Hydroxylammonium Bromide.—The procedure[12] of Adams was used for preparation of the salt, 60% yield, m.p. 137.5–138.5° dec.

Anal.[12] Calcd. for $H_2NOH \cdot HBr$: equiv. wt., 56.98. Found: equiv. wt., 56.70.

Hydrogen Iodide Salt of Hydroxylamine.—The procedure[12] of Adams was used for preparation of the salt, m.p. 97–99° dec.; lit.[14] for $H_2NOH \cdot HI$, m.p. 83–84° (dec.); lit. for $(H_2NOH)_3 \cdot HI$, m.p. *ca.* 100° dec.[13] and 103–104°.[31]

Hydroxylammonium Phosphate.—The method[15] of Uhlenhuth gave the salt in 91% yield, m.p. 157.5–158.5° dec.

Anal. Calcd. for $(H_2NOH)_3 \cdot H_3PO_4$: N, 21.33; P, 15.72. Found: N, 21.22; P, 15.31.

Hydroxylammonium ethyl sulfate was obtained in 76% yield according to the reported procedure,[32] m.p. 101–103° dec., lit.[32] m.p. 102.5° dec.

General Procedure for Amination.—The general procedure and identification of products are basically the same as previously reported.[8] The data are outlined in Tables I and II. In the reaction of hydroxylammonium chloride with chlorobenzene the cooled reaction mixture was poured onto ice and sufficient concentrated sodium hydroxide solution was added to dissolve the aluminum hydroxide. The separated aqueous layer was extracted with ether which was then combined with the organic layer. The organic layer was extracted with hydrochloric acid and the usual procedure was then followed.

Distillation of the dried neutral fraction usually yielded only recovered toluene and slight traces of xylene disproportionation product. The reaction with hydroxylammonium phosphate also produced 17.6 g. of xylene, b.p. 134–145°, identified by infrared analysis, and 22.1 g. of viscous brown tar which would not distil at 135° (13 mm.). The reactions with hydroxylammonium chloride or bromide in the presence of aluminum bromide produced 19.76 g. and 18.05 g., respectively, of bromotoluene, b.p. 62–71° (14 mm.), $n^{20}\mathrm{D}$ 1.5506, identified by comparison of the spectrum with those of the authentic bromotoluene isomers.

A by-product from the amination by hydroxylammonium ethyl sulfate was a mixture of ethyltoluene isomers in 39% yield, b.p. 51–54° (17 mm.), $n^{20}\mathrm{D}$ 1.4951. The infrared spectrum was consistent with those[33] of the authentic ethyltoluene isomers.[34]

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.51; H, 9.82.

The hydroxylammonium acetate reaction also produced methylacetophenone in 14% yield, b.p. 108.5–109° (21 mm.), $n^{20}\mathrm{D}$ 1.5324; lit.[35] for *p*-methylacetophenone, b.p. 93.5° (7 mm.), $n^{20}\mathrm{D}$ 1.5335.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.70; H, 7.96.

Infrared analysis showed the sample to be exclusively *p*-methylacetophenone. The 2,4-dinitrophenylhydrazone was prepared and crystallized from acetic acid, m.p. 250–252°, lit.[36] m.p. 252–253°.

The reaction of bromobenzene with hydroxylammonium chloride also yielded 10 g. of benzene, 59.8 g. of dibromobenzene and 5.4 g. of residue in addition to recovered bromobenzene.

The amination of phenol by hydroxylammonium chloride produced 19 g. of black viscous residue in addition to recovered phenol.

Competitive Amination of Benzene–Toluene with Hydroxylammonium Chloride.—A mixture of anhydrous aluminum chloride (294 g., 2.2 moles), benzene (429 g., 5.5 moles), toluene (506 g., 5.5 moles) and hydroxylammonium chloride (76.5 g., 1.1 moles) was heated at 75–78° for 2 hr. and then worked up in the usual manner. The basic product consisted of an aniline–toluidine mixture, 19.1 g., b.p. 89–103° (31 mm.), and distillation residue (0.7 g.). The aniline–toluidine mixture was analyzed by gas chromatography as previously described.[8] A weight ratio, toluidine/aniline, of 3.34 was obtained with the toluidine standard consisting of 30% *ortho*, 18% *meta* and 52% *para* isomer. The relative rate, $k_{\text{toluene}}/k_{\text{benzene}}$, was calculated[16] to be 2.9.

Isomerization Studies with Chloroanilines.—The procedure, previously described,[6] involved use of *o*-, *m*- or *p*-chloroaniline (0.1 mole), chlorobenzene (2 moles), aluminum chloride (0.4 mole), water (0.1 mole) and hydrogen chloride. On the basis of infrared analysis, no isomerization of the individual isomers occurred. The recoveries obtained were: *ortho* (84%), *meta* (96%), *para* (97%).

