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Peroxomonophosphoric Acid Oxidation. V.[1] A Kinetic and Mechanistic Study of Oxidation of Aminobenzoic Acids in Acid Medium. Double Bell Shaped pH Rate Profile

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Anthranilic acid and *p*-aminobenzoic acid were oxidized with peroxomonophosphoric acid in aqueous acid medium to the corresponding azoxy derivatives. Suitable rate laws for the double bell shaped pH rate profile were derived and rationalized on the basis of protonation of the amino group and ionization of the carboxyl group. The mechanism of oxidation involves the nucleophilic attack of nitrogen on the electrophilic peroxo oxygen. The reactivity of different peroxomonophosphoric acid species has been estimated.

Reports have been given on the oxidation of 3-aminopyridine,[1] dimethyl sulfide,[2] dimethyl sulfoxide,[3] and benzaldehyde[4] by peroxomonophosphoric acid (PMPA). In the oxidation of sulfide, the sulfur functions as a nucleophile. While the dimethyl sulfoxide oxidation presents dualistic behavior, sulfur acts as a nucleophile in the acid medium, becoming an electrophile in alkaline medium. It is of interest to see whether amines which are good nucleophiles act by a mechanism similar to that of sulfides. There seems to be no kinetic and mechanistic study on the oxidation of aromatic amines except for a preliminary work by Boyland and Manson[5] who screened a number of amines towards their reactivity to PMPA to see whether they involve oxidative phosphorylation. Recently, Ogata and co-workers[6] studied the oxidation of *N,N*-dimethylaniline to *N,N*-dimethylaniline *N*-oxide and determined the relative reactivity of the various species of PMPA. We felt it necessary to extend the kinetic studies to aromatic amines such as anthranilic acid (OAB) and *p*-aminobenzoic acid (PAB). We wish to report some of the salient kinetic features of the reaction.

Experimental

All the chemicals were of analytical grade. Conductivity water was used in the preparation of the solutions and as a reaction medium. PMPA was prepared by acid hydrolysis of $K_4P_2O_8$.[7] The concentration was checked frequently by iodometry, the self-decomposition being negligible in the pH region examined. The acidity was adjusted by adding appropriate amounts of perchloric acid or standard buffers[8] and measured with a Systronics digital pH-meter 335. Sodium perchlorate was used for adjusting the ionic strength. Whenever necessary sodium perchlorate was generated by neutralizing the perchloric acid with carbonate free sodium hydroxide. Both the aminobenzoic acids were purified by recrystallization from water, their melting points (OAB-144 °C, PAB-191 °C) agreeing with those in literature (OAB-145 °C, PAB-192 °C). The kinetics was followed by measuring the rate of disappearance of PMPA, the estimation of which was made by iodometry in an acetic acid–acetate buffer of pH 4—5 with a drop of ammonium molybdate solution.[4] The rate constants were computed by the usual method and were found in duplicate runs to be reproducible within ±5%. Computations were carried out with a DCM minicomputer Microsystem 1121. The IR absorption spectra were recorded on a Perkin Elmer 137 spectrophotometer.

Product Study. PMPA=0.04 mol dm^{-3} (50 ml) and anthranilic acid 0.008 mol dm^{-3} (50 ml) were mixed at pH 1.3 and 45 °C and kept for 48 h. The product azoxybenzene-2,2′-dicarboxylic acid was extracted with diethyl ether (dark brown solid, yield 75%), checked for its purity by TLC and identified by its mp 225 °C (uncorrected) and IR (Nujol): 1690(s) (ArCOOH) and 1290(s) ($N{=}N{\rightarrow}O$) cm^{-1}. Under similar conditions the product azoxybenzene-4,4′-dicarboxylic acid isolated from *p*-aminobenzoic acid (a yellow solid, yield 80%) was identified by its mp 238 °C (uncorrected) and IR (Nujol): 1710(s) (ArCOOH) and 1300(s) ($N{=}N{\rightarrow}O$) cm^{-1}.

Results

The kinetics of oxidation of OAB and PAB by PMPA in aqueous medium was investigated at 308 K. The rate data for both OAB and PAB suggest second order kinetics at constant acidity, the rate law being

$$V = k'[\text{Aminobenzoic acid}]_t[\text{PMPA}]_t, \qquad (1)$$

where subscript t stands for total concentration and k' the observed second order rate constant.

