The Kinetics of Nitration and Nitrosation of 1-Methyl-2-phenylindolizine

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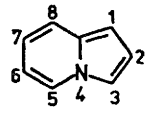
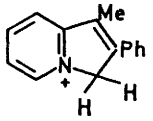
The rate profile for the 4'-nitration of 1-methyl-2-phenylindolizine in aqueous sulphuric acid at 24.9 °C shows that the reaction involves the conjugate acid. The reaction rate (relative to benzene) in 73% sulphuric acid is 1.78×10^{-2} and the partial rate factor at the 4'-position is 0.10. The kinetic form of the 3-nitrosation of 1-methyl-2-phenylindolizine in aqueous sulphuric acid indicates that the reaction involves the rate-determining attack of dinitrogen trioxide on the neutral molecule of the substrate. The rate coefficient for this reaction is *ca.* 10^8 mol^{-1} s^{-1} dm^3 at 24.9 °C.

THE orientation of electrophilic substitution in indolizine (I) and substituted indolizines appears to depend on the reagent and the experimental conditions. Nitration of the 2-methylindolizine in a mixture of nitric acid and sulphuric acid occurs at the 1-position [1] but nitration in acetic anhydride occurs at the 3-position.[2] A number of other electrophilic substitutions in 2-methylindolizine occur at the 3-position, including nitrosation and diazo-coupling.[3] The nitration of 2-phenylindolizine with an equivalent amount of nitric acid in sulphuric acid gives mainly 2-(4-nitrophenyl)indolizine with some 1-nitro-2-(4-nitrophenyl)indolizine,[1] but the nitrosation of 2-phenylindolizine occurs at the 3-position.[4]



(I)



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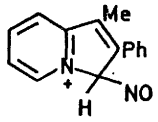

(III)

Several authors have suggested [2,3] that the substitutions at the 3-position derive from attack on the neutral indolizine molecule and that the anomalous substitutions elsewhere involve attack on some other species, either the conjugate acid [3] or a strongly hydrogen-bonded complex.[2] These substituted indolizines are more basic than the corresponding indoles (2-methylindolizine, $pK_a = 5.87$) [5] and ^{1}H n.m.r. studies show that both 2-methyl- and 2-phenyl-indolizine protonate essentially completely at the 3-position.[6] It is very reasonable therefore that protonation should block this position to further electrophilic attack.

The work now reported was carried out to provide kinetic evidence for this mechanistic distinction and quantitative information on the reactivity of the neutral molecule and conjugate acid of one substituted indolizine.

Nitration.—Our preliminary studies on the nitration of 2-phenylindolizine with a two-fold excess of nitric acid in aqueous sulphuric acid indicated a more complex product composition than that reported in the literature for, in addition to 2-(4-nitrophenyl)indolizine and 1-nitro-2-(4-nitrophenyl)indolizine, we obtained *ca.* 20% of an unidentified dinitro-compound, probably 3-nitro-2-(4-nitrophenyl)indolizine. We find, however, that 1-methyl-2-phenylindolizine also undergoes nitration in aqueous sulphuric acid at the 4'-position and is much more resistant to dinitration. A 90% yield of the 4'-nitro-derivative can be isolated under preparative conditions and the ' infinity ' spectra of reaction mixtures under the conditions used for kinetic runs corresponds very closely to that of the 4'-nitro-product even when the nitric acid is present in 20-fold excess. To avoid complications deriving from dinitration, the kinetic studies were carried out on 1-methyl-2-phenylindolizine.

The reaction was followed from the change in the u.v. absorption at 310 nm. Second-order rate coefficients were calculated according to equation (1) † and were effectively constant throughout a given run.

$$\text{Rate} = k_2[\text{1-Me-2-Ph-indolizine}][\text{nitric acid}] \quad (1)$$

Since the nitric acid was in a 5—20-fold excess, this constancy shows that the reaction is first-order with respect to the aromatic substrate and the constancy of

TABLE 1

Second-order rate coefficients for the nitration of 1-methyl-2-phenylindolizine in aqueous sulphuric acid at 24.9 °C