Isomer Distributions.—The procedure for the quantitative determination of isomer distributions has been reported previously.[8] The following peaks (μ) were taken as characteristic: bromoaniline (*ortho*, 14.0; *meta*, 13.1; *para*, 12.7); fluoroaniline (*ortho*, 13.45; *meta*, 13.1; *para*, 12.1). The data for the fluoroaniline standards were corrected for the *meta* contaminant (7.5%) present in *o*-fluoroaniline. The method was shown to be accurate within ±1.5% except for *m*-fluoroaniline (±4%).

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(31) O. Piloty and O. Ruff, *Ber.*, **30**, 1656 (1897).

(32) H. E. M. Specht, A. W. Browne and K. W. Sherk, *J. Am. Chem. Soc.*, **61**, 1083 (1939).

(33) F. D. Rossini and R. B. Rice, "Infra-red Spectral Data," American Petroleum Institute Research Project 44, 1956, Series No. 164, 165, 166, 349, 350 and 351.

(34) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1955, p. 524.

(35) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1924).

(36) J. L. Simonsen and A. R. Todd, *J. Chem. Soc.*, 188 (1942).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, R. I.]

The Mechanism of the Oxidation of Some Aromatic Amines by Peroxyacetic Acid

BY KHAIRAT M. IBNE-RASA AND JOHN O. EDWARDS

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The rates of oxidation of phenylhydroxylamine, aniline and three ring-substituted anilines by peroxyacetic acid have been measured. The oxidations follow second-order kinetics, being first order in each reactant. The Hammett relationship is followed with a ρ value of -1.86 in solvent ethanol. The dependence of rates on temperature has been studied; the energies of activation are low (12 to 16 kcal. mole^{-1}) and the entropies of activation are highly negative (-23 to -26 cal. mole^{-1} deg.^{-1}). Methylmethacrylate, an effective radical trap, does not inhibit the rate of reaction. *p*-Nitroaniline reacts about 25 times faster in water than in ethanol. There is a slight decrease in rate when the solvent is changed from H_2O to D_2O. Phenylhydroxylamine reacts faster than would be expected on the basis of its basicity and polarizibility. These results are consistent with a bimolecular nucleophilic attack of the amine on the outer oxygen of peroxyacetic acid.

Introduction

The oxidation of aromatic amines to phenylhydroxylamines and nitroso-, nitro-, azo- and azoxy-compounds with organic peracids has been reported by several groups of workers.[1-8]

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(1) A. Baeyer and V. Villiger, *Ber.*, **33**, 1569 (1900).

(2) A. Baeyer and V. Villiger, *ibid.*, **34**, 762 (1901).

(3) E. Bamberger and T. Scheutz, *ibid.*, **34**, 2262 (1901).

(4) N. Prileschajew, *ibid.*, **42**, 4811 (1909).

(5) J. D'Ans and A. Kneip, *ibid.*, **48**, 1136 (1915).

(6) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

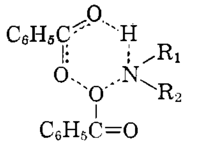
(7) D. Swern, *Chem. Revs.*, **45**, 34 (1949).

(8) R. R. Holmes and R. P. Bayer, *J. Am. Chem. Soc.*, **82**, 3454 (1960).

It is generally believed that the primary process involved is the stepwise oxidation of aniline to phenylhydroxylamine, then to nitrosobenzene, and finally to nitrobenzene. The azo and azoxy compounds arise from the competitive condensations between phenylhydroxylamine and nitrosobenzene and between the unreacted aniline and nitrosobenzene.[3,5,9]

D'Ans and Kneip[5] reported over 70% yields of the corresponding nitroso compounds when aniline, *p*-toluidine and *p*-nitroaniline were treated with a little more than two equivalents of the peracid (added in one portion) in aqueous medium. In each case the corresponding azoxy compound was isolated in over 20% yield. When the peracid was added dropwise, the yields of nitroso compounds were reduced and those of azoxy compounds increased. They also observed that when the reaction mixture was not cooled, substantial amounts of nitro compounds were formed. Emmons[10] has reported that nitro compounds are obtained in high yields (62–83%) when the aromatic amines are oxidized with peroxyacetic acid under boiling conditions.

There is evidence that the oxidation of amines with acyl peroxides or with peracids may proceed with the formation of free radicals or by a non-radical mechanism depending on the structure of the amine.[11] It has been suggested that the non-radical mechanism may operate with the formation of ions as intermediates[11] or may proceed by way of a cyclic activated complex I.[12] Denney and Denney[13] and Edwards[14] have pointed out that the essential feature of the non-radical mechanism may be a nucleophilic displacement by the nitrogen compound on the peroxidic oxygen.