Effect of Acidity. The kinetics was investigated over the pH range 0—7. The rate data are summarized in Table 1. The plots of log k' *vs.* pH (Figs. 1 and 2) have two bell shaped regions, 0—3 and 3—7. This indicates participation of different species of PMPA resulting from dissociation (Eqs. 4 and 16) as well as different aminobenzoic acid species either resulting from protonation of the amino group or dissociation of the carboxyl group (Eqs. 3 and 15).

It appears that the rate law has to include complex H^+ dependence for each of the pH regions. It is possible to write the rate law in a general form as

$$V = k'[\text{substrate}]_t[\text{PMPA}]_t[H^+]^n, \qquad (2)$$

where $-1<n<+1$.

Effect of Added Substances. At pH 1 ionic strength has little influence on the rate. A marginal influence is observed at pH 4.17 (Table 1). The reaction rate was found to be insensitive to the addition of radical trapping agents such as acrylamide. No influence was observed on rate by variation of solvents such as acetic acid.

Temperature Variation. Activation parameters have been evaluated from the linear Arrhenius plots of log k' *vs.* T^{-1} by measuring the rates of oxidation at four temperatures in the range 308—323 K (Table 2).

TABLE 1. SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF AMINOBENZOIC ACIDS BY PMPA SPECIES AT 308 K, $\mu=0.4$ mol dm^{-3} IN AQUEOUS MEDIUM AT VARIOUS pH

Substrate	pH	[Substrate] $\times 10^3$ / mol dm^{-3}	[PMPA] $\times 10^4$ / mol dm^{-3}	$k' \times 10^2$ / dm^3 mol^{-1} s^{-1}
Anthranilic acid	1.0	5.15	4.10	5.44
	1.0	2.65	4.62	5.51
	1.0	6.50	4.76	5.48
	1.0	9.70	3.67	5.14
	1.0	3.70	4.31	5.87
	1.0	3.65	8.94	5.01
	1.0	3.60	16.35	5.01
	1.0	3.65	4.37	5.81[a]
	1.0	3.74	4.01	5.56[b]
	1.0	3.70	4.01	5.18[c]
	1.0	3.66	4.06	5.20[d]
	1.0	3.64	4.49	5.03[e]
	6.67	3.81	3.55	1.66[f]
	0.3	3.66	5.36	3.60
	0.6	3.75	5.26	4.98
	0.83	3.65	3.69	5.41
	1.3	3.75	4.37	6.37
	1.7	3.57	4.17	5.60
	2.0	3.678	5.254	4.75
	2.24	3.63	4.17	3.73
	3.33	3.85	3.89	3.75
	3.73	3.69	4.69	4.17
	4.13	3.55	3.68	4.51
	4.17	3.62	4.08	3.86[g]
	4.17	3.62	4.18	4.98[h]
	4.85	3.68	4.51	5.84
	5.32	3.68	5.56	4.30
	5.59	3.68	4.82	3.82
	6.21	3.68	4.05	1.89
	6.65	3.59	2.82	1.76

Substrate	pH	[Substrate] $\times 10^3$ / mol dm^{-3}	[PMPA] $\times 10^4$ / mol dm^{-3}	$k \times 10^2$ / dm^3 mol^{-1} s^{-1}
Anthranilic acid	6.96	3.85	4.41	1.28
	7.20	3.75	4.91	1.15
	1.0	3.73	4.15	9.59[i]
	1.0	3.73	4.45	13.50[j]
	1.0	3.73	3.84	21.12[k]
	4.85	3.64	3.27	8.69[i]
	4.85	3.64	2.96	13.36[j]
	4.85	3.64	4.25	16.19[k]
p-Aminobenzoic acid	0.0	3.87	3.83	1.01
	0.12	3.81	3.54	1.12
	0.3	3.78	4.25	1.61
	0.52	3.78	3.49	2.18
	0.7	3.78	4.54	2.88
	1.0	3.54	4.27	6.81[i]
	1.0	3.54	4.67	11.40[j]
	1.0	3.54	5.37	17.23[k]
	1.0	3.79	4.32	5.43[l]
	1.0	3.70	3.86	4.83[m]
	1.0	3.70	4.53	5.41[n]
	1.0	3.85	3.52	5.14
	0.89	3.65	4.35	4.40
	1.36	3.81	3.26	4.22
	2.85	4.03	4.21	3.14
	3.39	4.03	4.08	2.99
	3.93	3.71	4.71	3.36
	4.50	3.71	4.19	3.98
	5.31	3.71	3.62	5.46
	5.87	4.03	3.41	2.97
	6.43	3.85	3.89	1.66
	7.03	3.85	3.48	1.09