H_2SO_4 (%)	10^5[ArH] / mol dm^{-3}	10^4[HNO_3] / mol dm^{-3}	k_2 / mol^{-1} s^{-1} dm^3
72.4	5.93	12.1	3.62×10^{-2}
74.5	8.68	4.22	2.41×10^{-1}
74.5	8.68	8.44	2.23×10^{-1}
75.1	6.34	6.34	3.70×10^{-1}
75.6	9.82	9.79	4.84×10^{-1}
75.6 [a]	9.82	9.79	4.81×10^{-1}
77.4	7.20	7.06	3.35
77.4	6.60	3.31	3.10
80.0	6.42	3.18	26.5

[a] In the presence of 3.19×10^{-4} mol dm^{-3} of sodium nitrite.

the values of k_2 for different initial concentrations of nitric acid shows that the reaction is first-order with respect to the stoicheiometric concentration of nitric acid. These values of k_2 are collected in Table 1 and the rate profile is compared with those of related compounds in Figure 1.

Nitrosation does not occur at an observable rate under the conditions used for these kinetic runs and so nitration through nitrosation followed by oxidation cannot occur. However, the nitrous acid catalysis of

† The reactants are written out in full in this and some subsequent equations to show that the rate coefficients are calculated with respect to the stoicheiometric concentrations, not the molecular concentrations.

nitration is not limited to this reaction path [7] and so experiments were carried out in the presence of added

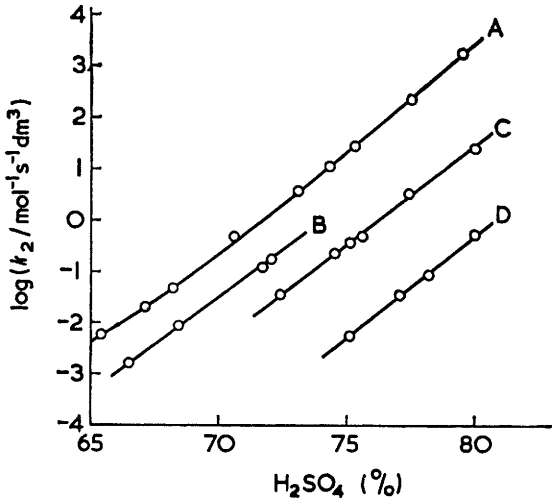

FIGURE 1 Rate profiles for nitration in aqueous sulphuric acid: A, benzene (ref. 11); B, the β-phenylethylammonium ion (ref. 13); C, the conjugate acid of 1-methyl-2-phenylindolizine; D, the 4-phenylpyridinium ion (ref. 12)

sodium nitrite. The comparison of the two kinetic runs in 75.6% sulphuric acid shows that such catalysis is absent.

As expected from the studies on 2-methylindolizine [2] the nitration of 1-methyl-2-phenylindolizine in acetic anhydride occurs at the 3-position for the product was shown to be identical with a specimen of the 3-nitro-derivative prepared by oxidation of the 3-nitroso-compound. The low yield of this product in the nitration reaction (33%) and the complexities of kinetic studies in acetic anhydride [8] led us to turn to nitrosation to provide information on the reactivity of the neutral system.

TABLE 2

Kinetics of nitrosation of 1-methyl-2-phenylindolizine in aqueous sulphuric acid and deuteriosulphuric acid at 24.9 °C. Interpolated values of rate coefficient in parentheses

H_2SO_4 (%)	h_0 [a]	10^5[ArH] mol dm^{-3}	10^3[HNO_2] mol dm^{-3}	10^4k_1 [b] s^{-1}	k_4 [c] mol^{-1} s^{-1} dm^3
9.99	2.13	9.06	4.53	1.78	18.5
9.99	2.13	9.06	5.00	(2.16)	(18.4)
9.99	2.13	9.06	9.06	7.19	18.6
7.79	1.51	8.00	4.00	2.01	19.0
7.79	1.51	8.00	5.00	(3.16)	(19.1)
7.79	1.51	8.00	6.00	4.73	19.8
7.79	1.51	8.00	8.00	8.46	20.0
7.79	1.51	8.00	10.00	13.00	19.6
6.27	1.05	7.16	3.58	3.11	25.5
6.27	1.05	8.61	4.31	3.93	22.2
6.27	1.05	9.26	4.63	5.36	26.2
6.27	1.05	9.26	5.00	(6.02)	(25.3)
6.27	1.05	18.5	9.26	24.1	29.5
6.27 [d]	1.05	7.16	3.58	6.96	
D_2SO_4 mol dm^{-3}					
0.66	1.05 [e]	8.12	4.07	0.656	4.37
0.66	1.05 [e]	10.2	5.09	0.885	3.58
0.66	1.05 [e]	16.2	8.14	2.79	4.42