I

Ross observed second-order kinetics for the oxidation of triethylamine by hydrogen peroxide[15] and, recently, Ogata and Tabushi reported similar results for the oxidation of *p*-substituted N,N-dimethylanilines by Caro acid.[16] The second-order rate constants are high and substituents influence the rate in the direction consistent with the amine acting as a nucleophile.

The present investigations were undertaken to determine rates and activation parameters for the peroxyacetic acid (hereafter peracid) oxidation of aromatic amines and to correlate these values with the possible mechanisms.

Results

Analysis of Products and Kinetic Technique.—Nitrosobenzenes absorb in the visible region between 810 and 740 mμ.[17] At low concentrations (0.01 to 0.02 *M*) in ethanol, Beer's law is obeyed. The extinction coefficient of nitrosobenzene in ethanol was determined to be 45 at 755 mμ.

The kinetic technique involved measuring the rate of appearance of the nitrosobenzenes spectrophotometrically, under conditions which favored the formation of nitroso compounds as the predominant products of oxidation. Ethanolic solutions containing 0.005 to 0.020 *M* aniline and 0.061 to 0.122 *M* peracid (freed from H_2SO_4 which is present in the commercially available product to the extent of 1%) were placed in spectrophotometric cells and the appearance of the nitrosobenzene followed as a function of time. The wave lengths 755, 750 and 746 mμ were monitored for nitrosobenzene, *p*-chloronitrosobenzene and *p*-methylnitrosobenzene, respectively. The absorbancy at infinite time was taken as a measure of the total nitroso compound formed in a particular kinetic run; the yields of the nitroso compounds were thus found to be 98% from *p*-toluidine, 94% from aniline, 74% from *p*-chloraniline and over 99% from phenylhydroxylamine.

In a few experiments the reaction mixture after the complete oxidation of 0.01 *M* *p*-toluidine with 0.122 *M* peracid was diluted 200-fold with ethanol and its ultraviolet spectrum studied. The spectrum showed three maxima at 315, 288 and 226 mμ, in agreement with Nakamoto and Rundle's work.[17] The absorbancy values at 315 and 288 mμ confirmed a 98% yield of *p*-methylnitrosobenzene. By a similar method the yield of nitrosobenzene from the oxidation of aniline under the kinetic conditions was found to be 94%.

In one set of kinetic runs on the oxidation of aniline, the peracid was used without prior destruction of the 1% of H_2SO_4. Under these conditions lower yield of nitrosobenzene (about 74%) was observed and the formation of the secondary condensation products favored. Under similar conditions the yield of nitrosobenzene from phenylhydroxylamine was not suppressed. These observations are in agreement with those of Ogata and Takagi[18] and Ogata, Tsuchida and Takagi,[19] who have reported that the condensation of anilines with nitrosobenzenes to form azo compounds is acid catalyzed, while the condensation of phenylhydroxylamine with nitrosobenzene in 100% methanol is slightly retarded by acid.

Rate Law.—The second-order rate constants for the oxidation of phenylhydroxylamine to nitrosobenzene were calculated from the integrated form of the differential rate equation

$$dx/dt = k(a - x)(b - x) \qquad (1)$$

For the two-step oxidation of anilines, the second-

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[9] I. P. Gragerov and A. F. Levit, *Zhur. Obskch. Khim.*, **30**, 3726 (1960).

[10] W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5528 (1957).

[11] O. A. Chaltikyan, E. N. Atanasyan, A. A. Sarkisyan, G. A. Marmaryan and D. S. Gaibakyan, *Zhur. Fiz. Khim.*, **32**, 2601 (1958).

[12] Ya. K. Syrkin and I. I. Moiseev, *Russian Chem. Rev. (Uspekhi Khimii)*, **29**, 209 (1960), Eng. Trans.

[13] D. B. Denney and D. Z. Denney, *J. Am. Chem. Soc.*, **82**, 1389 (1960).

[14] J. O. Edwards, "Nucleophilic Displacement on Oxygen in Peroxides," paper given at the Peroxide Reaction Mechanism Conference, Brown University, Providence, R. I., June, 1960.

[15] S. D. Ross, *J. Am. Chem. Soc.*, **68**, 1484 (1946).

[16] Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Japan*, **31**, 969 (1958).

[17] K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

[18] Y. Ogata and Y. Takagi, *ibid.*, **80**, 3591 (1958).

[19] Y. Ogata, M. Tsuchida and Y. Takagi, *ibid.*, **79**, 3397 (1957).

