ozone. Except for a novel pathway in participating solvents, the features of the reaction are similar to the reactions of simpler alkynes with ozone. The mechanistic details of the reaction in nonparticipating solvents could not be established unequivocally. The thermal lability of a yellow intermediate in the reaction contrasts greatly with its stability toward nucleophilic attack.

Experimental Section

Di-*tert*-butylacetylene (Chemsamco), methyl pivalate, pivalic acid, and pivalic anhydride (Aldrich) were >99% pure by gas chromatography and were used as received. Pivalil was collected from several reaction mixtures by preparative gas chromatography or by ordinary chromatography on alumina by elution with CHCl$_3$. The yellow liquid showed ϵ 20.4 at 360 nm in CHCl$_3$ at 25 °C, but the extinction coefficient decreased at lower temperatures. Solvents were reagent or spectroscopic grade. Dichloromethane was dried over molecular sieve (Linde 4A) before use. Ozone was produced from a Welsbach Model 14 ozonizer from oxygen at 7–8 psi and passed into solutions in Pyrex test tubes or (in later runs) in 10 × 100 mm Kimble tubes which could be sealed with a plastic screw cap. The solutions were cooled in dry ice/acetone (−78 °C) or liquid nitrogen/solvent baths.

The analysis of the evolved gases (run 13) was accomplished by ozonizing the sample in a tube with a ground glass joint and an adapter with a stopcock, so that the sample could be degassed by cooling to −196 °C and thawing to −78 °C. After degassing, the evacuated tube was closed off with the stopcock and allowed to warm to 25 °C, and the gases above the solution were admitted to a mass spectrometer (Consolidated Electrodynamics Corp. Model 21-620) and gas chromatograph (Hewlett Packard Model 800 equipped with FID and an 8 ft × $^1/_8$ in Porapak Q column) for analysis.

Gas chromatography–mass spectroscopy of some of the reaction mixtures was carried out with a Finnigan Model 4000 with an INCOS data system, on a 6 ft × 2 mm i.d. column packed with 3% OV-17 on Gas Chrom Q (120 mesh). With the "gentle" donor CH$_5^+$–NH$_4^+$ in the CIMS mode, we were able to see the P + 1 ions for all of the *tert*-butyl derivatives in this work, which undergo extensive fragmentation with EIMS. For routine analysis, we used a Varian Model 1700 TC gas chromatograph and a $^1/_4$ in. × 6 ft column packed with 10% OV-1 on Chromosorb W (column A) or a Hewlett-Packard Model 5700A FID instrument with a $^1/_8$ in. × 10 ft column packed with 10% SP2100 on 100/120 Supelcoport (column B), with mesitylene or hexamethylethane as internal standards. The ^{1}H NMR spectra were measured with a Varian CFT-20 instrument with internal Me$_4$Si as a reference (δ 0).

The Pyrex jacketed cell for low-temperature spectral measurements was made as a constant-temperature cell by Mr. Kenneth Tracewell (Chemsamco) from an outer tube 1$^5/_{16}$ in. × 3$^3/_4$ in. with two inner 10/30 ground glass inlet tubes. The cell was held in place with short pieces of Tygon tubing, which joined the inlet tubes to two copper tubes that were anchored into holes drilled through the sample compartment of a Cary Model 14 spectrometer. The jacket was evacuated with an oil pump. The inner cell compartment was a squared piece of tubing with o.d. $^1/_2$ in. Cold samples were introduced into the cells by syringe through a serum cap. The temperature of the solution was monitored with a copper–constantan thermocouple enclosed in a glass tube and inserted through the serum cap. The thermocouple was calibrated with ice/water and with chloroform slush (−63.5 °C), and the output was displayed continuously on a strip chart recorder. The spectral range in Figure 1 was scanned in about 25 s, during which the temperature change of the solution was less than about 3 °C.

Acknowledgment. We thank Mr. Bruce Hidy, Mr. Robert Iden, and Mr. Thomas Householder of Battelle Laboratories for spectral measurements, and Dr. John R. Nixon for assistance with the NMR spectrometer.

Registry No. 1a, 17530-24-4; ozone, 10028-15-6.

