Oxide.—The method of Chernova and Khokhlov[10] was not successful for the preparation of these oxides from the amines in our laboratory. Oxidation of the amines was accomplished by peroxybenzoic acid.[15] A stoichiometric quantity of peroxybenzoic acid in $CHCl_3$ (100 ml of 0.05 *M*) was added dropwise with stirring to a solution of the amine in $CHCl_3$ (0.86 g in 50 ml) at −35°. After 2 hr the solution was warmed to room temperature. After all the peracid had reacted, the $CHCl_3$ was removed under vacuum and the residue washed with ether. An equivalent of 6 *M* HCl was then added to give the amine oxide hydrochloride which could be recrystallized from acetone. The hydrochloride of *N,N*-dimethyl-1-naphthylamine *N*-oxide melts at 170° dec and *N,N*-dimethyl-2-naphthylamine *N*-oxide hydrochloride melts at 146–148° dec with nmr signals (acetone-d_6–D_2O, 5:1), at δ 9.5–7 (m, 7) and 3.76 [s, $NO(CH_3)_2$, 6]. The amine oxide was obtained using Ag_2O and recrystallized from acetone. *N,N*-Dimethyl-2-naphthylamine *N*-oxide had mp 152–155° dec and nmr (acetone-d_6–D_2O, 5:1) δ 9–7 (m, 7) and 3.93 [s, $NO(CH_3)_2$, 6]. *N,N*-Dimethyl-1-naphthylamine *N*-oxide rapidly hydrated and gave a variable melting point.

Irradiation of Trimethyl- and Triethylamine *N*-Oxides.—The amine oxide (1 g) was dissolved in methanol and the solvent allowed to evaporate in a rotating, cylindrical vessel leaving a thin film of the oxide. This solid was irradiated in a vacuum with a medium-pressure, mercury-arc lamp in a quartz immersion well until all the amine oxide had disappeared from the surface (1–3 hr). The products, in a cold trap attached the vessel, were analyzed by gspc using a Poropak Q column (10 ft × 0.25 in., 60–120°).

The irradiation solution of trimethylamine *N*-oxide was degassed and irradiated with the medium-pressure lamp in quartz. The products were separated from unreacted amine oxide by bulb-to-bulb distillation and analyzed by glpc. Besides their glpc retention times, trimethylamine was identified by its nmr spectrum, dimethylamine by mp 167–169°, mmp 166–168° (lit.[16] mp 171°) of its hydrochloride salt, water by its melting point and color change with anhydrous copper sulfate, and dimethylformamide by its ir spectrum.

Registry No.—Trimethylamine *N*-oxide, 1184-78-7; triethylamine *N*-oxide, 2687-45-8; *N,N*-dimethylaniline *N*-oxide, 874-52-2; 2-hydroxy-*N,N*-dimethylaniline, 3743-22-4; 1-*N,N*-dimethylnaphthylamine *N*-oxide, 830-70-6; 2-*N,N*-dimethylnaphthylamine *N*-oxide, 34418-90-1; *N,N*-dimethyl-1-naphthylamine *N*-oxide hydrochloride, 39717-26-5; *N,N*-dimethyl-2-naphthylamine *N*-oxide hydrochloride, 39717-27-6; peroxybenzoic acid, 93-59-4.

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[15] J. R. Moyer and N. C. Manley, *J. Org. Chem.*, **29**, 2099 (1964).

[16] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 52nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1971–1972, p C101.

Triangular Kinetic Schemes. An Elaboration

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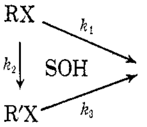
We recently reported[1] the derivation of the analytical equations governing triangular kinetic schemes of the type particularly common to solvolytic processes. Judging by the response to this paper, some amplification of the assertions given there is in order.



