Tetrahedron. Vol. 28, pp. 15 to 19. Pergamon Press 1972. Printed in Great Britain

KINETICS OF THE PEROXYDISULFATE OXIDATION OF *p*-NITROSOPHENOL[1]

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(*Received in Japan* 31 *March* 1971: *Received in the UK for publication* 17 *May* 1971)

Abstract— The stoichiometry and kinetics for oxidation of *p*-nitrosophenol to *p*-nitrophenol by potassium peroxydisulfate in an alkaline aqueous solution have been studied. The oxidation follows the second-order kinetics, being first-order in each reactant. The energy of activation is 19·2 kcal mol^{-1} and the entropy of activation is 14·7 e.u. The rate of oxidation is not affected by gaseous oxygen or allyl acetate, a radical trapper. The pH dependence on the rate has been studied. These results are consistent with a bimolecular nucleophilic attack of the nitrogen atom of nitrosophenoxide ion on the peroxy oxygen of peroxydisulfate ion.

AROMATIC nitroso compounds are oxidised by organic peracid to the corresponding nitro compounds.[2] The oxidation may involve either a nucleophilic attack of the peroxide anion of peracid on the nitrogen atom of the nitroso group or an electrophilic attack of peroxide oxygen on a nitrogen atom of the nitroso group.[3]

The present study used potassium peroxydisulfate as peroxide and *p*-nitrosophenol as nitroso compound and they were reacted in an aqueous buffer solution. It was found that the peroxydisulfate oxidises *p*-nitrosophenol quantitatively to *p*-nitrophenol in an alkaline aqueous solution at 50°.

The rate of reaction was followed by the iodometry of peroxydisulfate. The effects of alkali, salt, and temperature were measured for the mechanistic speculation of the reaction.

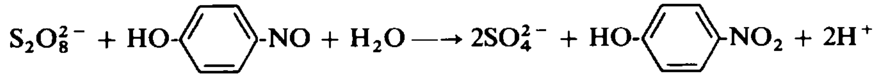
RESULTS

Stoichiometry. Table 1 shows that the consumption of peroxydisulfate and *p*-nitrosophenol and the formation of *p*-nitrophenol. A plot of moles of peroxydisulfate consumed *vs.* product formed is almost linear. No effect of atmospheric oxygen was observed, *i.e.*, no difference of the stoichiometry or rate was observed between the reactions under air and nitrogen atmospheres. The observed stoichiometry leads to Eq. 1.

TABLE 1. STOICHIOMETRY OF THE PEROXYDISULFATE OXIDATION OF *p*-NITROSOPHENOL AT 50°

Time (min)	consumed $K_2S_2O_8$ (M)	consumed *p*-nitrosophenol (M)	formed *p*-nitrophenol (M)
40	0·00209	0·00231	0·00203
80	0·00352	0·00366	0·00316
120	0·00509	0·00499	0·00500

Initial concentration: $K_2S_2O_8$, 0·02M: *p*-Nitrosophenol, 0·01M: NaOH, 0·05M



(1)

Effect of concentration of reactants. (a) *Peroxydisulfate.* The disappearance of potassium peroxydisulfate was measured at an initial molar ratio of *p*-nitrosophenol *vs.* peroxydisulfate of 10:1 at 50°. The rate was first-order with peroxydisulfate as obvious in a plot of the logarithm of peroxydisulfate concentration *vs.* time:

$$-d[S_2O_8^{2-}]/dt = k'[S_2O_8^{2-}].$$

(b) p-*Nitrosophenol.* In view of the data in Table 2, a plot of log k' *vs.* log *p*-nitrosophenoxide ion gives a straight line with a slope of unity. Alkali peroxydisulfate should be completely dissociated at this pH range. Hence, the rate is expressed as

$$v = k\,[p\text{-nitrosophenoxide ion}]\,[S_2O_8^{2-}].$$

TABLE 2. THE EFFECT OF INITIAL CONCENTRATION OF *p*-NITROSOPHENOL ON FIRST-ORDER RATE CONSTANTS IN AN ALKALINE AQUEOUS SOLUTION AT 50°

p-Nitrosophenol (M)	First-order rate constant $10^5\,k'(\text{sec}^{-1})$
0·015	6·27
0·020	9·21
0·025	9·68
0·035	11·95

Initial concentration: $K_2S_2O_8$, 0·003M: NaOH, 0·05M

Effect of temperature. The reaction was studied at 46·0°, 50·0° and 54·0°. Table 3 shows the second-order rate constants at various temperatures. A plot of logarithm of the second-order rate constant against an inverse of absolute temperature gives a straight line. The energy of activation for the oxidation of *p*-nitrosophenol in an alkaline aqueous solution was calculated from the slope of line to be 19·6 kcal mol^{-1}. The entropy of activation was − 14·6 cal mol^{-1} deg^{-1}. These values are comparable

TABLE 3. THE EFFECT OF TEMPERATURE ON THE PEROXYDISULFATE OXIDATION OF *p*-NITROSOPHENOL

Temperature	Second-order rate constant $10^3\,k(\text{M}^{-1}\,\text{sec}^{-1})$
46·0	3·20
50·0	4·39
54·0	6·28

Initial concentration: $K_2S_2O_8$, 0·003M: *p*-Nitrosophenol, 0·02M; NaOH, 0·05M to these for the oxidation with peroxide, which are 12—19 kcal mol^{-1} for E_a and -13 to -30 cal mol^{-1} deg^{-1} for $\Delta S^{\ddagger}$.

Effect of pH and ionic strength. No decomposition of peroxydisulfate was observed below pH 7. The pH effect on the second-order rate constant in a solution of almost constant ionic strength of 0·10 is shown in Table 4.