Peroxomonophosphoric Acid Oxidation. 7.[1] Studies of the Kinetics and Substituent Effect in the Oxidation of Aniline

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The kinetics of the oxidation of aniline and 12 substituted anilines by peroxomonophosphoric acid (PMPA) have been measured. The reactions are first order in PMPA and first order in amine. The rate laws are given in eq 10 and 13. The unprotonated amine is the reactive species. Correlation of log rates with σ, σ^+, σ^-, and ΔpK_a yielded values of ρ (−1.37), ρ^+ (−1.31); ρ^- (−1.38), and β (0.58), respectively. The values suggest an electron-deficient reaction center, and the Brønsted coefficient, β, indicates considerable bond formation in the transition state. All the ortho substituents provide steric retardation for the formation of the transition state. Oxidation of aniline gives azobenzene, azoxybenzene, *p*-aminophenol, and *p*-benzoquinone routed through the reactive intermediate phenylhydroxylamine. The individual reactivities of various ionized PMPA species with the amine have been estimated.

There have been extensive studies in the oxidation of aniline by peroxo acids like perbenzoic acid,[2] peracetic acid,[3-5] Caro's acid,[6] and trifluoroperacetic acid,[7] and a general picture of the mechanism is now available. A S$_N$2 intermediate is formed by nucleophilic attack of the amine lone pair on the electrophilic peroxo oxygen which decomposes to phenylhydroxylamine in a rate-limiting step. Further oxidation leads to nitroso- and eventually to nitrobenzene (eq 1).

$$\mathrm{ArNH_2 \rightarrow ArNHOH \rightarrow ArNO \rightarrow ArNO_2} \quad (1)$$

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(1) Part 6: S. N. Mahapatro, A. K. Panda, and G. P. Panigrahi, *Bull. Chem. Soc. Jpn.*, **56** (1981).

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

(3) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5528 (1957).

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

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

(6) I. P. Gragerov and A. F. Levit, *Zh. Obshch. Khim.*, **30**, 3726 (1960).

(7) W. D. Emmons and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 4623 (1953).

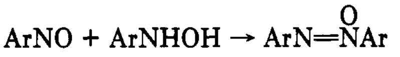
Table I. Oxidation Rates[a] for Varying Initial Concentration of PMPA and Amines

10^2[amine], M	10^4[PMPA], M	$10^4k_1'$, s^{-1}	$10^2k_2'$, M^{-1} s^{-1}
	Aniline[b]		
1.2	4.1	8.59	7.16
1.5	26.0	10.63	7.09
1.5	16.0	10.65	7.10
0.4	4.5	3.12	7.80
0.8	4.5	5.9	7.38
0.055	4.5		6.98[c]
	p-Nitroaniline[d]		
2.6	4.8	13.4	5.16
1.03	4.8	5.37	5.22
0.31	4.8	1.55	4.99
2.24	21.4	10.88	4.86
2.24	43.0	10.64	4.75

[a] At 35 °C. [b] In aqueous medium and at pH 4.4. [c] Obtained directly from a second-order rate expression. [d] In 50% aqueous acetonitrile (v/v) and at pH 1.3.

Quantitative yields of nitroso and nitrobenzene are never obtained because of competing condensation reactions leading to azo and azoxybenzenes[6,8] (eq 2 and 3).

$$\mathrm{ArNH_2} + \mathrm{ArNO} \rightarrow \mathrm{ArN{=}NAr} \qquad (2)$$


(3)

$$\mathrm{ArNO} + \mathrm{ArNHOH} \rightarrow \mathrm{ArN{=}}\overset{\mathrm{O}}{\mathrm{N}}\mathrm{Ar} \qquad (3)$$

Oxidation of aromatic amines by inorganic peroxo acids like peroxydisulfate (PDS), peroxodiphosphate (PDP), and peroxomonophosphoric acid (PMPA) have not been studied in detail except for the Boyland–Sims oxidation,[9] i.e., the oxidation of aniline to *o*-aminophenyl sulfate by peroxydisulfate. The *o*-aminophenyl sulfate could arise by electrophilic attack of the peroxo oxygen on the nitrogen and subsequent rearrangement or by direct C-attack.[10] The substituent effect in this oxidation pointed to N attack. Boyland and Manson[11] in a preliminary study screened several aromatic amines for their reactivity toward PDP and PMPA. Aniline was inert to PDP, whereas PMPA oxidized aniline to *p*-aminophenol and *p*-aminophenyl dihydrogen phosphate in presence of acetone but not in acetonitrile or water alone. Our interest in the PMPA oxidation of aniline arose mainly because of the following reasons.