[a] Interpolated from the results of P. Tickle, A. G. Briggs, and J. M. Wilson, *J. Chem. Soc.* (*B*), 1970, 65. [b] Defined by equation (2). [c] Defined by equation (3). [d] In the presence of 0.1 mol dm^{-3} sodium bromide. [e] At this acidity, $d_0 = h_0$ (E. Högfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15).

Nitrosation.—The nitrosation of 1-methyl-2-phenylindolizine is known to occur at the 3-position.[9] The reaction of nitrous acid with 1-methyl-2-phenylindolizine occurs readily in dilute sulphuric acid and the u.v. spectra of the solutions change, as expected, to that of the 3-nitroso-derivative. Kinetic runs have been carried out using a large excess of nitrous acid and the extent of reaction has been determined from the change in the optical density at 420 nm. Under these conditions, there is no evidence for subsequent reactions of the 3-nitroso-compound. The large excess of nitrous acid gives rise to pseudo-first-order kinetics during a given run and the resulting first-order rate coefficients (k_1) [calculated from equation (2)] are listed in Table 2.

$$\text{Rate} = k_1[\text{1-Me-2-Ph-indolizine}] \qquad (2)$$

The plots of log k_1 against log [HNO_2] in Figure 2 have slopes of 2.0—2.1, indicating that the reaction is second-order with respect to the stoicheiometric concentration of nitrous acid. These graphs have been used to calculate values of k_1 for [HNO_2] = 5×10^{-3} mol dm^{-3} at each acidity and the results are shown in parentheses in Table 2. They indicate that a change in acidity from 6.27% sulphuric acid to 9.99% sulphuric acid decreases

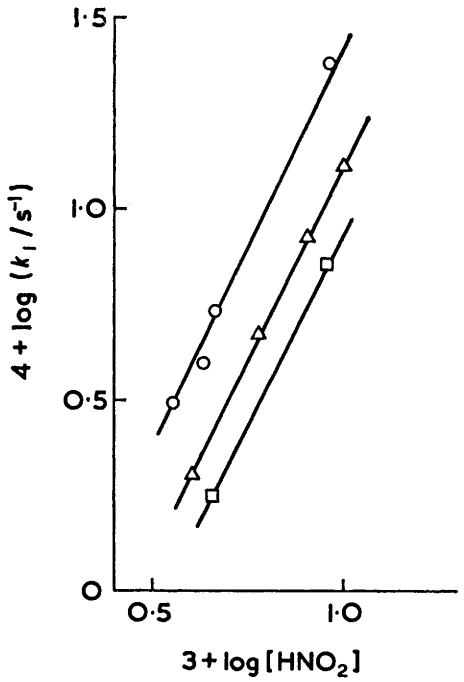

FIGURE 2 The dependence of the first-order rate coefficients for the nitrosation of 1-methyl-2-phenylindolizine on the concentration of nitrous acid. ○ .... in 6.27% H_2SO_4; △ .... in 7.97 H_2SO_4; □ .... in 9.99% H_2SO_4

k_1 by about a factor of three. This suggests an inverse dependence on some acidity function and so values of

k_4 have been calculated using equation (3).* The results, in the last column of Table 2, show that k_4

$$\text{Rate} = k_4[\text{1-Me-2-Ph-indolizine}][\text{nitrous acid}]^2h_0^{-1} \quad (3)$$

decreases somewhat with acidity but the mean value is 21.7 ± 3.7.

The first-order rate coefficients in Table 2 include that for one run carried out in the presence of 0.1 mol dm^{-3} sodium bromide: the result shows that some bromide ion catalysis is present. The reaction rates in deuteriosulphuric acid (0.66 mol dm^{-3}) were also measured (Table 2). This molarity is the same as that of 6.27% sulphuric acid and a comparison of the mean values of k_4 at the two acidities gives $k_4^H/k_4^D = 6.3 \pm 0.6$.

