**Table III. Contributions to Steric Energy of Benzcycloalkenyl Cations**

| cation | ring size | $E_{\text{bend}}$[a] | $E_{\text{stretch}}$[a] | $E_{\text{torsion}}$[a] | $E_{\text{van der Waals}}$[a] |
|---|---|---|---|---|---|
| **24a** | 5 | 5.9 | 0.5 | 7.0 | 3.6 |
| **24b** | 6 | 0.6 | 0.5 | 6.0 | 7.5 |
| **24c** | 7 | 3.8 | 0.9 | 9.0 | 11.0 |
| **24d** | 8 | 7.2 | 1.2 | 9.1 | 12.6 |

[a] kcal/mol.

(especially the $C_2$–$C_3$ bond) are slightly shorter than the corresponding lengths in **22** because of contractions induced by the additional resonance and positive charge in **24**. Bond lengths and stretching constants were arbitrarily assigned to correspond to these assumptions.[16] Torsional constants about such bonds were those for $sp^2$–$sp^3$ double bonds. The effect of the approximations is to render absolute values of the computed carbonium ion energies and of $\Delta\Delta H_f°$ meaningless, but, as noted previously, the various errors should largely cancel when the homologous series **24a–d** is examined. The computed values of $\Delta\Delta H_f°$ (Table II) support the impression from model building that cations **24** (and **21**) should form with difficulty in the medium ring systems. The molecular mechanics calculations show further that the largest single contributor to the increased $\Delta\Delta H_f°$ in the seven- and eight-membered ring systems is, as expected, van der Waals' (nonbonded) repulsions (Table III).

## Experimental Section

**General.** NMR spectra were recorded on a Varian A60-A spectrometer. Gas chromatographic analyses and preparative separations were carried out using a Varian 90-P chromatograph. Products were collected by preparative VPC for identification by NMR and mass spectroscopy. Most cycloalkanones were commercial samples, except for cyclodecanone, which was prepared from sebacoin (obtained from P. S. Wharton) by the method of Reusch and Le Mahieu,[17] and cycloundecanone, which was prepared by the method of Garbisch and Wohllebe.[18] Dibromo ketones were prepared by literature procedures.[19]

**Mercury reductions** were carried out by a standard procedure.[3,5] Analysis of mixtures was by integration of peak areas;[20] products were collected by preparative VPC and identified by NMR and mass spectroscopy. The α-acetoxycycloalkanones obtained in this work are practically all known compounds[22] whose spectral properties agreed with literature values where available or expectation where not.

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# Kinetics of the Peroxymonophosphoric Acid Oxidation of Aromatic Amines[1]

Yoshiro Ogata,* Kohtaro Tomizawa, and Takashi Morikawa

*Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan*

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Oxidation of *N*,*N*-dimethylaniline (**1a**) and methyldiphenylamine (**1b**) with peroxymonophosphoric acid in aqueous acetonitrile at 30 °C gives the corresponding *N*-oxides. The oxidation obeys the rate equation: $v = k_2[\text{amine}]_t[\text{peracid}]_t$. The effect of the acidity of solution shows that neutral amine alone can react with peracid, the rate being determined by a nucleophilic attack of amine on peracid oxygen. The reactivity of $H_3PO_5$ to amine is ~100 times higher than that of $H_2PO_5^-$, and the reactivity of **1a** to peracid is ~100 times higher than that of **1b**. These results are discussed on the basis of both a plot of rate constant vs. pH and acidity constants of $H_3PO_5$ and conjugate acids of amines.