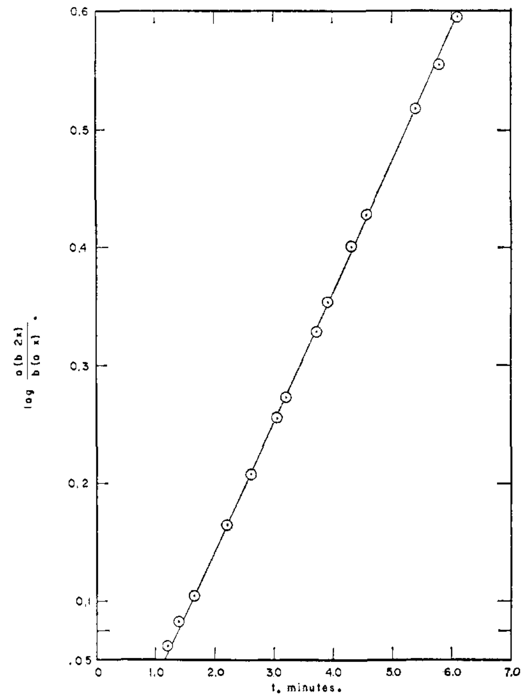

Fig. 1.—Second-order plot for the oxidation of aniline with peracid in ethanol at 30°.

order rate constants were calculated by using eq. 2

$$k = \frac{2.303}{(b - 2a)} \log \frac{a(b - 2x)}{b(a - x)} \qquad (2)$$

which is the integrated form of the differential rate eq. 3

$$dx/dt = k(a - x)(b - 2x) \qquad (3)$$

where a and b are the initial concentrations of amine and peracid, respectively, and x is the amount of nitroso compound formed at time t. Figure 1 shows a typical second-order plot for the oxidation of aniline by peracid at 30° in ethanol. The linearity of the plot, after the induction period has been passed, indicates that the over-all reaction obeys second-order kinetics. The induction period is typical of series reactions and our kinetic treatment employs the steady-state approximation for the concentration of the intermediate phenylhydroxylamine, because the rate of oxidation of phenylhydroxylamine was found to be faster than the rate of oxidation of aniline (Table II). The validity of the steady-state approximation was tested under pseudo first-order conditions. For a case of series first-order reactions like

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Frost and Pearson have given the equations[20]

$$C = A_0 [1 - (1 + k_1/k_2)e^{-k_1t}] \qquad (4)$$

$$C = A_0 [1 + 1/k_1 - k_2 (k_2e^{-k_1t} - k_1e^{-k_2t})] \qquad (5)$$

$$B = A_0k_1/k_2 - k_1 (e^{-k_1t} - e^{-k_2t}) \qquad (6)$$

Equation 4 employs the steady-state approximation for B while 5 and 6 are exact equations. In the present system A_0 and C symbolize the initial concentration of aniline and the concentration of nitrosobenzene formed at the time t, respectively; k_1 and k_2 are the pseudo first-order rate constants for the oxidation of aniline to phenylhydroxylamine and the oxidation of phenylhydroxylamine to nitrosobenzene, respectively.

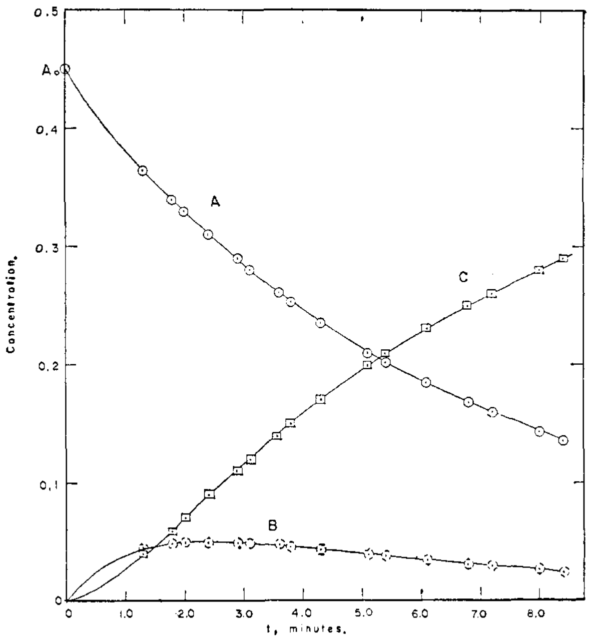

Fig. 2.—Concentration-time curves for aniline (A), phenylhydroxylamine (B), and nitrosobenzene (C) in the oxidation of aniline with peracid.

The pseudo first-order rate constant for the oxidation of aniline with peracid (0.122 M) in ethanol at 20°, obtained by using eq. 4 which employs the steady-state approximation, was found to be $2.30 \pm 0.1 \times 10^{-3}$ sec.$^{-1}$. For two runs the value of this pseudo first-order rate constant was calculated by using the exact eq. 5, k_2 having been determined separately and found to be 15.0×10^{-3} sec.$^{-1}$. The value of k_1 thus obtained was $2.45 \pm 0.05 \times 10^{-3}$ sec.$^{-1}$, which is in close agreement with the value of k_1 (2.30×10^{-3} sec.$^{-1}$) obtained using the steady-state approximation.