(1)

The exact solution[1a] (in closed form) of the differential equations appropriate to eq 1 provides the relationship[2]

$$[\mathrm{HX}]_t = [\mathrm{RX}]_0\left[1 + \frac{(k_3 - k_1)e^{-(k_1+k_2)t} - k_2e^{-k_3t}}{k_1 + k_2 - k_3}\right] \quad (2)$$

The instantaneous "first-order" titrimetric rate constant (k_{inst}) can be obtained as follows.

$$\ln\left(\frac{[\mathrm{HX}]_\infty}{[\mathrm{HX}]_\infty - [\mathrm{HX}]_t}\right) = \ln\left[\frac{k_1 + k_2 - k_3}{k_2e^{-k_3t} + (k_1 - k_3)e^{-(k_1+k_2)t}}\right] \quad (3)$$

$$k_{\mathrm{inst}} = \frac{\mathrm{d}}{\mathrm{d}t}\ln\left(\frac{[\mathrm{HX}]_\infty}{[\mathrm{HX}]_\infty - [\mathrm{HX}]_t}\right) \quad (4)$$

$$= \frac{\mathrm{d}}{\mathrm{d}t}\ln\left[\frac{k_1 + k_2 - k_3}{k_2e^{-k_3t} + (k_1 - k_3)e^{-(k_1+k_2)t}}\right] \quad (5)$$

Extraction of the derivative, then multiplication by $\exp(k_3t)$, leads to

$$k_{\mathrm{inst}} = \left[\frac{k_2k_3 + (k_1 - k_3)(k_1 + k_2)e^{Kt}}{k_2 + (k_1 - k_3)e^{Kt}}\right] \equiv \frac{N}{D} \quad (6)$$

$$\text{where } K = k_3 - k_1 - k_2$$

The proof that the sense of curvature of "first-order" plots of titrimetric data ($\ln [\mathrm{HX}]_\infty/[\mathrm{HX}]_\infty - [\mathrm{HX}]_t$ *vs.* time) depends only on the relative magnitudes of k_1 and k_3 can be seen by examining the first derivative of k_{inst}

$$\text{curvature} = \frac{\mathrm{d}k_{\mathrm{inst}}}{\mathrm{d}t} = \frac{D\frac{\mathrm{d}N}{\mathrm{d}t} - N\frac{\mathrm{d}D}{\mathrm{d}t}}{D^2} \quad (7)$$

The *sign* of curvature is a function of the numerator in eq 7, which expands to

$$\begin{aligned}\text{sign} &= [k_2 + (k_1 - k_3)e^{Kt}][(k_1 - k_3)(k_1 + k_2)Ke^{K_t}] - \\ &\qquad [k_2k_3 + (k_1 - k_3)(k_1 + k_2)e^{Kt}][(k_1 - k_3)Ke^{Kt}] \\ &= k_2(k_1 + k_2 - k_3)K(k_1 - k_3)e^{Kt} \\ &= (k_3 - k_1)K^2k_2e^{Kt}\end{aligned} \quad (8)$$

Since the last three terms are strictly positive, the nature of curvature is determined by $(k_3 - k_1)$; if $k_3 > k_1$, the plot will be concave upward and k_{inst} will increase with time, while if $k_3 < k_1$, the curve will exhibit negative curvature and k_{inst} will fall off with time. Clearly, the *magnitude* of curvature (which can be calculated with eq 7) will depend on the relative magnitudes of all three rate constants. If $k_1 = k_3$, the effect of the k_2 pathway will be titrimetrically unobservable.[1a]

It has on occasion been incorrectly stated that extrapolation of k_{inst} (as defined by eq 4) to $t = 0$ provides a value of $(k_1 + k_2)$, even though Winstein and coworkers have used such graphical extrapolations to ob-

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[1] (a) R. S. Macomber, *J. Org. Chem.*, **36**, 2182 (1971). (b) For a description of similar schemes, including those with reversible reactions, see R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).

[2] For the relevant equations when $k_3 = k_1 + k_2$, see footnote 9 of ref 1a.