As a promising substitute oxidant for percarboxylic acid, peroxymonophosphoric acid was successfully applied to aromatic hydroxylation[2] and Baeyer–Villiger reaction[3] and they were kinetically studied. It has been reported that aniline is oxidized by peroxymonophosphoric acid to *p*-aminophenol and *p*-aminophenyldihydrogen phosphate, and 2-naphthylamine is oxidized to 2-amino-1-naphthol, etc., while *N*,*N*-dimethyl-2-naphthylamine is oxidized to its *N*-oxide.[4]

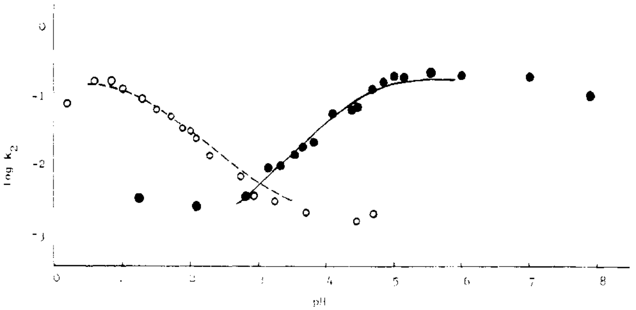


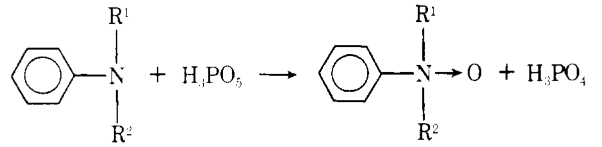
**Figure 1.** Plot of log $k_2$ vs. pH for the reaction of amines with $H_3PO_5$ in 50% aqueous acetonitrile at 30 °C. (●) The value of log $k_2$ for the reaction of dimethylaniline (**1a**) with $H_3PO_5$. (○) The value of log $k_2$ for the reaction of methyldiphenylamine (**1b**) with $H_3PO_5$. The solid line represents a theoretical plot (log $k_{calcd}$) calculated by eq 19 and the broken line represents a theoretical plot (log $k_{calcd}$) calculated by eq 26.

Various peroxides were used for the conversion of tertiary aromatic amines to their $N$-oxides, e.g., hydrogen peroxide for $N,N$-dimethylaniline[5] and perhydrol for methyldiphenylamine.[6] But the kinetics and mechanism of oxidation of the tertiary amine were reported only on the Caro's acid oxidation[7] and on the selenium dioxide catalyzed hydrogen peroxide oxidation.[8]

The present paper describes principally the kinetics and mechanism of the oxidation of tertiary aromatic amines with peroxymonophosphoric acid in aqueous acetonitrile to give $N$-oxides.

## Results

Oxidation of tertiary aromatic amines, $N,N$-dimethylaniline (**1a**) and methyldiphenylamine (**1b**), with peroxymonophosphoric acid in aqueous acetonitrile at 30 °C afforded the corresponding $N$-oxides (**2a,** 82.3%; **2b,** 63.5%) but triphenylamine (**1c**) was not oxidized under these conditions (eq 1).



(1)

1a, $R^1 = R^2 = Me$
b, $R^1 = Me; R^2 = Ph$
c, $R^1 = R^2 = Ph$

2a, $R^1 = R^2 = Me$
b, $R^1 = Me; R^2 = Ph$

The products were determined by NMR, IR, UV, and high-pressure liquid-phase chromatography (LC). The rate was followed iodometrically by the consumption of peracid and it was consistent with the rate estimated by following amines by LC.

The rate data show that the second-order kinetics (eq 2) are satisfied, where the subscript t denotes total concentration.

$$v = k_2[\text{amine}]_t[\text{peracid}]_t \qquad (2)$$

Tables I and II list the effect of initial concentration on the rate with **1a** and with **1b,** respectively.

**Effect of Acidity.** To examine the effect of the protonation of amines and of the dissociation of peracid on the rate, the rate was measured in a region of pH 1.25–7.90 for the reaction of **1a** and a region of pH 0.20–4.70 for **1b** (Tables III and IV). Figure 1 shows a plot of log $k_2$ vs. pH and the following rate equations (eq 3 and 4) are derived from the figure for **1a**:

$$v = \frac{k_2'}{[H^+]}[\mathbf{1a}][\text{peracid}] \quad \text{at pH 3–5} \qquad (3)$$