In a single kinetic run on the oxidation of aniline with peracid (0.122 M) in ethanol at 20°, eq. 6 was used to calculate the concentrations of the intermediate phenylhydroxylamine (B) at various time intervals. The initial concentration of aniline (A_0) and the concentration of nitrosobenzene (C) at time t are known directly from the experiment; k_1 was calculated by using the exact eq. 5 and k_2 was determined in an independent experiment. The value A, the concentration of unreacted aniline at time t was then calculated by using the eq. 7

$$A = A_0 - B - C \qquad (7)$$

A plot of the concentrations A, B and C as a function of time is given in Fig. 2, which illustrates the fact that aniline is oxidized to nitrosobenzene through the intermediate formation of a reactive species (phenylhydroxylamine).

Table I lists the second-order rate constants for the oxidation of aniline at 20° in ethanol, under

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[20] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153 and 159.

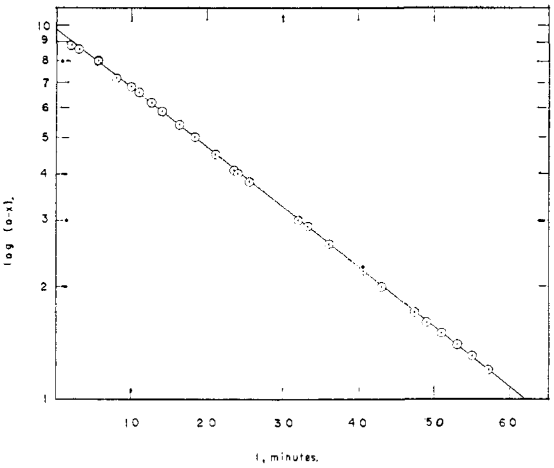

Fig. 3.—Pseudo-first-order plot for the oxidation of *p*-nitroaniline with peracid in water at 30°.

varying initial concentration of the reactants, confirming that the reaction is first order in each reactant. The rates of oxidation of *p*-nitroaniline with peracid were measured in ethanol, water and deuterium oxide by following the disappearance of *p*-nitroaniline at 410 mμ. The concentration of *p*-nitroaniline was varied between 5×10^{-5} to 1×10^{-4} *M* while that of peracid between 6.1×10^{-2} to 1.22×10^{-1} *M*. The absorbancy at time *t* was taken as a measure of unoxidized aniline at time *t* and plots of absorbancy *versus* time are linear to as far as the reaction was carried (in some cases to 90%). Figure 3 shows a typical pseudo-first-order plot for the oxidation of *p*-nitroaniline at 30° in water. The pseudo-first-order rate constants are independent of the initial concentration of *p*-nitroaniline, but they vary linearly with the peracid concentration, indicating that the rate is

TABLE I

[Peracid], *M*	[Aniline], *M*	$k_2 \times 10^2$, l. mole^{-1} sec.$^{-1}$
0.122	0.010	2.06 ± 0.07
.122	.020	1.98
.061	.01	2.02

$$\frac{-\mathrm{d}\,[p\text{-nitroaniline}]}{\mathrm{d}t} = k_2\,[p\text{-nitroaniline}][\text{peracid}]$$

The rates in water and deuterium oxide were measured at *p*H 6, where the *p*-nitroaniline ($K_b = 1 \times 10^{-12}$) is not protonated. In a few runs the *p*H was varied between 4.68 to 6.78 and no effect was observed on the rate of reaction.

Table II lists the second-order rate constants for the oxidation of phenylhydroxylamine and the various anilines at different temperatures and the activation parameters calculated from these rate constants.

Hammett Relation.—It is seen (Table II) that electron-donating *p*-substituents increase the rate of reaction while the electron-withdrawing groups retard the rate. A plot of log k_s/k_0 *versus* σ-values, using $\sigma = +1.27$ for *p*-nitro group,[21] is linear with a slope of −1.86.

TABLE II

SECOND-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS

Compound	Solvent	Temperature, °C.	$k_2 \times 10^4$, l. mole^{-1} sec.$^{-1}$	E_a kcal., mole^{-1}	$\Delta S^{\ddagger}$ cal., mole^{-1} deg.$^{-1}$
p-Toluidine	Ethanol	11.6	239		
		20.0	462 ± 3		
		30.0	941 ± 25	13	−23
Aniline	Ethanol	11.1	103 ± 1		
		20.0	206 ± 7		
		30.0	414 ± 8	13	−25
p-Chloroaniline	Ethanol	20.0	64.6 ± 0.9		
		30.0	136 ± 1	13	−26
p-Nitroaniline	Ethanol	30.0	1.94 ± 0.05		
		40.0	4.47 ± .15	16	−26
p-Nitroaniline	Water	10.0	10.6 ± .1		
		20.0	24.5 ± .3		
		30.0	52.6 ± 2.1	13.5	−26
p-Nitroaniline	D_2O	30.0	45.4 ± 1.1		
Aniline	Water	22.0	3500 ± 500		
Phenylhydroxylamine	Ethanol	25.2	1580 ± 40		
		20.0	1230		
		14.6	958 ± 52		
		10.0	671	8	−37