DISCUSSION

The ^1H n.m.r. spectrum of 1-methyl-2-phenylindolizine in acidic media shows that the molecule is protonated at the 3-position.[6] The pK_a of this substrate has not been measured but that of 1,2-dimethylindolizine is 7.32 [5] and studies on substituted 6- and 7-ethoxycarbonylindolizines indicate that the replacement of a 2-methyl group by a 2-phenyl group decreases the basicity by 1.1 to 1.24 units.[10] The pK_a of 1-methyl-2-phenylindolizine has therefore been taken as *ca.* 6.1.

The slope of the rate profile for the nitration of 1-methyl-2-phenylindolizine is very similar to that for benzene [11] (Figure 1) and therefore indicates that reaction is occurring through the bulk component of the prototropic equilibrium: *i.e.* the conjugate acid (II). The reactivity of the conjugate acid relative to benzene is 1.78×10^{-2} in 73% sulphuric acid giving a partial rate factor of 0.10 for substitution at the *para*-position of the benzene ring (assuming 90% *para*-substitution). These figures show also that there can be no significant contribution from reaction through the equilibrium concentration of the neutral molecule for, at this acidity, the concentration of the neutral molecule should be less than that of the conjugate acid by a factor of *ca.* 10^{12} (assuming the protonation to follow H_0) but the rate of nitration of the neutral molecule cannot exceed that of the conjugate acid by more than a factor of *ca.* 10^3 because of the limit imposed by diffusion control.[11]

The interaction of the benzene ring with the nitrogen pole in the ion (II) involves both a conjugated and a saturated carbon chain. This complicates the estimation of the reactivity expected for this structure. It is significant however that the observed reactivity is between that of the 4-phenylpyridinium ion [12] and the β-phenylethylammonium ion [13] (Figure 1) for the linkages of the benzene ring to the nitrogen pole in these structures contain some of the structural elements present in the ion (II). The observed reactivity is therefore consistent with reaction through the conjugate acid.

The interpretation of the kinetic form for the nitrosation of 1-methyl-2-phenylindolizine [equation (3)] requires more care, for the conclusions depend on whether the rate-determining step is considered to be the formation of the σ-complex (III) or the proton loss from this σ-complex. If the formation of (III) is considered to be rate-determining, then the kinetic form implies that the rate-determining step is a reaction between a molecule of the unprotonated substrate ($C_{15}H_{13}N$) and dinitrogen trioxide. Taking the equilibrium constant for the formation of dinitrogen trioxide [14] as 0.2 mol^{-1} dm^3 and the pK_a of 1-methyl-2-phenylindolizine as 6.1, the value of k_2' [equation (4)] comes to

$$\text{Rate} = k_2'[C_{15}H_{13}N][N_2O_3] \quad (4)$$

be 1.4×10^8 mol^{-1} s^{-1} dm^3. This indicates a reaction within one or two powers of ten of the encounter limit.

If the rate determining step is taken to be proton loss from the σ-complex (III), the kinetic form of equation (3) implies that the proton must be accepted by a nitrite ion. It is then impossible to draw conclusions concerning the kinetics of the nitrosation stage, except that the rate of this stage must greatly exceed that given by equation (3).

We prefer the first of these alternatives, mainly because of the relative concentrations of nitrite ions and water molecules in the solution. The ratio of the rate coefficients $k_{NO_2^-}/k_{H_2O}$ for proton acceptance from the σ-complex by nitrite ions with water should not exceed the inverse of the ratio of the dissociation constants of the corresponding conjugate acids ($K_{H_3O^+}/K_{HNO_2}$) for otherwise the Brönsted coefficient β would exceed unity. Taking [15,16] $K_{H_3O^+} = 55.5$ and $K_{HNO_2} = 4.6 \times 10^{-4}$ gives $k_{NO_2^-}/k_{H_2O} < 1.2 \times 10^5$. In a solution containing the highest concentrations of nitrous acid used (10^{-2} mol dm^{-3}) at the lowest acidity (6.27% H_2SO_4), the ratio $[NO_2^-]/[H_2O] = 8.5 \times 10^{-8}$. Thus, the nitrite ions should be unable to compete effectively with the water molecules in proton acceptance from the σ-complex.