a) $\mu=0.65$ mol dm^{-3}. b) $\mu=0.15$ mol dm^{-3}. c) 10% AcOH. d) 30% AcOH. e) Acrylamide, 3.1×10^{-3} mol dm^{-3}. f) Acrylamide 3.25×10^{-3} mol dm^{-3}. g) $\mu==0.15$ mol dm^{-3}. h) $\mu=0.8$ mol dm^{-3}. i) At 313 K. j) At 318 K. k) At 323 K. l) $\mu=0.6$ mol dm^{-3}. m) 20% AcOH. n) 40% AcOH.

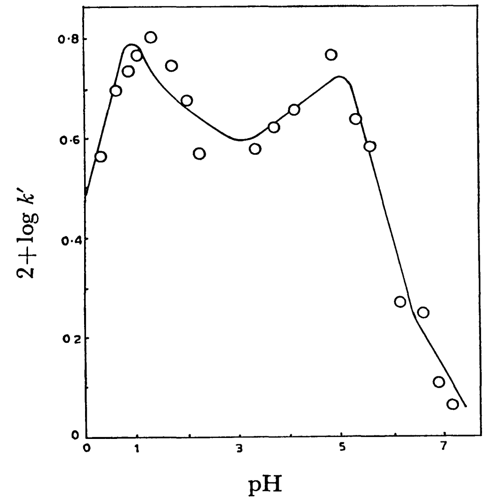


Fig. 1. Plots of log k' *vs.* pH (pH range 0 to 7) for OAB, ⊙ experimental points, — theoretical line obtained from Eq. 14 for pH 0 to 3 and Eq. 25 for pH 3 to 7.

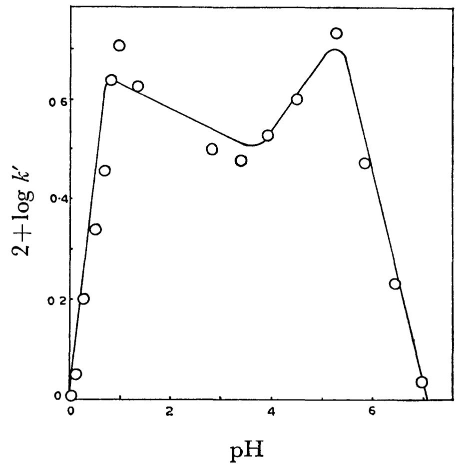


Fig. 2. Plots of log k' *vs.* pH (pH range 0 to 7) for PAB. ⊙ experimental points, — theoretical line obtained from Eq. 14 for pH 0 to 3 and Eq. 25 for pH 3 to 7.

TABLE 2. VALUES OF $\Delta H^{\ne}$ AND $\Delta S^{\ne}$ FOR THE OXIDATION OF AMINOBENZOIC ACIDS IN WATER AND $\mu=0.4$ mol dm^{-3} CALCULATED AT 308 K

pH	Substrate	$\frac{\Delta H^{\ne}}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^{\ne}}{\text{J K}^{-1}\text{mol}^{-1}}$
1.0	OAB	66.6	−52.4
4.85	OAB	55.2	−89.2
1.0	PAB	66.0	−55.6

Discussion

In view of the rate-pH profile the following equilibria seem to be likely in the pH region 0—1.

$$\mathrm{BH^+} \overset{K_\mathrm{H}}{\rightleftharpoons} \mathrm{B} + \mathrm{H^+} \tag{3}$$

where B stands for aminobenzoic acid and BH+ for N-protonated aminobenzoic acid.

$$\mathrm{H_3PO_5} \overset{K_1}{\rightleftharpoons} \mathrm{H_2PO_5^-} + \mathrm{H^+} \tag{4}$$

The magnitude of $K_1(=8.0\times10^{-2})$ suggests that the peracid exists in a neutral form[9] as H_3PO_5 below pH 1. Similarly the protonation equilibria for the aminobenzoic acids suggest that it may exist both as BH+ and B in the pH range 0—1. The inverse first order acid dependence in the region indicates the participation of free aminobenzoic acid but not the protonated species. The step may involve reaction between the neutral species of the substrate molecule and H_3PO_5 only.

