with diazomethane in the usual fashion, yielding 0.96 g. (80%) of XIV, m.p. 154.5–155°. Its infrared spectrum in carbon tetrachloride showed a sharp intense carbonyl band at 5.75 μ and its n.m.r. spectrum in chloroform showed two sharp singlets at 6.42 and 8.56 τ, relative areas 2:1.

Anal. Calcd. for $C_{13}H_{18}O_8$: C, 51.65; H, 6.00. Found: C, 51.81; H, 6.12.

Mechanism of the Oxidation of Nitrosobenzenes by Peroxoacetic Acid

BY KHAIRAT M. IBNE-RASA, CARL G. LAURO AND JOHN O. EDWARDS

The oxidation of nitrosobenzenes by peroxoacetic acid in aqueous ethanolic media has been found to obey second-order kinetics with first-order dependence on each reactant. The oxidation is not acid catalyzed. The rate is enhanced by a factor of about 22 when the solvent is changed from ethanol to water. Electron-releasing *p*-substituents on nitrosobenzene accelerate the rate of oxidation, while the electron-withdrawing groups have the opposite effect. Peroxochloroacetic acid and Caro acid oxidize nitrosobenzene about 30 and 7 times, respectively, as fast as does peroxoacetic acid in 47% ethanol at 30°. The energy of activation (E_a) for the oxidation of nitrosobenzene by peroxoacetic acid in 47% ethanol is 16.1 kcal. mole^{-1} and the entropy of activation ($\Delta S^{\pm}$) −22 cal. mole^{-1} deg.$^{-1}$. The rate of oxidation is not retarded by nitrobenzene, which is a radical trap. Added perchlorate ions do not have any significant influence on the rate of oxidation. A mechanism consistent with these data is suggested.

Introduction

A kinetic study of the peroxoacetic acid oxidation of some anilines to phenylhydroxylamines and then to nitrosobenzenes was reported in a previous paper.[1] The results of a similar study of the next step, the oxidation of nitrosobenzenes to nitrobenzenes, are now presented. These investigations were undertaken partly because of our general interest in reactions involving nucleophilic displacement on oxygen[1,2] and partly because very few reactions of nitroso compounds have been the subjects of detailed kinetic studies in the past.[3]

It has been suggested that the oxidation of nitroso to nitro compounds by peroxy acids involves a nucleophilic attack by the peroxoacid on the nitrogen of the nitroso group.[4] There is, in principle, at least one more pathway available for the oxidation; the nitroso nitrogen might perform a nucleophilic attack on the outer oxygen of the peroxy acid, the reactants thus acting in a manner reverse to that suggested by Bunton. One of the aims of this work was to discriminate, if possible, between the above two mechanisms.

The present studies indicate that in acidic aqueous ethanolic media the oxidation follows a mechanistic path analogous to that suggested for aromatic amines[1]; *i.e.*, the peroxy acid behaves as an electrophile rather than as a nucleophile as suggested by Bunton.

Results

Kinetic Technique and Product Analysis.—The kinetic technique involved measuring the rate of disappearance of the nitrosobenzenes spectrophotometrically. Aqueous ethanolic solutions containing 0.01 to 0.02 *M* of a nitrosobenzene and 0.130 to 0.260 *M* peroxoacetic acid were placed in thermostated spectrophotometric cells and the disappearance of the nitroso compound followed as a function of time. The absorbancy at time "*t*" (A_t) was taken as a measure of the unreacted amount of nitrosobenzene at that time. In most

cases the peroxy acid was present in large excess relative to the nitroso compound to provide pseudo-first-order conditions. Plots of log A_t *vs.* time were linear to over three half-lives. Pseudo-first-order rate constants (k_1) were calculated from the slopes of these plots. The k_1 values were then divided by the initial concentration of peroxoacetic acid to get the second-order constants (k_2) listed in Table I.

TABLE I

EFFECT OF MEDIUM, TEMPERATURE AND SUBSTITUENTS ON SECOND-ORDER RATE CONSTANTS

Initial [peroxoacetic acid] = 0.260 *M*, initial [Ar·NO] = 0.01 *M*

Compound	Solvent[a]	Temp. ±0.1°C.	$k_2 \times 10^4$, 1. mole^{-1} sec.$^{-1}$
Nitrosobenzene	96% EtOH	50.0	5.15
	56% EtOH	50.0	18.4
	47% EtOH	50.0	27.2 ± 0.4
	36% EtOH	50.0	40.2
	16% EtOH	50.0	78.8
	47% EtOH	40.0	12.1 ± 0.1
	47% EtOH	30.0	5.15
p-Chloronitrosobenzene	47% EtOH	50.0	15.8
p-Bromonitrosobenzene	47% EtOH	50.0	14.7
p-Nitrosotoluene	47% EtOH	50.0	63.4
p-Nitrosoanisole	47% EtOH	50.0	200

[a] By "*x*% EtOH" is meant "*x*" volumes of ethanol contained in 100 volumes of reaction solution.