The interpretation in terms of nitrosation by nitrous anhydride is consistent with the fact [17] that proton loss ceases to be rate determining in the nitrosation of indoles as the basicity of the indole is increased above $pK_a = -3.5$, for the indolizine considered here is far more basic than this limit. The interpretation is also consistent with the catalysis of the reaction by sodium bromide (Table 2) for this can occur through nitrosation by nitrosyl bromide. The isotope effect observed in deuteriosulphuric acid ($k_4^H/k_4^D = 6.3$) is somewhat larger than might be expected on this interpretation for it must then be ascribed to the product of the isotope effects on the equilibria involved in the protonation of the indolizine and the formation of nitrous anhydride instead of to a primary isotope effect † on the proton loss from (III). The concentration of the neutral indolizine molecule should be less in the deuteriated medium by a factor [18] of 3—6 but the isotope effect on the equilibrium concentration of the nitrous anhydride

* The acidity function h_0 is used here merely as a convenient measure of the acidity of the medium. The appropriate acidity function for the protonation of indolizines is not known.

† Hydrogen-isotope exchange at the 3-position is rapid when indolizines are added to deuteriotrifluoroacetic acid [6] and we have assumed that this is true also for the dilute deuteriosulphuric acid used here.

is more difficult to estimate. The nearest analogy may be the hydration of aldehydes where the ratio of the unhydrated to the hydrated form is less in the deuteriated medium by a factor [18] of *ca.* 0.85. The product of such isotope effects could, therefore, give rise to the observed result.

Thus, the nitration and nitrosation of 1-methyl-2-phenylindolizine exemplify the reactivity of the conjugate acid and the neutral molecule respectively. There is no need to postulate a hydrogen-bonded complex of the neutral molecule as one reacting species. There is also no evidence in these results for a mechanism of nitrosation in which a positive nitrosating agent attacks the protonated substrate but in which a proton is displaced in forming the transition state. Such a mechanism is important in the *N*-nitrosation of the more basic aromatic amines.[19]

Unfortunately, the present work cannot be used to compare the reactivity of the neutral indolizine molecule with that of related substrates. Rate-determining nitrosation by dinitrogen trioxide is not a common mechanism for aromatic *C*-nitrosation, for dinitrogen trioxide appears to be too weak an electrophile to attack phenoxide ions [20] and although some indoles will react with dinitrogen trioxide, the formation of the nitrosating agent is normally rate-determining.[17] The only example of a kinetic form corresponding to equation (3) in the nitrosation of indoles has been considered to involve a rate-determining proton abstraction by a nitrite ion from the intermediate σ-complex.[17] Thus, although the reaction rate and kinetic form of equation (3) are consistent with the high reactivity of indolizine derivatives, the result does not permit relative rates to be calculated. We hope to obtain evidence on this matter from studies on other electrophilic substitutions.

EXPERIMENTAL

Materials.—Sulphuric acid (*d* 1.84), nitric acid (*d* 1.42), and sodium nitrite were AnalaR reagents: the first two were standardised by the titration of a known weight with sodium hydroxide. 1-Methyl-2-phenylindolizine [6] and 1-methyl-3-nitroso-2-phenylindolizine [9] were prepared and purified as described in the literature.

1-Methyl-2-(4-nitrophenyl)indolizine. This compound was prepared by the dropwise addition at 25 °C of nitric acid (0.23 g, 70%) in sulphuric acid (5 ml) to a solution of 1-methyl-2-phenylindolizine (0.52 g) in sulphuric acid (77.6%). After 1 h, the reaction mixture was poured onto ice, neutralised (NH_4OH), and extracted with chloroform. After drying ($MgSO_4$), the chloroform was evaporated off and the product dissolved in benzene and chromatographed on a silica column with benzene as the eluant. The product (0.58 g, yield 90%) had m.p. 188 °C after recrystallisation from benzene–light petroleum (Found: C, 71.5; H, 4.9; N, 10.8. $C_{15}H_{12}N_2O_2$ requires C, 71.4; H, 4.8; N, 11.1%). The ^1H n.m.r. spectrum in CD_3COCD_3 had δ 2.47 (3 H, s), 6.4—8.4 (9 H, m). The identification as the 4′-isomer is based on the clear AB quartet between δ 7.7 and 8.4.