(1) We have recently shown that PMPA oxidizes 3-aminopyridine to 3,3′-azoxypyridine[12] and anthranilic acid to azoxybenzene-2,2′-dicarboxylic acid[13] in essentially quantitative yields. Boyland's[11] finding of *p*-aminophenol and *p*-aminophenyl dihydrogen phosphate as the only products in the PMPA oxidation of aniline conflicted with our preliminary product analysis where we could identify at least four products, viz., (i) azobenzene, (ii) azoxybenzene, (iii) *p*-aminophenol, and (iv) *p*-benzoquinone. No nitrobenzene could be detected.

(2) The ionization of H_3PO_5 to $H_2PO_5^-$, HPO_5^{2-}, and PO_5^{3-} of decreasing electrophilic ability,[14] presents an opportunity to estimate their reactivity toward nucleophilic amine, which is not possible in other organic peroxo acids.

Table II. pH Dependence of the PMPA-Amine Reaction[a]

amine (concn, M)	pH	$10^2k_2'_{\mathrm{obsd}}$, M^{-1} s^{-1}	$10^2k_2'_{\mathrm{calcd}}$, M^{-1} s^{-1}
aniline (1.5 × 10^{-2})	3.91	4.6	4.2
	4.35	7.2	8.5
	4.74	13.8	12.2
	5.10	11.7	13.1
	5.70	7.8	8.5
	5.88	7.3	6.9
	6.55	3.5	2.9
p-nitroaniline (2.5 × 10^{-3})	0.0	3.3	3.2
	0.3	6.4	5.6
	0.63	9.8	8.7
	1.0	12.6	11.8
	1.3	9.4	11.4
	2.15	3.2	4.0
	2.67	1.32	1.68
	3.01	0.90	1.05
	3.48	0.63	0.67
	4.09	0.7	0.51
	4.76	0.54	0.41
	5.54	0.26	0.213
	6.13	0.13	0.093
	6.35	0.082	0.067
	7.09	0.031	0.031

[a] At 35 °C in aqueous medium with PMPA (4.5 × 10^{-4} M).

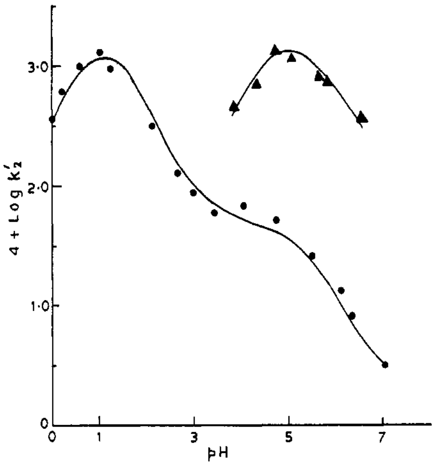


Figure 1. Plot of log k_2' vs. pH for the reaction of amines with PMPA at 35 °C in aqueous medium: ▲, aniline; ●, *p*-nitroaniline. The solid line represents the theoretical plot of log $k_2'_{\mathrm{calcd}}$ against pH (data from Table II).

Kinetic Results and Discussion

First-order rate constants (k_1', s^{-1}) have been computed from the slopes of the linear log [PMPA] vs. time plots. The plots are linear for well over 2 half-lives. The rates of oxidation of aniline could be measured in a limited pH range, 4–7,[15] whereas oxidation rates for *p*-nitroaniline have been obtained in the entire acidic pH range of 0–7. Variations in the initial PMPA concentration and amine showed first-order dependence on each at constant acidity (Table I). Thus at constant acidity, the simplest rate expression is given by eq 4, where k_2' is the observed second-order rate constant and t denotes the total analytical concentration.

$$\mathrm{rate} = k_2'[\mathrm{PMPA}]_t[\mathrm{amine}]_t \qquad (4)$$

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(8) P. Ruggli and J. Rohner, *Helv. Chim. Acta*, **25**, 1553 (1925).

(9) E. Boyland, D. Manson, and P. Sims, *J. Chem. Soc.*, 3623 (1953).

(10) E. J. Behrman, *J. Am. Chem. Soc.*, **89**, 2424 (1967).

(11) E. Boyland and D. Manson, *J. Chem. Soc.*, 4689 (1957).