Medium Effects.—Although a detailed study of solvent effects was not undertaken, the difference in reactivity of *p*-nitroaniline in water and in ethanol is striking ($k_{H_2O}/k_{C_2H_5OH} = 25$). An estimate of k_{H_2O} for unsubstituted aniline may be made from the data of Table II, using the assumption that the solvent effect on rate is the same for all anilines; k_{H_2O} aniline calculated in this way is 50×10^{-2} l. mole.$^{-1}$ sec.$^{-1}$ at 20°. This estimate cannot be far from the actual value because a rough value of this rate constant was obtained experimentally ($35 \pm 5 \times 10^{-2}$ l. mole.$^{-1}$ sec.$^{-1}$). The rate of oxidation of *p*-nitroaniline in D_2O was found to be slightly slower than that in H_2O ($k_{H_2O}/k_{D_2O} = 1.15$).

Radical Inhibitors.—The rate of oxidation of *p*-toluidine and *p*-chloroaniline (0.010 *M*) with peracid (0.122 *M*) in ethanol was measured in presence of methyl methacrylate (0.2 *M*), which is an efficient radical trap.[22] No effect was observed on the rates of oxidation. The yield of *p*-nitrosotoluene was not affected by methyl methacrylate, but that of *p*-nitrosochlorobenzene was slightly reduced.

Effect of Sulfuric Acid.—In a set of kinetic runs in which aniline was oxidized with peracid in presence of sulfuric acid (0.002 *M*), the second-order rate constant in ethanol at 30° was $2.70 \pm 0.04 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. The energy of activation was calculated to be 13.8 kcal. mole.$^{-1}$ and $\Delta S^{\ddagger}$ equalled −22 cal. mole.$^{-1}$ deg.$^{-1}$.

Gaseous Products.—A small quantity of a gas, which was neither CO_2 nor O_2, was evolved immediately after mixing peracid (0.10 *M*) with anilines (0.05 *M*) in ethanol at 5°. The evolution of the gas stopped within two minutes after the mixing of the reactants. There were no gases evolved as the oxidation progressed.

Hydrogen Peroxide.—It was found that there is no observable reaction when *p*-nitroaniline is treated with hydrogen peroxide in water at *p*H 6.

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[21] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Co., Inc., New York, N. Y., 1940, p. 188.

[22] C. G. Swain, W. Stockmayer and T. Clarke, Jr., *J. Am. Chem. Soc.*, **72**, 5426 (1950).

Oxidation of Azobenzenes.—In a trial run azobenzene (0.02 *M*) was treated with peracid (0.104 *M*) in ethanol at 25°. The rate of loss of azobenzene was found to be much slower than the oxidation of aniline under similar conditions as only about 20% reaction occurred in 15 hours.

Discussion

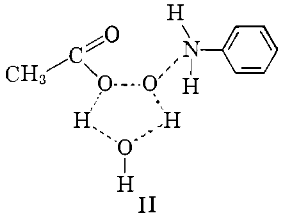
Reaction Mechanism.—The results of the present investigations which are pertinent to mechanism are summarized as follows: (1) The over-all oxidation of anilines with peroxyacetic acid follows second-order kinetics, being first-order in each reactant. Aniline is oxidized to phenylhydroxylamine in the slow step of the reaction, followed by a comparatively more rapid oxidation of phenylhydroxylamine to nitrosobenzene. (2) Electron-donating substituents on the aniline accelerate the rate of oxidation, while electron-withdrawing groups retard the rate. The Hammett relationship is followed, with a ρ-value of -1.86 in ethanol. (3) The energies of activation are low and the entropies of activation highly negative. (4) *p*-Nitroaniline reacts about 25 times faster in water than in ethanol. In water the rate is independent of *p*H in the range 4.68 to 6.78. The entropies of activation in both these solvents are the same ($\Delta S^{\ddagger} = -26$ cal. mole.$^{-1}$ deg.$^{-1}$). (5) Methyl methacrylate, an effective radical inhibitor, does not alter the rate of reaction and no gases are evolved during the oxidations. (6) Hydrogen peroxide does not react at a measurable rate with *p*-nitroaniline in aqueous medium at *p*H 6.