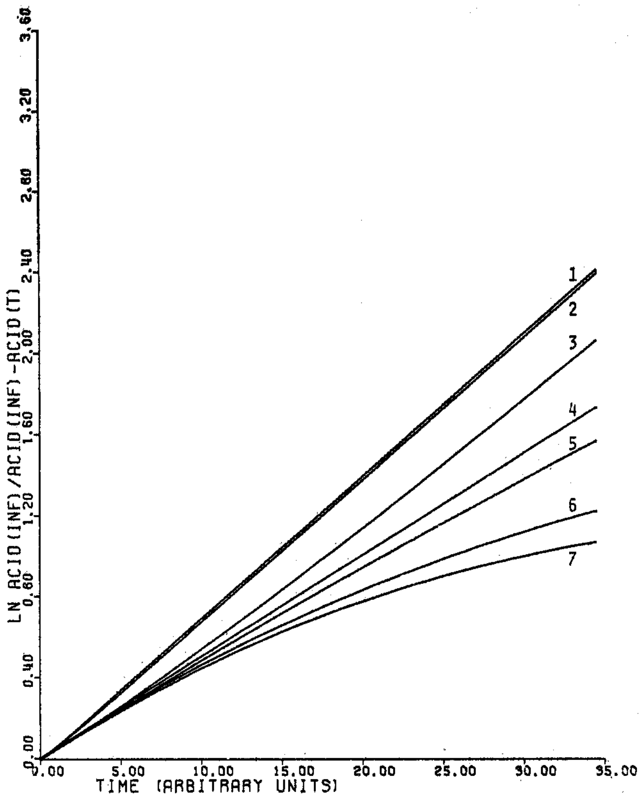

Figure 1.—Titrimetric plots for $k_1 = 0.05$, $k_2 = 0.02$, and $k_3 = 2.0$ (curve 1), 0.7 (2), 0.1 (3), 0.05 (4), 0.035 (5), 0.01 (6), 0.001 (7). Each curve covers *ca.* 4 half-lives.

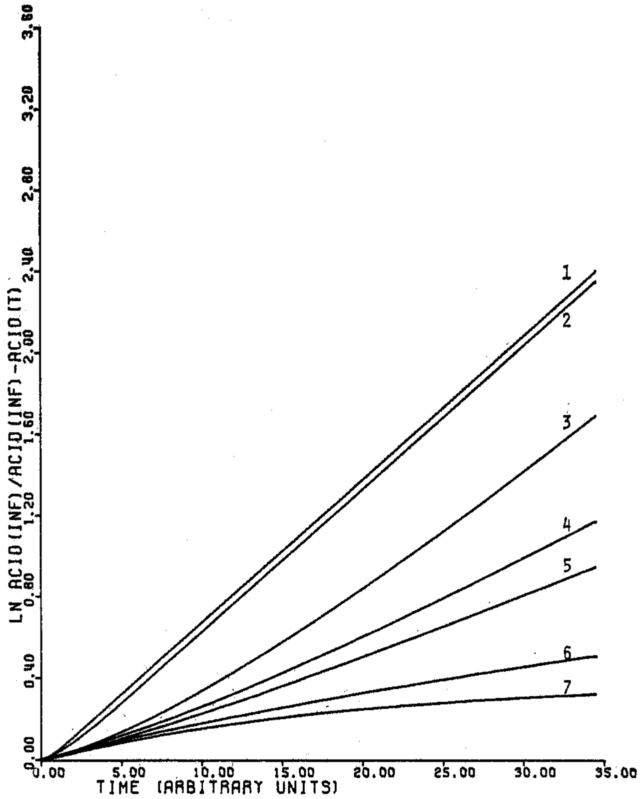

Figure 3.—Titrimetric plots for $k_1 = 0.02$, $k_2 = 0.05$, and $k_3 = 2.0$ (curve 1), 0.7 (2), 0.1 (3), 0.05 (4), 0.035 (5), 0.01 (6), 0.001 (7). Each curve covers *ca.* 4 half-lives.