1-Methyl-3-nitro-2-phenylindolizine was prepared by the addition at 5 °C of nitric acid (0.23 g, 70%) in acetic anhydride (5 ml) to a solution of 1-methyl-2-phenylindolizine (0.52 g) in acetic anhydride (5 ml). After 3 h, the reaction mixture was poured onto ice and treated as described above for the preparation of the 4′-nitro-product. The product (0.21 g, 33%) had m.p. 173 °C (Found: C, 71.8; H, 4.9; N, 10.8. $C_{15}H_{12}N_2O_2$ requires C, 71.4; H, 4.8; N, 11.1%). The identification as the 3-nitro-isomer is based on the preparation of an identical product by oxidation of the known [9] 1-methyl-3-nitroso-2-phenylindolizine (0.6 g) with *meta*-chloroperbenzoic acid (0.6 g) at 5 °C in benzene–acetone (9 : 1; 50 ml). After 45 min the reaction mixture was shaken with diluted ammonium hydroxide and the product from the organic layer separated and purified as outlined above: m.p. and mixed m.p. 173 °C, ^1H n.m.r. (CD_3COCD_3) had δ 2.15 (3 H, s) and 6.8—8.1 (9 H, m).

Kinetics.—Separate solutions of nitric acid and 1-methyl-2-phenylindolizine in aqueous sulphuric acid were brought to 24.9 °C, mixed, and then rapidly transferred to a 1-cm spectrophotometer cell maintained at the same temperature. The concentration of product (x) was calculated from the change in the optical density (D) at 310 nm using equation (5) where a is the initial concentration of the

$$x = (D - \varepsilon_1 a)/(\varepsilon_2 - \varepsilon_1) \quad (5)$$

indolizine and ε_1 and ε_2 are the extinction coefficients at this wavelength of 1-methyl-2-phenylindolizine and its 4′-nitro-derivative respectively. These values (3 623—4 056) and (9 780—10 250) were determined at each acidity from solutions of the respective compounds. A typical kinetic run is illustrated in Table 3.

TABLE 3

Nitration of 1-methyl-2-phenylindolizine (6.34×10^{-5} mol dm^{-3}) with nitric acid (6.35×10^{-4} mol dm^{-3}) in aqueous sulphuric acid (75.1%) at 24.9 °C

Time/min	5	15	25	35
D [eqn. (5)]	0.262	0.309	0.349	0.384
$10^5 x$ [eqn. (5)] [a]	0.45	1.21	1.85	2.42
$10k_2$ / mol^{-1} s^{-1} dm^3	3.87	3.75	3.70	3.68
Time/min	55	75	95	115
D [eqn. (5)]	0.440	0.486	0.519	0.541
$10^5 x$ [eqn. (5)] [a]	3.32	4.06	4.59	4.95
$10k_2$ / mol^{-1} s^{-1} dm^3	3.64	3.71	3.72	3.64

[a] Calculated using $\varepsilon_1 = 3\,688$, $\varepsilon_2 = 9\,890$.

TABLE 4

Nitrosation of 1-methyl-2-phenylindolizine (9.26×10^{-5} mol dm^{-3}) with nitrous acid (4.63×10^{-3} mol dm^{-3}) in aqueous sulphuric acid (6.27%) at 24.9 °C

Time/min	5	10	15	20
D [eqn. (5)]	0.105	0.167	0.215	0.255
$10^5 x$ [eqn. (5)]	2.03	3.22	4.15	4.92
$10^4 k_1$ [a]/s^{-1}		5.99	5.78	5.67
Time/min	25	30	35	40
D [eqn. (5)]	0.287	0.315	0.338	0.360
$10^5 x$ [eqn. (5)]	5.54	6.08	6.52	6.95
$10^4 k_1$ [a]/s^{-1}	5.53	5.48	5.39	5.43

[a] Integrated from the time of the first reading. The least squares slope of the plot of $\log(a - x)$ against time gives $k = 5.36 \times 10^{-4}$ s^{-1}.

The kinetics of nitrosation were followed in a similar way using the change in the optical density at 420 nm. At this wavelength, the absorption of the reactants is negligible

and that of the 3-nitroso-product corresponds to $\varepsilon_2 = 5\,180$. A typical kinetic run is given in Table 4. The rate coefficients (k_1) in Table 2 were calculated from the slopes of plots of log $(a - x)$ against time. For both sets of reactions, the optical densities at $t = \infty$ were in good agreement with those calculated for complete reaction.

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