$$v = k_2[\mathbf{1a}][\text{peracid}] \quad \text{at pH 6–8} \qquad (4)$$

**Table I. Second-Order Rate Constant $k_2$ at Various Initial Concentrations for the $H_3PO_5$ Oxidation of 1a in 50% Aqueous Acetonitrile at 30 °C and pH 4.46**

| initial concn of 1a × $10^2$ M | initial concn of $H_3PO_5$ × $10^3$ M | $k_2$ ($M^{-1}$ $s^{-1}$) × $10^2$ |
|---|---|---|
| 1.08 | 1.25 | 6.42 |
| 2.16 | 1.25 | 6.65 |
| 2.16 | 2.49 | 6.18 |
| 4.31 | 2.49 | 6.94 |
| 4.31 | 3.74 | 6.72 |

**Table II. Second-Order Rate Constant $k_2$ at Various Initial Concentrations for the $H_3PO_5$ Oxidation of 1b in 50% Aqueous Acetonitrile at 30 °C and pH 1.90**

| initial concn of 1b × $10^2$ M | initial concn of $H_3PO_5$ × $10^3$ M | $k_2$ ($M^{-1}$ $s^{-1}$) × $10^2$ |
|---|---|---|
| 0.748 | 1.26 | 3.59 |
| 1.49 | 1.26 | 3.42 |
| 2.99 | 1.89 | 3.20 |
| 2.24 | 2.53 | 3.19 |
| 2.24 | 3.78 | 3.34 |

The plot of log $k_2$ vs. pH at pH 3–5 (Figure 1) shows a good linearity with a slope of +1, whereas the plot of log $k_2$ vs. pH at pH 1–4 for **1b** gave a curve with a slope of −0.6 to −0.8 (eq 5).

$$v = k_2'[H^+]^{0.6\text{–}0.8}[\mathbf{1b}][\text{peracid}] \qquad (5)$$

This fact suggests that both $H_3PO_5$ and $H_2PO_5^-$ take part in this oxidation on account of $pK_1$ (= $-\log K_1$) = $1.3_7$, which will be discussed below.

Phosphoric acid, present originally or added to the $H_3PO_5$, did not affect the rate and product, because the acidity of solution was controlled with the buffer.

## Discussion

In view of the pH profile of $k_2$ (Figure 1), the effects of the protonation of amine and dissociation of peracid on the rate should be considered (eq 6–8), where B is an amine.

$$BH^+ \overset{K_H}{\rightleftharpoons} B + H^+ \qquad (6)$$

$$H_3PO_5 \overset{K_1}{\rightleftharpoons} H_2PO_5^- + H^+ \qquad (7)$$

$$H_2PO_5^- \overset{K_2}{\rightleftharpoons} HPO_5^- + H^+ \qquad (8)$$

The quantity of $K_H$ indicates the dissociation constant of conjugate acid of amine and the quantities of $K_1$ and $K_2$ indicate first and second dissociation constants of peracid, respectively.

The value of $pK_H$ (= $-\log K_H$) in 50% aqueous acetonitrile at 30 °C was found to be $4.6_0 \pm 0.2$ for **1a,**[9] $0.5_0 \pm 0.2$ for **1b,**[9] and 0.0 for **1c.**[10] This suggests that the amine **1a** exists as its conjugate acid ($BH^+$) at pH below 3 and the ratio of [B]/[$BH^+$] increases with increasing pH, and practically all of amine **1a** exists as a neutral base (B) at pH over 6, while most of **1b** exists as free base at pH over 1. Since the oxidation involves an electron transfer from amine nitrogen to peracid, only neutral amine can react with peracid.