The steps of the reaction below pH 1 may be as follows.

$$\mathrm{BH^+} \overset{K_\mathrm{H}}{\rightleftharpoons} \mathrm{B} + \mathrm{H^+} \tag{5}$$

and

$$\mathrm{B} + \mathrm{H_3PO_5} \xrightarrow{k_1} \text{Products.} \tag{6}$$

The total concentration of the base can be expressed as

$$[\mathrm{B}]_\mathrm{t} = [\mathrm{B}] + [\mathrm{BH^+}].$$

Hence

$$[\mathrm{B}]_\mathrm{t} = [\mathrm{B}] + \frac{[\mathrm{B}][\mathrm{H^+}]}{K_\mathrm{H}}$$

or

$$[\mathrm{B}]_\mathrm{t} = [\mathrm{B}]\{1+[\mathrm{H^+}]/K_\mathrm{H}\} = \frac{\mathrm{B}(K_\mathrm{H}+[\mathrm{H^+}])}{K_\mathrm{H}}$$

or

$$[\mathrm{B}] = \frac{[\mathrm{B}]_\mathrm{t}K_\mathrm{H}}{(K_\mathrm{H}+[\mathrm{H^+}])}. \tag{7}$$

Hence the rate is expressed by

$$V = k_1[\mathrm{B}][\mathrm{H_3PO_5}]_\mathrm{t} \tag{8}$$

$$= k_1\frac{K_\mathrm{H}}{K_\mathrm{H}+[\mathrm{H^+}]}[\mathrm{B}]_\mathrm{t}[\mathrm{H_3PO_5}]_\mathrm{t}$$

$$= k'[\mathrm{B}]_\mathrm{t}[\mathrm{H_3PO_5}]_\mathrm{t}, \tag{9}$$

where

$$k' = \frac{k_1K_\mathrm{H}}{K_\mathrm{H}+[\mathrm{H^+}]}, \tag{10}$$

which can be rearranged to

$$\frac{1}{k'} = \frac{1}{k_1} + \frac{[\mathrm{H^+}]}{k_1K_\mathrm{H}}. \tag{11}$$

Plot of $1/k'$ *vs.* [H+] was found to be linear (corr. coeff= 0.988 and 0.99) in both cases, confirming the rate law. The plot gives K_H values of 0.53 and 0.16 and value of $k_1=0.071$ and 0.054 dm^3 mol^{-1} s^{-1} for OAB and PAB, respectively.

In order to interpret the bell shaped nature of log k' *vs.* pH plot in the pH region 0—3, it seems necessary to consider the dissociation of both protonated OAB and PAB and that of H_3PO_5 to $H_2PO_5^-$ as well.

The other species of peracid, *viz.* HPO_5^{2-} and PO_5^{3-}, are not relevant in the pH region under consideration since the second and third dissociation constants of PMPA are of the order of 10^{-6} and 10^{-13}, respectively.[9] The probable steps of the reaction might be as follows.

$$\mathrm{BH^+} \overset{K_\mathrm{H}}{\rightleftharpoons} \mathrm{B} + \mathrm{H^+} \tag{5}$$

$$\mathrm{B} + \mathrm{H_3PO_5} \xrightarrow{k_1} \text{Products} \tag{6}$$

$$\mathrm{B} + \mathrm{H_2PO_5^-} \xrightarrow{k_2} \text{Products} \tag{12}$$

which lead to the rate expression,

$$-\frac{\mathrm{d}[\mathrm{PMPA}]_\mathrm{t}}{\mathrm{d}t} = \frac{k_1K_\mathrm{H}[\mathrm{H^+}]+k_2K_1K_\mathrm{H}}{K_1K_\mathrm{H}+(K_1+K_\mathrm{H})[\mathrm{H^+}]+[\mathrm{H^+}]^2}[\mathrm{B}]_\mathrm{t}[\mathrm{PMPA}]_\mathrm{t}$$

$$= k'[\mathrm{B}]_\mathrm{t}[\mathrm{PMPA}]_\mathrm{t}, \tag{13}$$

where

$$k' = \frac{k_1K_\mathrm{H}[\mathrm{H^+}]+k_2K_1K_\mathrm{H}}{K_1K_\mathrm{H}+(K_1+K_\mathrm{H})[\mathrm{H^+}]+[\mathrm{H^+}]^2}. \tag{14}$$

