k_7K_8K_5 + k_8'K_5'K_4'K_3)/(1 + K_3)\} \times [\text{H}^+][\text{NO}_3^-](a - x) \quad (4)$$

where  $a$  = initial concentration of nitrosophenol. The rate equation is consistent with the observed rate expression. The initial attack on the nitrogen atom of benzoquinone oxime by nitrogen dioxide seems to be preferred to that on the carbon atom. In spite of a large equilibrium constant,  $K_3$ , in organic solvents,<sup>6</sup> the electrophilic radical attack of nitrogen dioxide on the oxygen atom of nitrosophenol is probably more favorable than that on the nitrogen atom of the oxime because of the more electronegative nature of oxygen atom. Hence, it is impossible to decide here if the main pathway is *via* nitroso or *via* oxime.

The fact that the slope of a line obtained from the plot of  $\log k$  vs.  $H_0$  is  $-1.2$  instead of  $-1$  suggests that protonated nitrogen dioxide ( $\text{HNO}_2^+$ ) may participate a little as an attacking species in a parallel reaction,<sup>2-4</sup> although nitrosophenol is so reactive that it needs almost no highly reactive species such as  $\text{HNO}_2^+$  for the present reaction and hence,  $\text{NO}_2\cdot$  is the principal attacking species.

Side reactions may occur, but their rates are extremely slow and hence they are hardly detectable, unless the reaction mixture is treated for several hours with nitric acid from which nitrous acid has been removed by addition of urea.

### Experimental Section

**Materials.**—*p*-Nitrosophenol was prepared by nitrosation of phenol<sup>10</sup> and recrystallization from methanol: mp 135–136° dec (lit.<sup>11</sup> mp 135–136°);  $\lambda_{\text{max}}$  300 m $\mu$  ( $\epsilon$  18,500). *p*-Nitrophenol had mp 113° (lit.<sup>12</sup> mp 113–114°); uv bands at  $\lambda_{\text{max}}$  312 m $\mu$  ( $\epsilon$  10,000).

**Kinetic Procedure.**—The rate was measured by the same method as that in the previous report<sup>2</sup> except that the extract was washed with saturated aqueous sodium chloride instead of aqueous sodium bicarbonate. *p*-Nitrosophenol was not always extracted completely and the content of *p*-nitrophenol was measured by means of a simultaneous equation at the following wavelengths: *p*-nitrosophenol, 290 m $\mu$  ( $\epsilon$  16,600), 312 (16,700); *p*-nitrophenol, 290 (6590), 312 (10,000).

**Registry No.**—*p*-Nitrosophenol, 104-91-6; *p*-nitrophenol, 100-02-7; nitric acid, 7697-37-2.

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(8) J. H. Boyer and H. Alul, *J. Amer. Chem. Soc.*, **81**, 4237 (1959).

(9) J. L. Riebsomer, *Chem. Rev.*, **36**, 183 (1945).