Of the several mechanisms which have been suggested for the oxidation of amines by peroxyacids or peroxides[9,11–14] some can be definitely eliminated on the basis of the above results, at least insofar as the present system is concerned. A radical chain mechanism cannot be operative here because methyl methacrylate does not alter the rate of reaction (item 5) and because no gases are evolved during the oxidation. Acetoxy radical, if formed, would be expected to give CO_2, C_2H_6, CH_4, etc. It is also difficult to write a radical chain mechanism which would fit the observed kinetic law. Furthermore a radical chain mechanism as also a mechanism involving free radicals as intermediates[11] would demand high energies of activation since homolytic bond cleavages would be involved. The low values of energies of activation obtained for the present system are, therefore, considered evidence against both a radical chain mechanism and a non-chain mechanism involving free radicals as intermediates. Gragerov and Levit[9] have reported O^{18}-exchange experiments which exclude the possibility of the formation of OH· in the oxidation of aromatic amines by Caro acid in aqueous medium. The suggestion that there is greater charge separation in the transition state than in the ground state of the reactants[11] appears unlikely in the present system, because if that were the case the entropy of activation would be predicted to be more negative in ethanol than in water,[23] which is not in accord with our experimental results (item 4).

Syrkin and Moiseev[12] have suggested that the peroxidic oxidation of aliphatic secondary amines proceeds by way of a cyclic activated complex I. While this might well be the case in non-hydroxylic solvents, this type of cyclic transition state would not easily explain the great difference in reactivity when the solvent is changed from water to ethanol (item 4).

Our kinetic data show that both amine and peracid are involved in the transition state and suggest that the nitrogen atom of the amine performs a nucleophilic displacement on the sterically less hindered peroxidic oxygen. The effect of *p*-substituents on the rate of oxidation (item 2) is consistent with the amine acting as a nucleophile. The magnitude of the value of ρ (-1.86) in ethanol is also consistent with this postulate, the value of ρ for the nucleophilic displacement by N,N-dimethylaniline on the carbon of methyl iodide in methanol being -2.142.[24] The low values of energies of activation and the highly negative entropies of activation lend further support to this view, because for many known cases of nucleophilic displacements on peroxide oxygen low values of these parameters have been reported.[25–29]

A transition state which arises from a simple nucleophilic displacement giving acetate ion and phenylhydroxyammonium ion cannot, however, explain the solvent effect and the relative entropies of activation in water and in ethanol. Such a transition state would of necessity be polar (greater charge separation) and cannot be accepted as such on the basis of arguments presented earlier in this section. It is therefore considered that a solvent molecule also is involved in the transition state II through hydrogen bonding which tends to decrease the polarity of the transition state.



II

The difference in reactivity between the aqueous and the ethanolic systems is ascribed to the difference between the acidities of the two solvents and not to the difference in their polarity. The highly negative entropies of activation are also better explained by assuming such a cyclic transition state. It is analogous to the transition state proposed by Bateman and Hargrave[29] for the oxidation of cyclohexylmethyl sulfide with alkyl hydroperoxides. The solvent effects and the trend of activation parameters observed by them are similar to the observations in the aniline system. The small lowering of rate in D_2O as compared

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(23) Reference 20, p. 122.

(24) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(25) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4783 (1953).

(26) D. H. Fortnum and J. O. Edwards, *J. Org. Chem.*, submitted for publication.

(27) D. H. Fortnum, C. J. Battaglia, S. R. Cohen and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).

(28) C. G. Overberger and R. W. Cummins, *ibid.*, **75**, 4250 (1953).

(29) L. Bateman and K. P. Hargrave, *Proc. Roy. Soc.* (*London*), **224A**, 389 (1954).

with water is also indicative of hydrogen bonding in the transition state.

The four-parameter equation,[30] which correlates nucleophilic reactivity with polarizability and basicity, suggests that the rate constant for the oxidation of aniline with peroxyacetic acid in aqueous medium should be near to the rate constant of bromide ion oxidation[27] under similar conditions. This latter value (25.8×10^{-2} l. mole.$^{-1}$ sec.$^{-1}$) is reasonably comparable in size to the rate constant estimated experimentally here ($40\text{–}50 \times 10^{-2}$ l. mole.$^{-1}$ sec.$^{-1}$). This similarity is considered additional evidence for a mechanism involving nucleophilic displacement by aniline.

The transition state II also suggests that the rate of oxidation of the amine should be independent of *p*H in the range in which the amine is unprotonated. Such was found to be the case for *p*-nitroaniline where the rate of oxidation was measured between the *p*H range 4.68 to 6.78 (item 4). The suppression of the rate of oxidation of aniline in ethanol by small amounts of sulfuric acid is also explained on the ground of aniline protonation. Ogata and Tabushi[16] have reported similar effects in the oxidation of N,N-dimethylanilines by Caro acid.