In a few experiments, which had been started with 0.01 *M* of a nitrosobenzene, 2 ml. of the reaction solution at infinite time was diluted with water to 250 ml. The ultraviolet spectra of these diluted solutions were studied and compared with those of 8 × 10^{-5} *M* aqueous solutions of authentic samples of the corresponding nitrobenzene. The yield of nitrobenzene from the oxidation of nitrosobenzene was thus found to be quantitative and the conversion of *p*-chloronitrosobenzene to *p*-chloronitrosobenzene was better than 95%.

Kinetic Law.—The linearity of the first-order plots indicates that the reaction is first order with respect to the nitroso compound. The dependence of the pseudo-first-order rate constants on the initial concentrations of the reactants was also studied for the oxidation of nitrosobenzene. The pseudo first-order rate constant

(1) K. M. Ibne-Rasa and J. O. Edwards, *J. Am. Chem. Soc.*, **84**, 763 (1962).

(2) J. O. Edwards in "Peroxide Reaction Mechanisms," edited by J. O. Edwards, Interscience Publishers, Inc., New York, N. Y., 1962, pp. 67–106.

(3) B. G. Gowenlock and W. Luttke, *Quart. Rev.*, (London) **12**, 321 (1958).

(4) C. A. Bunton in "Peroxide Reaction Mechanisms," edited by J. O. Edwards, Interscience Publishers, Inc., New York, N. Y., 1962, p. 21.

was found to be independent of the initial concentration of nitrosobenzene, but it varied linearly with the initial concentration of peroxoacetic acid. The first-order dependence of the oxidation on each of the two reactants was thus confirmed.

In one kinetic run in 47% EtOH, the initial concentrations of nitrosobenzene (a) and the peroxy acid (b) were 0.02 M and 0.130 M, respectively. A plot of log $a(b - x)/b(a - x)$, where "x" symbolizes the amount of nitrosobenzene reacted at time "t," vs. time was linear to over 80% reaction. The second-order rate constant calculated from the slope of this plot was equal to 25.9 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$ at 50°, which agrees well with the value (27.2 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$) given in Table I. It was thus demonstrated that the oxidation obeys the second-order kinetic law.

The apparent pH of the reaction solutions of the runs of Table I was $\simeq 2$. In a few experiments appropriate amounts of ethanolic KOH were added to vary the apparent pH between 2 and 5. For the oxidation of nitrosobenzene in 47% EtOH at 50°, the values of $k_2 \times 10^4$ l. mole^{-1} sec.$^{-1}$ were 27.2, 27.2 and 28.8 at apparent pH values of 2.5, 3.9 and 5.0, respectively. The reaction rate is thus independent of pH in the region studied.

Activation Parameters.—The activation energy and the entropy of activation for the oxidation of nitrosobenzene in 47% ethanol, as calculated from the rate constants of Table I, are 16.1 kcal. mole^{-1} and -22 cal. mole^{-1} deg.$^{-1}$, respectively.

Medium Effect.—It is seen from Table I that the rate of oxidation of nitrosobenzene decreases significantly with the increasing ethanolic content of the solvent. An estimated value of the second-order rate constant for the oxidation of nitrosobenzene in water (zero ethanolic content) was obtained by extrapolation of the data of Table I. This value was 114 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$ at 50°. Thus the oxidation is about 22 times as fast in water as in ethanol. It is interesting to note that the exaltation in rate due to change of solvent from ethanol to water is essentially that observed in the oxidation of anilines.[1]

The second-order rate constant for the oxidation of aniline by peroxoacetic acid in ethanol, extrapolated from the data of reference 1, is 1650 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$ at 50°. In the solvent ethanol, therefore, aniline is oxidized about 320 times more rapidly than nitrosobenzene.

In one kinetic run the oxidation of nitrosobenzene (0.01 M) was carried out in presence of 0.2 M NaClO$_4$ (T 50°, solvent 47% EtOH). The second-order rate constant for this run was calculated to be 25.4 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$. The ionic strength, therefore, does not seem to influence the rate significantly.

Substituent Effects.—It is also seen from Table I that the electron-donating p-substituents accelerate the rate of oxidation, while the electron-withdrawing p-substituents have the opposite effect. The value of ρ, the Hammett reaction constant, based on the rates of p-methyl-, p-chloro- and p-bromonitrosobenzenes, is -1.58.