A least-squares solution of Eq. 14 was attempted using the reported value of K_1. The K_H value obtained kinetically from $1/k'$ *vs.* [H+] plot (Eq. 11) in the region of pH 0—1 was used. k_1 and k_2 values are estimated from Eq. 14, the results being summarized in Table 3. These values are in line with the order of reactivity between peracid species[6] ($H_3PO_5>H_2PO_5^-$). In order to check the validity of the rate law, the computed k_1 and k_2 values were employed to calculate the pH-log k' profile (Figs. 1 and 2). Agreement between the experimental points and theoretical line is satisfactory.

TABLE 3. RATE CONSTANTS OF DIFFERENT PMPA SPECIES IN dm^3 mol^{-1} s$^{-1}\times10^2$

Substrate	k_1	k_2	k_3	$\left(k_4\frac{K_\mathrm{a}}{K_2}+k_5\right)$	k_6
OAB	8.1	4.1	4.02	24.7	1.20
PAB	6.3	3.5	2.83	23.5	0.88

k_1 values from the composite rate law (Eq. 13) compare well with those obtained from the k'^{-1} *vs.* [H+] plot in the pH region 0—1 where the neutral species of PMPA alone was assumed to be effective. Indifference of rate to added salt at pH 1 can also be rationalized by the steps postulated above.

To account for the pH dependence of rate in the pH region 3—7, it is reasonable to assume that both the substrate as well as PMPA species are dissociated and all species resulting from dissociation are involved in controlling the rate.

$$\mathrm{B} \overset{K_\mathrm{a}}{\rightleftharpoons} \mathrm{B^-} + \mathrm{H^+} \tag{15}$$

$$\mathrm{H_2PO_5^-} \overset{K_2}{\rightleftharpoons} \mathrm{HPO_5^{2-}} + \mathrm{H^+},\quad K_2 = 4.2\times10^{-6}, \tag{16}$$

where B has the same meaning as before and B− is

$NH_2C_6H_4COO^-$.

In the pH region under discussion, the major oxidant species[9] are $H_2PO_5^-$ and HPO_5^{2-}. The total PMPA concentration $[PMPA]_t$ can therefore be assumed to consist of $H_2PO_5^-$ and HPO_5^{2-}. Similarly, total substrate concentration $[B]_t$ can be assumed to be due to B and B^-:

$$[B]_t = [B] + [B^-] \tag{17}$$

and

$$[PMPA]_t = [H_2PO_5^-] + [HPO_5^{2-}]. \tag{18}$$

In view of the overall second order dependence at constant pH, the steps of the reaction in the pH region may be described as

$$B + H_2PO_5^- \xrightarrow{k_3} \text{Products} \tag{19}$$

$$B^- + H_2PO_5^- \xrightarrow{k_4} \text{Products} \tag{20}$$

$$B + HPO_5^{2-} \xrightarrow{k_5} \text{Products} \tag{21}$$

$$B^- + HPO_5^{2-} \xrightarrow{k_6} \text{Products.} \tag{22}$$

These steps also explain the marginal salt effect on the rate at pH 4.17 (Table 1). From Eqs. 19—22, the rate law can be written as

$$-\frac{d[PMPA]_t}{dt} = k_3[B][H_2PO_5^-] + k_4[B^-][H_2PO_5^-]$$
$$+ k_5[B][HPO_5^{2-}] + k_6[B^-][HPO_5^{2-}]. \tag{23}$$

Equation 23 can be rearranged to give the rate expression

$$-\frac{d[PMPA]_t}{dt} = \frac{k_3[H^+]^2+\left(k_4\frac{K_a}{K_2}+k_5\right)K_2[H^+]+k_6K_aK_2}{(K_a+[H^+])(K_2+[H^+])} \times [PMPA]_t[B]_t$$
$$= k'[PMPA]_t[B]_t, \tag{24}$$

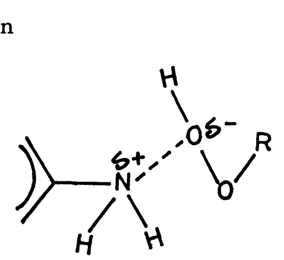
where

$$k' = \frac{k_3[H^+]^2+\left(k_4\frac{K_a}{K_2}+k_5\right)K_2[H^+]+k_6K_aK_2}{(K_a+[H^+])(K_2+[H^+])}. \tag{25}$$