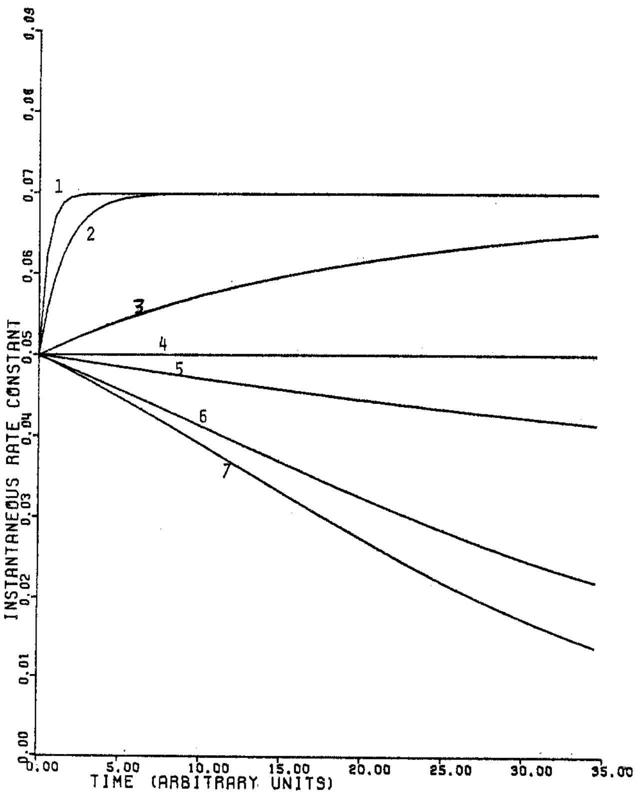

Figure 2.—Plots of k_{inst} *vs.* time for the data in Figure 1.

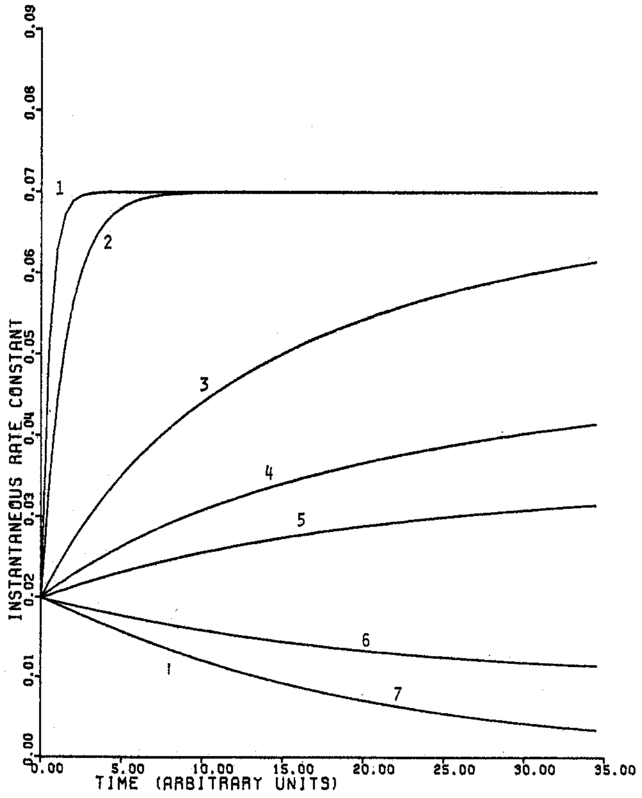

Figure 4.—Plots of k_{inst} *vs.* time for the data in Figure 3.