$pK_1$ (= $-\log K_1$) of peroxymonophosphoric acid was found to be $1.3_7 \pm 0.2$ and $pK_2$ (= $-\log K_2$) was found to be $7.6_0 \pm 0.2$.[9] Therefore, peracid exists in a neutral form ($H_3PO_5$) at pH below 1 and the ratio of [$H_2PO_5^-$]/[$H_3PO_5$] increases with increasing pH and virtually all of peracid exists in a form of $H_2PO_5^-$ at pH 3–7. By a further increase of pH over 8 the

**Table III. Second-Order Rate Constant $k_2$ for the $H_3PO_5$ Oxidation of 1a at Various pH in 50% Aqueous Acetonitrile at 30 °C**

| pH | $k_2$ ($M^{-1}$ $s^{-1}$) × $10^2$ | log $k_2$ |
|---|---|---|
| 1.25 | 0.310 | −2.51 |
| 2.10 | 0.234 | −2.63 |
| 2.77 | 0.324 | −2.49 |
| 3.15 | 0.832 | −2.08 |
| 3.33 | 0.912 | −2.04 |
| 3.54 | 1.35 | −1.87 |
| 3.65 | 1.74 | −1.76 |
| 3.82 | 2.09 | −1.68 |
| 4.10 | 5.37 | −1.27 |
| 4.39 | 6.18 | −1.21 |
| 4.46 | 6.61 | −1.18 |
| 4.70 | 12.5 | −0.902 |
| 4.85 | 15.8 | −0.800 |
| 4.99 | 18.8 | −0.726 |
| 5.14 | 18.1 | −0.742 |
| 5.57 | 22.0 | −0.658 |
| 5.99 | 19.3 | −0.700 |
| 7.01 | 19.5 | −0.711 |
| 7.90 | 10.6 | −0.975 |

**Table IV. Second-Order Rate Constant $k_2$ for the $H_3PO_5$ Oxidation of 1b at Various pH in 50% Aqueous Acetonitrile at 30 °C**

| pH | $k_2$ ($M^{-1}$ $s^{-1}$) × $10^2$ | log $k_2$ |
|---|---|---|
| 0.20 | 7.71 | −1.13 |
| 0.60 | 15.6 | −0.807 |
| 0.85 | 15.8 | −0.802 |
| 1.02 | 12.5 | −0.903 |
| 1.30 | 8.71 | −1.06 |
| 1.52 | 5.92 | −1.23 |
| 1.73 | 4.87 | −1.31 |
| 1.90 | 3.31 | −1.48 |
| 2.01 | 2.88 | −1.54 |
| 2.11 | 2.36 | −1.63 |
| 2.29 | 1.29 | −1.89 |
| 2.75 | 0.631 | −2.20 |
| 2.94 | 0.331 | −2.48 |
| 3.25 | 0.282 | −2.55 |
| 3.72 | 0.196 | −2.71 |
| 4.46 | 0.146 | −2.84 |
| 4.70 | 0.186 | −2.73 |

second dissociation affording $HPO_5^{2-}$ becomes appreciable. Taking into account that peracid is a cationoid reagent ($-O-O^{\delta+}-H$), the reactivity of peracid should decrease in the order: $H_3PO_5 > H_2PO_5^- > HPO_5^{2-}$.

**Kinetics.** As stated above, this oxidation is a nucleophilic reaction of neutral amine with peracid, where the rate-determining step may be the electron transfer from amine nitrogen to peracid resulting in the addition of $OH^+$ to amine nitrogen.

$$BH^+ \overset{K_H}{\rightleftharpoons} B + H^+ \tag{6}$$

$$H_3PO_5 \overset{K_1}{\rightleftharpoons} H_2PO_5^- + H^+ \tag{7}$$

$$H_2PO_5^- \overset{K_2}{\rightleftharpoons} HPO_5^{2-} + H^+ \tag{8}$$

$$HPO_5^{2-} \overset{K_3}{\rightleftharpoons} PO_5^{3-} + H^+ \tag{9}$$

$$B + H_3PO_5 \xrightarrow[\text{slow}]{k_3} B\text{-}OH^+ + H_2PO_4^- \tag{10}$$

$$B + H_2PO_5^- \xrightarrow[\text{slow}]{k_4} B\text{-}OH^+ + HPO_4^{2-} \tag{11}$$

$$B\text{-}OH^+ \xrightarrow[\text{fast}]{} B\text{-}O + H^+ \tag{12}$$

The total concentration of amine, $[B]_t$, is expressed as:

$$[B]_t = [B] + [BH^+] \tag{13}$$

From eq 6 and 13

$$[B] = \frac{1}{1 + [H^+]/K_H}[B]_t \tag{14}$$

where

$$K_H = \frac{[B][H^+]}{[BH^+]} \tag{15}$$

Also the total concentration of peracid, $[H_3PO_5]_t$, is expressed as

$$[H_3PO_5]_t = [H_3PO_5] + [H_2PO_5^-] + [HPO_5^{2-}] + [PO_5^{3-}] \tag{16}$$

In this oxidation, $PO_5^{3-}$ ($K_3 \doteqdot 2 \times 10^{-12}$ in $H_2O$ at 30 °C)[11] is negligible because pH is 0.2–8 under these experimental conditions.

**Dimethylaniline (1a).** In view of the value of $pK_1$ ($1.3_7$) and $pK_2$ ($7.6_0$) of peracid, the most part of peracid exists as first dissociated peracid ($H_2PO_5^-$) at pH 3–7, i.e., $[H_3PO_5]_t \simeq [H_2PO_5^-]$. On the other hand, in view of the $pK_H$ value of $4.6_0$ for **1a**, virtually all of **1a** is protonated at pH below 3, the concentration of neutral amine increases with increasing pH, and virtually all of the amine exists as a neutral form at pH over 5. Therefore, the concentration of neutral amine is represented by

$$[B] = \frac{1}{1 + [H^+]/K_H}[B]_t \quad \text{at pH 3–5} \tag{14}$$

Hence

$$v = \frac{k_4}{1 + [H^+]/K_H}[B]_t[H_3PO_5]_t \quad \text{at pH 3–5} \tag{17}$$

While

$$v = k_4[B]_t[H_3PO_5]_t \quad \text{at pH 6–8} \tag{18}$$

From the plateau in the pH profile in Figure 1, log $k_4 = -0.71_1$ or $k_4 = 0.19_5$ $M^{-1}$ $s^{-1}$.

$$k_{\text{calcd}} = \frac{k_4}{1 + [H^+]/K_H} \tag{19}$$

The plot of log $k_{\text{calcd}}$ vs. pH ($3 < \text{pH} < 5$) gave an excellent agreement with the observed curve as shown in Figure 1.

**Methyldiphenylamine (1b).** The rate constant ($k_2$) for **1b** decreases with increasing pH (Figure 1). The plot suggests that the difference of oxidation activities between $H_3PO_5$ and $H_2PO_5^-$ is fairly large and also that the distribution of these active species in solution is affected by pH especially at pH 1–3, because $pK_1$ is $1.3_7$, whereas **1b** exists mostly as a neutral form at pH > 1; i.e., $[B] = [B]_t$.

$$B + H_3PO_5 \xrightarrow[\text{slow}]{k_3} B\text{-}OH^+ + H_2PO_4^- \tag{10}$$

$$B + H_2PO_5^- \xrightarrow[\text{slow}]{k_4} B\text{-}OH^+ + HPO_4^{2-} \tag{11}$$

Therefore, the rate at pH 1–3 is expressed as:

$$v = [B]_t(k_3[H_3PO_5] + k_4[H_2PO_5^-]) \tag{20}$$

Equations 7 and 16 lead to

$$v = \frac{1}{1 + K_1/[H^+]}(k_3 + k_4K_1/[H^+])[B]_t[H_3PO_5]_t \quad \text{at pH 1–3} \tag{21}$$

At pH >4, practically all peracid exists as $H_2PO_5^-$, hence eq 11 alone operates for this oxidation.