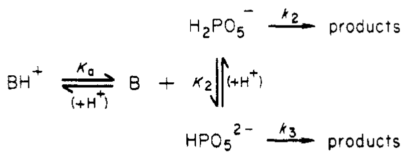
(12) S. N. Mahapatro, G. P. Panigrahi, and A. K. Panda, *Curr. Sci.*, **49**, 227 (1980).

(13) G. P. Panigrahi and A. K. Panda, *Bull. Chem. Soc. Jpn.*, **54**, 1554 (1981).

(14) Y. Ogata, K. Tomizawa, and T. Morikawa, *J. Org. Chem.*, **44**, 352 (1979).

(15) The pK_a of the anilinium ion is 4.6. At pH 4.6, aniline is 50% protonated. Rate measurements below pH 4 showed complication, and the linearity of log [PMPA] vs. time could not be seen. On mixing there was a rapid drop of titer (~30%) followed by a very slow oxidation. We do not know the reason for this. We believe that below pH 4 aniline is totally protonated (>90%), and the rapid initial decrease might be due to some reversible equilibrium between the protonated and unprotonated amine.

Scheme I[a]



[a] B = $C_6H_5NH_2$, $K_2 = 4.2 \times 10^{-6}$, and $K_a = 2.512 \times 10^{-5}$.

Table III. Individual Rate Constants (M^{-1} s^{-1}) of Different PMPA Species at 35 °C

amine	k_1	k_2	k_3
aniline	~50[a]	0.256	0.0144
p-nitroaniline	0.4804	0.0049	0.000223

[a] Reference 17.

The pH dependence of the oxidation reaction for aniline and *p*-nitroaniline have been studied, and the rate constants are given in Table II. The pH-rate profile clearly reflects the involvement of various PMPA species and unprotonated amine, which is in consonance with our earlier observation that in anthranilic acid[13] the unprotonated amine is the reactive species.

Rate Law for Aniline Oxidation. A plot of log k_2' vs. pH (Figure 1) results in a bell-shaped curve with a rate maximum at pH 4.75. In the pH range 4–7, H_3PO_5 exists mainly as $H_2PO_5^-$ and HPO_5^{2-}.[16] We envisage the reaction scheme shown in Scheme I.

In this [H⁺] range

$$[\mathrm{PMPA}]_t = [H_2PO_5^-] + [HPO_5^{2-}] \qquad (5)$$

$$[H_2PO_5^-] = \frac{[H^+]}{K_2 + [H^+]}[\mathrm{PMPA}]_t \text{ and } [HPO_5^{2-}] = \frac{K_2}{K_2 + [H^+]}[\mathrm{PMPA}]_t \qquad (6)$$

but

$$[\mathrm{amine}]_t = [B] + [BH^+] \qquad (7)$$

or

$$[B] = \frac{K_a}{K_a + [H^+]}[\mathrm{amine}]_t \qquad (8)$$

Hence, the rate law for aniline becomes

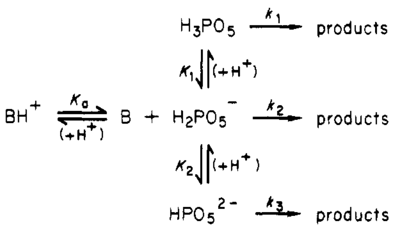
$$-\frac{d[\mathrm{PMPA}]_t}{dt} = k_2\frac{[H^+]}{K_2 + [H^+]}[\mathrm{PMPA}]_t\frac{K_a}{K_a + [H^+]}[\mathrm{amine}]_t + k_3\frac{K_2}{K_2 + [H^+]}[\mathrm{PMPA}]_t\frac{K_a}{K_a + [H^+]}[\mathrm{amine}]_t \qquad (9)$$

$$= \frac{k_2[H^+] + k_3K_2}{K_2 + [H^+]}[\mathrm{PMPA}]_t\frac{K_a}{K_a + [H^+]}[\mathrm{amine}]_t \qquad (10)$$

Hence from eq 4

$$k_2' = \frac{(k_2[H^+] + k_3K_2)K_a}{(K_2 + [H^+])\,(K_a + [H^+])} \qquad (11)$$

Scheme II[a]



[a] B = $p\text{-}O_2NC_6H_4NH_2$, $K_1 = 8.0 \times 10^{-2}$, $K_2 = 4.2 \times 10^{-6}$, and $K_a = 7.762 \times 10^{-2}$.