The rates of oxidation of nitrosobenzene by peroxochloroacetic acid and by Caro acid also have been measured.[5] In 47% ethanol and at 30°, the second-order rate constants are 167 $\times$ 10^{-4} and 35 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$, respectively. Thus peroxochloroacetic acid oxidizes nitrosobenzene about 32 times as fast as does peroxoacetic acid ($k_2 = 5.15 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ at 30° in 47% EtOH) and Caro acid is about 7 times as effective as peroxoacetic acid.

(5) E. Koubek of these laboratories has measured these rates in connection with some other work.

Radical Inhibitor.—The rate of oxidation of nitrosobenzene (0.01 M) with peroxoacetic acid (0.130 M) in 47% EtOH was measured in presence of nitrobenzene (0.2 M) which is a reasonably efficient radical trap.[6] There was observed essentially no effect on the rate of oxidation.

Attempts to study the oxidation in alkaline media were not successful. Although an expected complication was the spontaneous decomposition of the peroxoacid, the chief hindrance proved to be the conversion of nitrosobenzene to a yellow product immediately upon the addition of base.

Discussion

The experimental observations that (a) the oxidation obeys clean-cut second-order kinetics, (b) nitrobenzene, a radical trap, does not inhibit the rate of reaction and (c) the energy of activation is low ($E_a = 16$ kcal. mole^{-1}) suggest that the reaction proceeds neither by a radical chain mechanism nor by a mechanism involving free radicals as intermediates.[1]

The mechanism suggested by Bunton,[4] which bears similarity to the peroxoacid cleavage of ketones[7] in the sense that both are initiated by a nucleophilic attack of the peroxoacid upon the substrate, may be depicted as
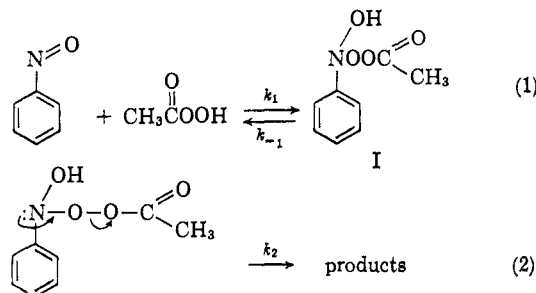
This mechanism (eq. 1 and 2), if operative, would give rise to several specific situations any one of which might apply to the present system. These are considered one by one as follows.

Situation 1.—The formation of the intermediate I may occur in a rapid reversible step (eq. 1) followed by the unimolecular decomposition of I into the products in the rate-determining step of the reaction (eq. 2). It may further be assumed that the equilibrium (eq. 1) largely favors the formation of I. The situation, then, demands that the reaction be zero order in the reactant which is present in excess, with the rate constant being k_2.[8] The observed kinetics, first-order dependence on each reactant even when the peroxoacid is in excess, show that the above assumption is not applicable to the system under investigation. Furthermore, a mechanism requiring the rapid conversion of nitrosobenzene into a stable intermediate is untenable on the ground that the measured rate is the rate of disappearance of nitrosobenzene.

Situation 2.—It may again be assumed that I is formed in a reversible step (eq. 1) but that $k_2 \gg k_{-1}$, i.e., the intermediate is in a steady state, its concentration relative to the reactants is small and its formation is the rate-controlling step with the rate constant being k_1. The observed value of ρ (-1.58) for the p-substituted nitrosobenzenes, however, rules out this possibility. It is obvious that for the nucleophilic attack by the peroxoacid on the nitrogen to be kinetically significant, the predicted value of ρ would be moderate and positive. Thus, for example, a

(6) C. G. Swain, W. H. Stockmayer and J. T. Clark, J. Am. Chem. Soc., 72, 5426 (1950).

(7) M. F. Hawthorne and W. D. Emmons, ibid., 80, 6398 (1958).

(8) L. G. Cannell, ibid., 79, 2929 (1957).

p-chloro substituent would make the nitrogen electron deficient and hence more amenable to the nucleophilic attack. In addition peroxochloroacetic acid has been observed to oxidize nitrosobenzene about 30 times more rapidly than does peroxoacetic acid. Because peroxochloroacetic acid is a poorer nucleophile than the unsubstituted peroxoacid, its greater reactivity as an oxidizing agent is irreconcilable with any mechanism in which nucleophilic attack by the peroxoacid is of kinetic importance.