$$v = k_4[\mathrm{B}][\mathrm{H_2PO_5^-}] \tag{22}$$

i.e.,

$$v = k_4[\mathrm{B}]_t[\mathrm{H_3PO_5}]_t \qquad \text{at pH} > 4 \tag{23}$$

From Figure 1, $k_4$ is calculated to be $1.7_4 \times 10^{-3}$ M$^{-1}$ s$^{-1}$. While at pH 0.5–1 most parts of amine **1b** and peracid exist as their neutral form, so that the rate is represented by

$$v = k_3[\mathrm{B}][\mathrm{H_3PO_5}] \tag{24}$$

i.e.,

$$v = k_3[\mathrm{B}]_t[\mathrm{H_3PO_5}]_t \qquad \text{at pH 0.5–1} \tag{25}$$

From Figure 1, $k_3$ is calculated to be $1.5_8 \times 10^{-1}$ M$^{-1}$ s$^{-1}$. The decrease of $k_2$ with decreasing pH at pH 0.2 may be due to a decrease of the concentration of neutral amine because p$K_H$ is $0.5_0$.

The above results give elementary rate constants $k_3$ and $k_4$ for reactions 10 and 11, respectively:

$$k_{\text{calcd}} = \frac{1}{1 + K_1/[\mathrm{H^+}]}(k_3 + k_4K_1/[\mathrm{H^+}]) \tag{26}$$

at pH 1–2, from $k_3 \gg k_4K_1/[\mathrm{H^+}]$

$$k_{\text{calcd}} \simeq \frac{k_3}{1 + K_1/[\mathrm{H^+}]} \tag{27}$$

The second term, $k_4K_1/[\mathrm{H^+}]$, contributes also to $k_{\text{calcd}}$ at pH over 2.5. Therefore, the theoretical plot of log $k_{\text{calcd}}$ vs. pH is a curve at pH 2.5–3.5 (Figure 1). This plot gave an excellent agreement with the observed value ($k_2$) as shown in Figure 1.

**Reactivity of Amine and Peracid.** The rate constants for the reaction of methyldiphenylamine (**1b**) with $H_3PO_5$ and $H_2PO_5^-$ are $1.5_8 \times 10^{-1}$ M$^{-1}$ s$^{-1}$ ($k_{3(\mathbf{1b})}$) and $1.7_4 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ $2k_{4(\mathbf{1b})}$), respectively. Hence, the reactivity of $H_3PO_5$ is about 100 times higher than that of $H_2PO_5^-$. This may be due to the decrease of the positive charge on peracid oxygen (-O-O$^{\delta+}$-H) or to the repulsion between peracid anion and nonbonding electron on the nitrogen of amine.

On the other hand, by comparison of the rate constant of the reaction of $H_2PO_5^-$ with **1a** and **1b** ($k_{4(\mathbf{1a})} = 1.9_5 \times 10^{-1}$ M$^{-1}$ s$^{-1}$, $k_{4(\mathbf{1b})} = 1.7_4 \times 10^{-3}$ M$^{-1}$ s$^{-1}$), the reactivity of **1a** to peracid is about 100 times higher than that of **1b**. This may be due to the fact that the electron density on nitrogen of **1a** is raised by the electron releasing two methyl groups but the electron density of **1b** is lowered by electron attracting two phenyl groups and also by the delocalization of the electron to the phenyl group. Therefore, the marked stability of triphenylamine (**1c**) for peracid oxidation is attributable to an electron-attracting effect of three phenyl groups and to steric hindrance.

## Experimental Section

IR and UV spectra were recorded on a Perkin-Elmer 337 spectrophotometer and a Hitachi 124 spectrophotometer, respectively. NMR spectra were recorded on a Hitachi R-24B NMR spectrometer using $Me_4Si$ or $Me_3Si(CH_2)_3SO_3Na$ as an internal standard. LC analysis was performed with a Yanagimoto L-1030 liquid chromatograph using Yanapak DMS column (2 × 250 mm). The pH measurement was carried out with a Hitachi-Horiba M-7 pH meter.