Table IV. Substituent Effect in the Oxidation of Anilines ($XC_6H_4NH_2$)

no.	X	ΔpK_a[a]	σ[b]	σ^-[c]	k_2', M^{-1} s^{-1}
1	H	0	0	0	0.060
2	*p*-CH_3	0.5	−0.17	−0.17	0.114
3	*m*-CH_3	0.12	−0.069		0.084
4	*o*-CH_3	−0.15	−0.1	−0.13	0.058
5	*o*-Cl	−1.96	0.020	0.68	0.0061
6	*m*-Cl	−1.10	0.373		0.020
7	*p*-Cl	−0.62	0.227	0.226	0.0456
8	*o*-Br	−2.07	0.21	0.70	0.00502
9	*p*-Br	−0.74	0.232	0.232	0.0326
10	*p*-I	−0.82	0.18	0.276	0.0356
11	*o*-NO_2	−4.86	0.78		0.00013
12	*m*-NO_2	−2.13	0.71		0.00674
13	*p*-NO_2	−3.49	0.778	1.27	0.0011

[a] $\Delta pK_a = pK_a$ (substituted aniline) − pK_a (aniline) (data from ref 18). [b] L. P. Hammett, "Physical Organic Chemistry", McGraw Hill, New York, 1970, p 356. [c] K. B. Wiberg "Physical Organic Chemistry", Wiley, New York, 1966, p 410; J. Shorter, "Correlation Analysis in Organic Chemistry", Clarendon Press, London, 1973, p 44.

From eq 11, least-squares values of k_2 and k_3 are obtained and are collected in Table III.

Rate Law for *p*-Nitroaniline Oxidation. The pH-rate profile for *p*-nitroaniline is broadly sigmoid (Figure 1). There is no oxidation in the alkaline pH. In the pH range studied Scheme II explains the rate data.

In this range of pH, PMPA exists[16] as H_3PO_5, $H_2PO_5^-$, and HPO_5^{2-}. Hence, the rate law is given by eq 12. By

$$-\frac{d[\mathrm{PMPA}]_t}{dt} = k_1[H_3PO_5][B] + k_2[H_2PO_5^-][B] + k_3[HPO_5^{2-}][B] \qquad (12)$$

putting H_3PO_5, $H_2PO_5^-$, and HPO_5^{2-} in terms of $[\mathrm{PMPA}]_t$ and [B] in terms of $[\mathrm{amine}]_t$, we get the rate law shown in eq 13, and from eq 4 we obtain eq 14.

$$-\frac{d[\mathrm{PMPA}]_t}{dt} = \frac{k_1[H^+]^2 + k_2[H^+]K_1 + k_3K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}[\mathrm{PMPA}]_t\frac{K_a}{K_a + [H^+]}[\mathrm{amine}]_t \qquad (13)$$

$$k_2' = \frac{(k_1[H^+]^2 + k_2K_1[H^+] + k_3K_1K_2)K_a}{([H^+]^2 + K_1[H^+] + K_1K_2)(K_a + [H^+])} \qquad (14)$$

Estimated values of k_1, k_2, and k_3 from eq 14 are collected in Table III.

The magnitudes of k_1, k_2, and k_3 in both the amines are quite good in the order of decreasing electrophilicity of the PMPA species.[14] The 50-fold difference between the k_2 as well as k_3 values for aniline and *p*-nitroaniline is reasonable and is to be expected from a difference of the nucleophilicity of the amino nitrogen. The calculated values of k_2' agree excellently well with that of the observed

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(16) C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, 4, 552 (1965).

(17) As the kinetics was complicated below pH 4 in the case of aniline, a value of k_1, which represents the reactivity of the H_3PO_5 and amine reaction, could not be calculated from the rate data. However, we have attempted to get a rough estimate of this value from the relation [log k_1(*p*-nitroaniline) − log k_1(aniline)]/σ (or ΔpK_a) = ρ (or β). The value obtained is of right order of magnitude.

(18) J. W. Smith, "Chemistry of the Amino Group", Saul Patai, Ed., Interscience, New York, 1968, Chapter 4, p 182.