Situation 3.—Lastly, the possibility exists that the mechanism of eq. 1 and 2 operates with $k_{-1} \gg k_2$; i.e., the decomposition of I into products is rate limiting with the rate constant being Kk_2; K symbolizes the equilibrium constant for eq. 1. The intermediate will be in a steady state and its concentration small relative to the reactants. A moderate and positive value of ρ for the equilibrium step (eq. 1) and a moderate but negative value of ρ for the decomposition of I into products (eq. 2) would be predicted. The net effect of p-substitution on "Kk_2" would thus be expected to be very small and perhaps negative. The observed value of ρ (-1.58), although qualitatively in the right direction, appears to be too negative to be consistent with prediction. The peroxoacid cleavage of ketones[7] occurs by a mechanism which is analogous to situation 3 here. The observed ρ-values are -1.10 and -1.45 for p-substituted acetophenones in the solvents ethylene chloride and acetonitrile, respectively. It is our opinion that, in the cleavage of ketones, the substituent effect on the decomposition of the Criegee intermediate, where migration of the phenyl group is involved, should be more pronounced than it is in the break down of the present intermediate I. Therefore the ρ-value in the present system should be less negative than it is in the reaction of ketones.

Another factor which is difficult to explain on the basis of a mechanism analogous to that of the cleavage of ketones is the insensitivity of the rate of the present reaction to changes in pH in the region studied (pH 2 to 5). The peroxoacid cleavage of ketones is invariably acid catalyzed,[7] the departure of the acetate ion being facilitated by protons. The absence of a similar catalytic effect of proton on the decomposition of the intermediate I cannot easily be explained.

It is proposed that the present data can most simply be explained by assuming that the nitroso nitrogen performs a nucleophilic attack on the outer oxygen of the peroxoacid in a fashion analogous to that suggested for the peroxoacid oxidation of anilines.[1] The transition state is composed of the peroxoacid, the nitroso compound and a molecule of the solvent. The direction and magnitude of the substituent effect (ρ -1.58), the values of activation parameters (E_a 16.1 kcal. mole^{-1}, $\Delta S^{\ddagger}$ -22 cal. mole^{-1} deg.$^{-1}$), the absence of acid catalysis and the solvent effect ($k_{H_2O}/k_{C_2H_5OH} \simeq 22$) are all consistent with such a mechanism. If the data of reference 1 on the oxidation of anilines be recalled (ρ -1.86 in ethanol, E_a 13 to 16 kcal. mole^{-1}, $\Delta S^{\ddagger}$ -23 to -26 cal. mole^{-1} deg.$^{-1}$, $k_{H_2O}/k_{C_2H_5OH} \simeq 25$, no acid catalysis) it will be seen that there is very close correspondence between the two systems.

Furthermore, this mechanism explains the greater reactivities of peroxochloroacetic acid and Caro acid relative to peroxoacetic acid as well as does the mechanism of situation 3, the varying abilities of chloroacetate, sulfate and acetate ions as leaving groups being responsible for differences in rates. Of particular significance, however, is the fact that Caro acid reacts more rapidly than does peroxoacetic acid by about the same factor in the present system ($k_{Caro}/k_{peracetic} = 7$)

than it does when bromide ion is the substrate ($k_{Caro}/k_{peracetic} = 4$),[2] suggesting similar roles for the peroxoacids in the two oxidations. Since bromide ion oxidation is known to involve nucleophilic displacement by the substrate upon the outer oxygen of the peroxoacid,[2] the analogous mechanism suggested above for the oxidation of nitrosobenzenes receives additional support from the observed relative reactivities of Caro and peroxoacetic acids.

The Abnormal Reactivity of p-Methoxy Compounds.—The reaction constant was calculated by using the rates of oxidation of p-methyl-, p-chloro- and p-bromonitrosobenzenes. The rate of the oxidation of p-nitrosoanisole showed a significant positive deviation from the Hammett plot.

The rate of oxidation of p-anisidine by peroxoacetic acid in ethanol at 20° also has been measured now. The second-order rate constant under these conditions is $984 \pm 48 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. The value of this constant predicted from the value of ρ (-1.86) as reported in reference 1, which is based on the rates of the unsubstituted, p-methyl-, p-chloro-, p-nitro- and p-bromoanilines (the last compound studied after the publication of reference 1 and $k_{p\text{-Br}}$ found to be 56.5 $\times$ 10^{-4} l. mole^{-1} sec.$^{-1}$ at 20° in ethanol), is 650×10^{-4} l. mole^{-1} sec.$^{-1}$. Thus p-anisidine also manifests abnormal reactivity toward the oxidizing agent.

Abnormal reactivities of systems where the reacting nucleophilic atom is adjacent to an atom bearing a free pair of electrons have been ascribed to what has been called the "α-effect".[1,9] In p-anisidine and p-nitrosoanisole the atom with a free pair of electrons is not in a position α to the reaction center, but the two are separated by a conjugated system. A possible explanation of the deviant behavior of the p-methoxy derivatives is the transmission of the "α-effect" through conjugation.

Experimental

(9) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).
(10) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **3**, 68 (1938).
(11) F. P. Greenspan and D. G. Mackeller, *Anal. Chem.*, **20**, 1061 (1948).