**Materials.** Acetonitrile was distilled over $P_2O_5$ (bp, 81–82 °C). Peroxymonophosphoric acid (2–2.5 M) was prepared by the method described in our previous paper.[3] Dimethylaniline (**1a**) was distilled under $N_2$ atmosphere before use: bp 89–91 °C (25 mm); UV log $\epsilon_{251\text{nm}}$ (MeOH) 4.12, log $\epsilon_{298\text{nm}}$ (MeOH) 3.26; NMR ($CCl_4$) $\delta$ 2.80 (s, 6 H, Me), 6.85 (m, 5 H, Ph). Methyldiphenylamine (**1b**) was prepared by the reaction of diphenylamine (16.9 g) with dimethyl sulfate (18.9 g):[12,13] bp 121–122 °C (1.5 mm); yield 9.39 g (51.3%); UV log $\epsilon_{244\text{nm}}$ (MeOH) 3.97, log $\epsilon_{291\text{nm}}$ (MeOH) 3.90; NMR ($CCl_4$) $\delta$ 3.20 (s, 3 H, Me), 7.0 (m, 10 H, Ph). Triphenylamine (**1c**) was obtained by the reaction of diphenylamine (21.6 g) with iodobenzene (25.0 g):[14] mp 127–128 °C; yield 17.0 g (56.6%); UV log $\epsilon_{290\text{nm}}$ (MeOH) 4.32; NMR ($CCl_4$) $\delta$ 7.0 (m, Ph). Dimethylaniline *N*-oxide (**2a**) was obtained from the reaction of **1a** (8.82 g) with 30% aqueous $H_2O_2$ (12.1 g):[5] mp 150.5–151.5 °C (recrystallized from petroleum ether); yield 6.49 g (65.0%); UV log $\epsilon_{254\text{nm}}$ (MeOH) 2.4, log $\epsilon_{288\text{nm}}$ (MeOH) 0.9; NMR ($D_2O$) $\delta$ 3.60 (s, 6 H, Me), 7.40 (m, 5 H, Ph); IR 950 cm$^{-1}$ (N–O). Methyldiphenylamine *N*-oxide (**2b**) was synthesized as follows: **1b** (0.20 g) was added to an acetone solution (4 mL) of 25% peracetic acid at room temperature in 1 day, the peracid remaining in the solution was decomposed by aq $Na_2S_2O_3$ and condensed to ca. 1 mL in vacuo. The condensate was chromatographed on Florisil (100–200 mesh) with benzene–methanol. The first eluent was **1b** unreacted, and the second eluent was *N*-oxide (**2b**): yield 0.128 g (59.0%); UV $\lambda_{\max}$ (MeOH) 284 nm, $\epsilon = 370$; mp 125–126 °C (recrystallized from benzene); NMR ($CDCl_3$) $\delta$ 3.95 (s, 3 H, Me), 7.5 (m, 10 H, Ph); IR 1015 cm$^{-1}$ (N–O).

pH in the solution was controlled by the use of the following buffer solutions: HCl ($0 < \text{pH} < 1$), 0.2 N HCl + 0.2 N KCl ($1 < \text{pH} < 2$), 1 N HCl + 1 N AcONa ($2 < \text{pH} < 4.5$), and $^1/_{15}$N $KH_2PO_4$ + $^1/_{15}$N $Na_2HPO_4$ ($4.5 < \text{pH} < 8$).

**Rates and Products.** To a 50% aqueous buffered MeCN solution of **1a** or **1b** was added a MeCN solution of $H_3PO_5$, the total volume being 50 mL. Aliquots (5 mL) were taken out at appropriate time intervals, and the remaining peroxymonophosphoric acid was titrated iodometrically. The second-order rate constant, $k_2$, was calculated according to eq 2, and the reproducibility was within ±5% for most runs. The concentration of remaining amine was measured by LC using a Yanapak DMS column, 80% aqueous MeOH as a developer, and phenol as an internal standard.

Products were identified and determined by IR, UV, NMR spectra, and LC analysis in comparison with authentic samples.

**Registry No.—1a,** 121-69-7; **1b,** 552-82-9; **1c,** 603-34-9; **2a,** 874-52-2; **2b,** 68258-04-8; peroxymonophosphoric acid, 13598-52-2.

## References and Notes

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