Table V. Correlation of log (Rates of Oxidation) of Substituted Anilines with σ, σ^+, and σ^-

exptl data used for	type of constant used	ρ	corr coeff	SD
all meta- and para-substituted compds	σ	−1.81	0.950	0.327
	σ^+	−1.72	0.953	0.346
all except p-NO$_2$	σ	−1.37	0.987	0.277
	σ^+	−1.31	0.987	0.290
all ortho-substituted compds	σ	−2.79	0.999	0.392
all para- and ortho-substituted compds	σ^-	−1.38	0.983	0.130

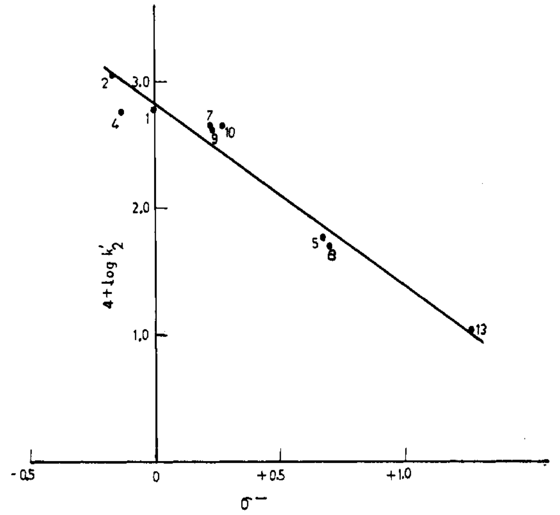


Figure 2. Plot of log k_2' against σ^- from data of Table IV.

k_2' values (Table II) and provide confidence to the multiple steps envisaged.

Substituent Effect. Rates have been measured for 12 substituted anilines in 20% aqueous acetonitrile (V/V) at pH 5.4 at 35 °C, and the rate constants are given in Table IV.

Hammett Relationship. The fact that electron-releasing substituents accelerate this reaction suggests that the reaction involves an electron-deficient center. Correlations with σ, σ^+, and σ^- have been attempted. The values of ρ, the correlation coefficient, and the SD values are collected in Table V.

It is seen that all the meta- and para-substituted compounds except the p-nitro one are in a line.[19] All the rates of oxidation of ortho substituents are consistently retarded and form a separate line. However, any reaction that involves demand on lone-pair electron density should show better correlation[33] with σ^- than with σ or σ^+. In fact, correlation of log k_2' with σ^- is linear and unlike in correlation with σ and σ^+; all the substituents (all para and ortho) could be seen to fall close to a single line (Figure 2) in correlation with σ^-. The values are of the same order of magnitude as those found by Edwards[5] for the oxidation of aniline by peracetic acid in ethanol at 30° ($\rho = -1.86$), and this also compares well with the metal ion catalyzed oxidation of anilines by *tert*-butyl hydroperoxide[20] ($\rho = -1.42$ to -1.97). The value indicates the development of cationic character on nitrogen during the transition state.

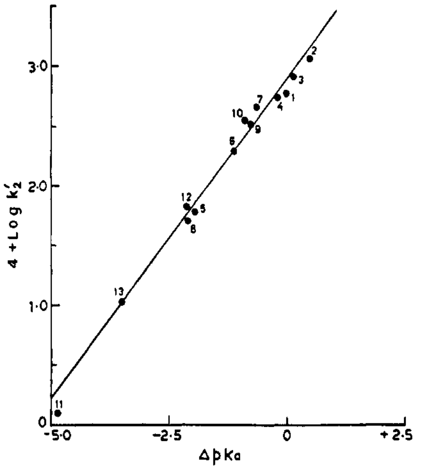
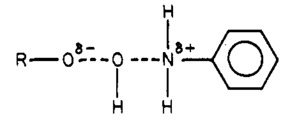


Figure 3. Plot of log k_2' against ΔpK_a from data of Table IV.

Brønsted Relationship. The correlation with pK_a or ΔpK_a is excellent (Figure 3) which indicates that the nitrogen basicity or the nucleophilicity finally controls the reaction. The Brønsted slope (β) of 0.58 suggests considerable bond formation in the transition state[21] and is entirely in agreement with the formation of the intermediate.

Activation Parameters. Thermodynamic parameters have been computed from the rate constants at four different temperatures and are recorded in Table VI.