TABLE 4. THE EFFECT OF pH ON THE PEROXYDISULFATE OXIDATION OF *p*-NITROSOPHENOL AT 50°

NaOH	NaCl	Second-order rate constant $10^3\,k(M^{-1}\,sec^{-1})$
0·05	None	4·39
0·02	0·08	0·98
0·04	0·06	3·81
0·05	0·05	5·17
0·08	0·02	4·99

Initial concentration: $K_2S_2O_8$, 0·003M: *p*-Nitrosophenol, 0·02M

The data of Table 4 shows that an increase of ionic strength increases the second-order rate constant, which suggests that reactive species are both anions, *i.e.*, *p*-nitrosophenoxide ion but not undissociated phenol reacts with peroxydisulfate ion.

Effect of a radical inhibitor. The rate of oxidation of *p*-nitrosophenol with peroxydisulfate ion in an alkaline aqueous solution was measured in the presence of allyl acetate, which is an effective radical trapper in peroxydisulfate oxidation.[4] No effect was observed on the rate.

DISCUSSION

The results of the present study are summerized as follows:

(1) The rate is expressed as

$$v = k\,[p\text{-nitrosophenoxide ion}]\,[S_2O_8^{2-}].$$

(2) Gaseous oxygen and a radical inhibitor, allyl acetate, affects neither rate nor consumption of peroxydisulfate.

(3) The activation parameters of this oxidation are analogous to those of peroxide oxidation reviewed by Edwards.[5]

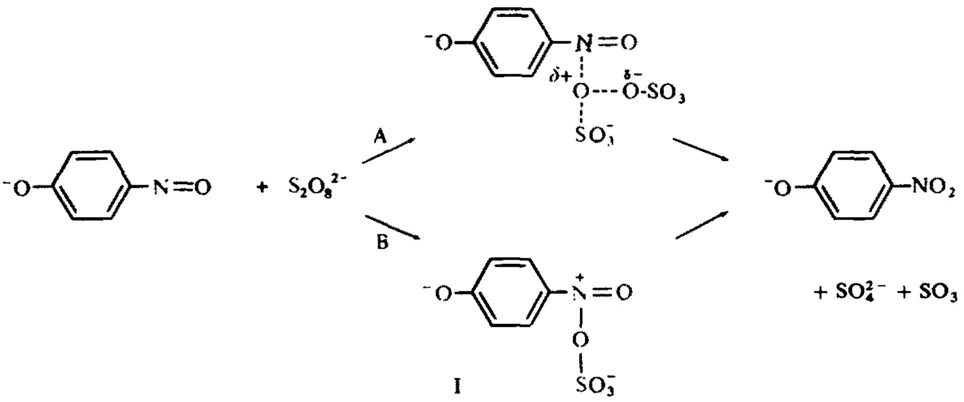
The data can be explained by assuming that the nitroso nitrogen performs a nucleophilic attack on the peroxy oxygen of the peroxydisulfate. No radical reaction is conceivable. This mechanism is analogous to the Elbs peroxydisulfate oxidation of phenols to form *o*- and *p*-dihydroxybenzenes[6, 7] and Boyland–Sims oxidation of anilines to form *o*-aminophenyl sulfates.[8]

These facts suggest two probable pathways (Scheme 1), which are kinetically indistinguishable, because the rate-limiting step of this reaction should be an attack of nitroso group nitrogen.

Path A involves a simultaneous cleavage of O—O and O—S bonds, while path B involves the formation of a tentative intermediate (I).

The Boyland–Sims oxidation is reported to have the following scheme[9] (Scheme 2). This is consistent with the dependence of the yield on the ratio of peroxydisulfate *vs.*

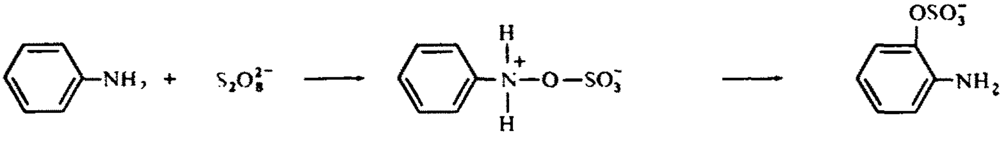
SCHEME 1.



amine, the behavior of phenylhydroxylamine-O-sulfonate and substituent effect with a negative ρ value of $-1{\cdot}41$.[9, 10]

The intermediate (I) of our reaction is analogous to II. The sulfate group of II can rearrange to the *ortho* carbon atom of the benzene, to give *o*-aminophenyl sulfate,

SCHEME 2.



II

but in the reaction of *p*-nitrosophenol, the electron-attracting nitroso group inhibits the rearrangement. (No 2-nitroso-5-hydroxyphenyl sulfate was observed.) The intermediate (I) seems to be very unstable, since no characteristic UV absorption was detectable during the reaction and the disappearance of *p*-nitrosophenol corresponded to the simultaneous formation of equivalent amount of *p*-nitrosophenol. Hence, path A seems to be the more probable.

EXPERIMENTAL

p-Nitrosophenol was prepared by nitrosation of phenol.[11] M.p. 135–136° dec (lit.[12] m.p. 135–136°): UV band at λ_{max} 300 mμ (ε 18,500). *p*-Nitrophenol m.p. 113° (lit.[13] m.p. 113–114°): UV band at λ_{max} 312 mμ (ε 10,000).

The reaction of *p*-nitrosophenol with aqueous peroxydisulfate was carried out as described by Behrman.[6] and followed by iodometric determination of peroxydisulfate. UV spectra of the mixture was measured by a Hitachi 124 model spectrophotometer.

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