Using the reported values[10] of K_a for OAB or PAB, the least-squares solution of Eq. 24 yields values of k_3, $(k_4\frac{K_a}{K_2}+k_5)$ and k_6 (Table 3). Substituting these least square values of k_3, $(k_4\frac{K_a}{K_2}+k_5)$ and k_6 in Eq. 25, log k'-pH profile was calculated (Figs. 1 and 2). The agreement between the experimental points and the theoretical line (Figs. 1 and 2) justifies the rate law.

The values of k_3, $\left(k_4\cdot\frac{K_a}{K_2}+k\right)$ and k_6 suggest minimum reactivity for the reaction with HPO_5^{2-} species compared with $H_2PO_5^-$ which is in agreement with the decreasing electrophilicity of HPO_5^{2-} over $H_2PO_5^-$. We see fair agreement between k_3 (reaction between B and $H_2PO_5^-$ in the pH range 3—7) and k_2 (reaction between B and $H_2PO_5^-$ in the pH range 0—3) for both the substrates. This is in favour of the rate laws postulated to account for the rate variation over the entire pH range.

Mechanism. Polar mechanisms in peroxide reactions have been advanced on the basis[11] of a) bimolecular kinetics, b) negative entropy of activation, and c) insensitivity to radical trapping agents.

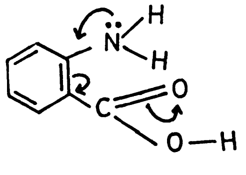


The present reactions confirm the above requirements and most probably involve polar transition states as shown in the following.
where $R{=}H_2PO_3$, HPO_3^-, or PO_3^{2-}.

Another question of importance is the nature of the peroxide attack, electrophilic *vs.* nucleophilic as dual character having been observed earlier[12,13] depending on the electronic environment. The species of PMPA namely H_3PO_5, $H_2PO_5^-$, HPO_5^{2-}, and PO_5^{3-} are in the decreasing order of electrophilicity. The fact that these aminobenzoic acids are not oxidized above pH 7 is strong evidence that the nucleophilic PMPA species are ineffective and the reaction essentially involves nucleophilic attack by the unprotonated amine on the electrophilic peroxo oxygen of the PMPA species. The rate should decrease with increase in pH.

The decrease in rate with increase in pH was not monotonic; there are two rate maxima-pH profiles, one at pH≈1, and the other at pH≈5, near the pK_a of the aminobenzoic acid. The rate maximum at pH 1 presents a situation where the concentration of the free base becomes maximum, the estimated K_H value being≈0.53. The amine is about 80% unprotonated at pH 1. The statistical distribution of H_3PO_5 and $H_2PO_5^-$ is 55 and 45% respectively. Even when the more electrophilic H_3PO_5 predominates at still lower pH, there is a marked decrease in rate because of the decrease in the unprotonated amine.

The second rate maximum around pH≈5 is unusual and the fact that this occurs near the pK_a of the carboxylic acid dissociation is of interest. The mesomeric effect taking place in the undissociated acid seems to cause a reduced nucleophilicity of nitrogen in I. In II, the carboxylate anion opposes the conjugation of amine lone pair and thus most probably increases the nucleophilicity of nitrogen.



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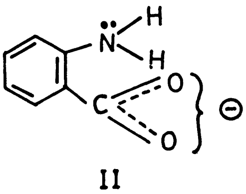

II

The formation of azoxybenzene-2,2′-dicarboxylic acid from anthranilic acid is of interest. The abnormal course of oxidation was recognized in the oxidation of 3-aminopyridine by H_2O_2/fuming H_2SO_4,[14] Caro's acid,[15] and PMPA.[1] Anthranilic acid is oxidized to the phenylhydroxylamine derivative in the rate limiting step and its oxidation to the nitroso derivative is fast as in the case of aniline, the rate of oxidation of aniline to phenylhydroxylamine being about five times lower than that of the oxidation of phenylhydroxylamine to nitrosobenzene.[16] The formation of azoxybenzene-2,2′-dicarboxylic acid involves the rapid condensation[17] between the nitroso and phenylhydroxylamine derivatives which are the reactive intermediates.

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