Reaction Mechanism. Of the several mechanisms suggested for the oxidation of aromatic amines by peroxo acids or peroxides, evidences in the present oxidation are more in favor of a polar transition state.[22] The relevant points are as follows. (a) There are second-order kinetics, first order each in the amine and PMPA. (b) The value of ρ is found to be −1.3 to −1.8. (c) Low $\Delta H^{\ddagger}$ and high negative $\Delta S^{\ddagger}$ values point to an orderly transition state. The homolytic cleavage of the peroxide bond[23] requires about 138 kJ mol^{-1}, and the low values of the enthalpy of activation observed are significant. (d) The insensitivity of the rates to added acrylamide, Cu^{2+}, or Fe^{2+} rule out a mechanism involving the homolytic scission of the peroxide bond. The transition state shown below must involve considerable charge separation. Such a transition state will be stabilized more in aqueous medium, and this is indeed observed as the reactions are considerably retarded in aqueous acetonitrile.



R = H_2PO_3, HPO_3^-, or PO_3^{2-}

The formation of p-aminophenol in considerable amounts is interesting. It could arise by acid catalyzed rearrangement of phenylhydroxylamine[24] formed in the rate-limiting step or by direct C attack at the para carbon. Such a mechanistic problem was encountered in the Boyland–Sims oxidation.[25] We believe that in the present

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[19] When an exalted value of 1.27 for the value of p-nitrogroup was used, the point for p-nitroaniline falls on the line. Such duality of substituent constants have been emphasized by Hammett (J. Shorter, "Correlation Analysis in Organic Chemistry", Clarendon Press, London, 1973, p 12).

[20] G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, **35**, 4007 (1970).

[21] L. Senatore, E. Ciuffarin, and A. Fava, *J. Am. Chem. Soc.*, **92**, 3035 (1970).

[22] D. Swern, *Chem. Rev.*, **45**, 1 (1949).

[23] L. Pauling, "The Nature of Chemical Bond and the Structure of Molecules and Crystals", Cornell University Press, Ithaca, NY, 1960, p 85.

[24] H. E. Heller, E. D. Hughes, and C. K. Ingold, *Nature (London)*, **168**, 909 (1951).

[25] N. Venkatasubramanian and A. Sabesan, *Can. J. Chem.*, **47**, 3710 (1969).

Table VI. Activation Parameters for the PMPA Oxidation[a] of Aniline and *p*-Nitroaniline

	k_2', M^{-1} s^{-1}, at					
amine	30 °C	35 °C	40 °C	45 °C	$\Delta H^‡$,[d] kJ mol^{-1}	$\Delta S^‡$,[d] J mol^{-1} K^{-1}
aniline[b]	0.098	0.138	0.165	0.217	39.5 ± 0.3 (9.4 ± 0.07)	−133 ± 1 (−31.8 ± 0.24)
p-nitroaniline[c]	0.085	0.126	0.150	0.195	39.2 ± 0.2 (9.4 ± 0.05)	−135 ± 1 (−32.2 ± 0.24)

[a] In aqueous medium. [b] At pH 4.70. [c] At pH 1.0. [d] In parentheses are $\Delta H^‡$ and $\Delta S^‡$ values expressed in kcal mol^{-1} and eu, respectively.

oxidation phenylhydroxylamine is the common intermediate for azoxybenzene, azobenzene, and *p*-aminophenol (*p*-benzoquinone being formed in low yields from *p*-aminophenol). The following support our contention. (a) There is a fairly good correlation between log rate and σ or pK_a, indicating nitrogen attack. If it were a case of N attack and C attack occurring in parallel reaction paths, the substituent effect would have been confused without any significant correlation. (b) The ortho substituents retard the reaction strongly, and this is to be expected if the rate-limiting step in the reaction is the formation of the intermediate.

Experimental Section

All the amines were from BDH and were distilled or recrystallized before use. Acetonitrile was distilled over P_2O_5 (bp 81–82 °C). Carbonate-free NaOH was prepared[26] and standardized against succinic acid with phenolphthalein as the indicator. $HClO_4$ (Baker analyzed, 70%), potassium hydrogen phthalate, KH_2PO_4, and NaOH were used to maintain the pH.

All the melting points were taken on a Wiswo-melt apparatus and are uncorrected. Ultraviolet spectra were recorded on a Carl Zeiss VSU2-P spectrophotometer. Preparative TLC was done with silica gel F-254.