Finally the observation that the *p*-nitroaniline does not react with hydrogen peroxide at a measurable rate in aqueous medium at *p*H 6 is consistent with a mechanism involving the transition state II. The much higher basicity of the hydroxyl ion as compared with that of the acetate ion makes it a poorer leaving group. In other systems involving nucleophilic displacements on the peroxide oxygen, hydrogen peroxide has invariably been found to be much less reactive than peroxyacetic acid under comparable conditions.[14]

Reactivity of Phenylhydroxylamine.—Phenylhydroxylamine ($pk_a = 3.3$)[19,31] is a weaker base than aniline and, if the arguments advanced by Jencks and Carriuolo[32] on the polarizability of hydroxylamine can be extrapolated to phenylhydroxylamine, there is no reason to believe that the latter compound possess abnormally high polarizability. Thus, although its polarizability is apparently normal and although it is a weaker base than the aniline, it exhibits greater nucleophilic reactivity than aniline in the present system ($k_{C_6H_5NHOH}/k_{C_6H_5NH_2} \simeq 6$ at 20° in ethanol). It has also been reported to show greater reactivity than aniline toward nitrosobenzenes.[18,19] Several instances of abnormally high nucleophilic reactivity of compounds in which the reacting atom is directly linked to an electronegative element with a free pair of electrons have been reported by Jencks and Carriuolo.[32] Edwards and Pearson[33] attribute this characteristic to the fact that besides polarizability and basicity, there is a third factor, a so-called Alpha Effect, which confers abnormal nucleophilic reactivity on these compounds. The electrostatic repulsions between the electron pair of the reacting atom and the free electron pair of the adjacent electronegative atom raise the ground state energy of the substrate thus lowering the energy of activation. In the transition state these repulsions are minimized when the electron pair of the reacting atom is used in forming the incipient new bond. The low energy of activation observed for the oxidation of phenylhydroxylamine (Table II) is consistent with the existence of an Alpha Effect in this substrate. The highly negative entropy of activation ($\Delta S^{\ddagger} = -37$ cal. mole.$^{-1}$ deg.$^{-1}$) may arise from additional restrictions on the transition state because of intramolecular hydrogen bonding in which the hydroxyl group is involved.

Side Reactions.—The competitive condensation reactions between unreacted aniline and nitrosobenzene and between phenylhydroxylamines and nitrosobenzenes give rise to the side products azobenzenes and azoxybenzenes, respectively. By using an excess of the oxidizing agent and by avoiding the presence of stronger acids, which catalyze the formation of azobenzenes[18] and retard the oxidation, high yields of nitroso compounds were achieved. Electron-releasing groups accelerate the rate of oxidation ($\rho = -1.86$ in ethanol) but do not influence the condensations equally favorably because the value of ρ for the condensation of substituted aniline with nitrosobenzene is -2.14 while that for the condensation of aniline with substituted nitrosobenzenes is $+1.22$.[18] The two effects therefore tend to cancel each other to a large extent. Consequently, highest yields of nitroso compounds are obtained when there is an electron-donating group on the aniline.

The azoxybenzene must arise solely from the condensation between nitrosobenzene and phenylhydroxylamines and none through the oxidation of azobenzene, because azobenzene was found to oxidize much more slowly than aniline.

Experimental

Materials.—Commercial peroxyacetic acid solutions, obtained from BECCO, were analyzed by the ceric sulfate–thiosulfate method.[34] The 1% sulfuric acid content was removed by taking a known volume of the standardized peracid in a known volume of absolute ethanol saturated with anhydrous sodium acetate. The precipitated sodium sulfate was coagulated by centrifugation and aliquots of the clear supernatant liquid were used to give the desired concentration of peracid.

Phenylhydroxylamine was prepared by reducing nitrobenzene with zinc dust[35] followed by recrystallization from benzene. The best grades available of anilines were further purified by recrystallization or distillation.

In a typical kinetic run 99 ml. of an ethanolic solution of peracid was brought to a desired temperature and then 1 ml. of 1.00 *M* aniline added. About 3 ml. of this solution, which contained 0.122 *M* of peracid and 0.010 *M* of aniline, was transferred to a thermostated spectrophotometric cell. The cells were maintained at a desired temperature to within 0.1°. Wave lengths 755, 750 and 746 mμ were monitored for the appearance of nitrosobenzene, *p*-chloronitrosobenzene and *p*-nitrosotoluene, respectively. It was confirmed that Beer's law is obeyed over the concentration used in the kinetic measurements and that no other reactant or product absorbed at the wave lengths chosen for kinetic measurements.

The wave length 410 mμ was monitored for the disappearance of *p*-nitroaniline in the solvents ethanol, water and D_2O.

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[30] J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1819 (1956).

[31] I. Bergman and J. C. James, *Trans. Faraday Soc.*, **50**, 60 (1954).

[32] W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

[33] J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

[34] F. P. Greenspan and D. G. Mackeller, *Anal. Chem.*, **20**, 1061 (1948).

[35] O. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 445.