tain values of k_1.[3] This misconception probably arises from a belief that the early stages of such reactions mimic the situation where $k_3 = 0$, but this is not the case. As can be seen from eq 6 at $t = 0$

$$k_{\text{inst}} = k_1 \tag{9}$$

but, as demonstrated below, k_{inst} rapidly increases to $k_1 + k_2$ when $k_3 \gg (k_1 + k_2)$. It *is* true, whether or not $k_3 = 0$, that $\mathrm{d}/\mathrm{d}t \ln ([\mathrm{RX}]_0/[\mathrm{RX}]_t) = k_1 + k_2$ at *all* stages of the reaction (and monitoring actual disappearance of RX, *e.g.*, spectrophotometrically, gives $k_1 + k_2$). However, $\mathrm{d}/\mathrm{d}t \ln [\mathrm{RX}]_t$ is only equal to $\mathrm{d}/\mathrm{d}t\, ([\mathrm{HX}]_\infty - [\mathrm{HX}]_t)$ when $k_3 = 0$ or $k_3 \gg k_1 + k_2$.[4] It is also instructive to consider the latter stages of the reaction. If $k_3 > (k_1 + k_2)$, k_{inst} will approach $(k_1 + k_2)$ as $t \rightarrow \infty$, whereas if $k_3 < (k_1 + k_2)$, k_{inst} approaches k_3, regardless of the sense of curvature.

Several further observations with eq 6 are pertinent. As expected,[1a] if $k_3 \gg k_1 + k_2$ (*i.e.*, as $k_3 \rightarrow \infty$), eq 6 becomes

$$k_{\text{inst}} = k_1 + k_2 \tag{10}$$

However, although eq 2 reduces to the appropriate form[4] upon substitution of $k_3 = 0$, the same is not true for eq 3–8. For example, while it is easily shown[4] that $k_{\text{inst}} = k_1 + k_2$ when $k_3 = 0$, eq 6 does not reduce to that result upon substitution of $k_3 = 0$. This is because the boundary conditions for obtaining eq 3 from 2 ($t \rightarrow \infty$) erase part of the k_3 dependence. An equivalent way of appreciating this is to realize that the equations derived here apply when the infinity titer reflects 100% conversion of starting material to acid. If $k_3 = 0$, the infinity titer will be $k_1/(k_1 + k_2)$ times the 100% infinity titer, and attempts to use this "observed" infinity titer for fitting eq 3–8 will lead to erroneous values for the rate constants. It is always preferable to use the theoretical (100% conversion) infinity titer to obtain the most information from plots of eq 3. When one is dealing with situations where k_3 is known to be negligibly small, the appropriate equations[4] should be generated from eq 2.

Finally, it is useful to examine the effect on titrimetric plots and k_{inst} of variations in k_3. By defining the half-life of the reaction as $0.69/(k_1 + k_2)$, then arbitrarily fixing the values of k_1 and k_2, one can vary k_3 and plot eq 3 and 6 as functions of time. For example, Figure 1 shows titrimetric plots where $k_1 = 0.05$, $k_2 = 0.02$ ($t_{1/2} = 10$ time units), and k_3 varies from 2.0 to 0.001. Figure 2 shows the behavior of k_{inst} over the same interval. A similar pair of plots is shown in Figures 3 and 4, where the values of k_1 and k_2 have been interchanged. These plots summarize the preceding discussion. If $k_3 > 10(k_1 + k_2)$, titrimetric plots will be essentially linear with slope $k_1 + k_2$. In the region $10(k_1 + k_2) > k_3 > k_1$, plots exhibit positive curvature, and k_{inst} approaches the lesser of k_3 or $(k_1 + k_2)$. When $k_3 = k_1$, the plot is again linear, but with slope k_1. Further decrease in k_3 gives rise to negative curvature, and k_{inst} approaches k_3. Again, for experimental fittings of these lines, one must use the theoretical infinity titer (*vide supra*).

An iterative nonlinear least squares Fortran IV program has been written to extract the values of k_1, k_2, and k_3 from experimental titrimetric (or equivalent) data, by obtaining the best fit of eq 3. A listing will be supplied upon request.

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[3] See, for example, W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

[4] Footnote 7, ref 1a.