Tetrapotassium peroxodiphosphate ($K_4P_2O_8$) was a gift sample from FMC Corp. A cerimetric estimation[27] of this sample accounted for 98% of the PDP. PMPA was prepared by acid hydrolysis of $K_4P_2O_8$ which is a two-stage consecutive reaction[28] (eq 15 and 16). The rate of PMPA hydrolysis to H_2O_2 is at least

$$H_4P_2O_8 + H_2O \rightarrow H_3PO_5 + H_3PO_4 \quad (15)$$

$$H_3PO_5 + H_2O \rightarrow H_2O_2 + H_3PO_4 \quad (16)$$

2 orders of magnitude slower than the rate of hydrolysis of PDP to PMPA and is negligible[16] at $[H^+] < 1$ M. This hydrolytic method has now become a standard source of PMPA.[29] For each individual experiment a fresh solution of PMPA was prepared. In a typical procedure, a known quantity of $K_4P_2O_8$ was weighed into a 100-mL standard flask and dissolved in 10 mL of conductivity water. A calculated amount of standard $HClO_4$ was added so as to get an acid strength of 0.5 M in 50 mL. This was made up to approximately 50 mL and thermostated at 35 °C for 3.5 h until hydrolysis was complete (>98%). For runs which necessiated the use of buffers, the acid after hydrolysis was completely neutralized by adding standard NaOH, and the calculated amounts of buffers were weighed into the flask to get the desired pH.[30] The pH of the solution was measured at the end of each run with the help of a Systronics 335 digital pH meter. PMPA was estimated iodometrically at pH 4–5 (HOAc–NaOAc buffer) with a drop of 1% ammonium molybdate solution.[31] The amount of H_2O_2[32] was never more than 2% in any given run. Independent runs with H_2O_2 showed that under the experimental conditions aniline was not oxidized by H_2O_2. The progress of the reaction was monitored by estimating the residual PMPA by iodometry at pH 4–5. Excellent linear plots were obtained from log PMPA vs. time plots. k_1' (s^{-1}), pseudo-first-order rate constants, were obtained from the slopes of these plots. k_2' (M^{-1} s^{-1}), second-order rate constant, was calculated from the relation shown in eq 17. All the experiments were done in duplicate and were

$$k_2' = k_1'/[\text{substrate}] \quad (17)$$

reproducible within ±5%. Least-squares analysis of the rate data were done with a DCM Microsystem 1121.

Product Analysis. $K_4P_2O_8$ (7.0 g, 0.02 mol) was dissolved in water (25 mL), and 5 mL of cold concentrated H_2SO_4 was added and the pH adjusted to 0.4. The mixture was left for 3.5 h to ensure complete hydrolysis. The pH was then readjusted to 4.5. Aniline (5 g, 0.055 mol) was added to it, and the mixture was stirred at 35 °C for 5 h. The mixture was extracted with hexane (5 × 100 mL). The hexane extract was acidified with 4 N HCl to remove excess aniline and the aqueous layer rejected several times. The hexane extract was rotary evaporated, which resulted in a dark brown solid (1.5 g). The crude product when treated with benzene (50 mL) gave a dark yellow solution and an insoluble residue which was recrystallized from ethanol (mp 185 °C) and was identified to be *p*-aminophenol (lit. mp 186 °C), yield 300 mg (3 mmol, 15%). The benzene solution on TLC with 50:50 benzene and petroleum ether (40–60 °C) showed three spots. Preparative TLC on silica gel yielded the following fractions: (1) azobenzene, yield 150 mg (0.27 mmol, 8%), mp 66 °C (lit. mp 68 °C), UV (EtOH) λ_{max} 320 nm; (2) azoxybenzene, yield 600 mg (3 mmol, 23%), mp 35 °C (lit. mp 36 °C), UV (EtOH) λ_{max} 230, 318 nm; (3) *p*-benzoquinone, yield 40 mg (0.37 mol, 3.7%), mp 113 °C (lit. mp 114 °C), UV (EtOH) λ_{max} 245 nm. All four compounds gave the correct C, H, and N analyses. When mixed with authentic samples the melting points were not depressed.

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Registry No. Aniline, 62-53-3; *p*-nitroaniline, 100-01-6; *p*-toluidine, 106-49-0; *m*-toluidine, 108-44-1; *o*-toluidine, 95-53-4; *o*-chloroaniline, 95-51-2; *m*-chloroaniline, 108-42-9; *p*-chloroaniline, 106-47-8; *o*-bromoaniline, 615-36-1; *p*-bromoaniline, 106-40-1; *p*-iodoaniline, 540-37-4; *o*-nitroaniline, 88-74-4; *m*-nitroaniline, 99-09-2; PMPA, 13598-52-2.

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