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Kinetics of Reactions of 1-Substituted 2,4-Dinitrobenzenes with Aniline and Piperidine in Acetone¹

Rita H. de Rossi* and Roberto A. Rossi

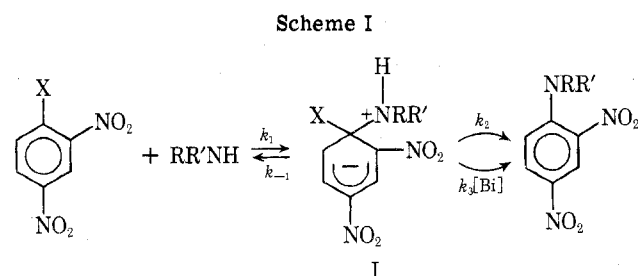
Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina

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The reactions of 1-X-2,4-dinitrobenzenes (X = Cl and F) with aniline and piperidine in acetone were studied. When X = Cl, no base catalysis is found, with $k_A = 0.434 \pm 0.011$ l. mol⁻¹ sec⁻¹ (piperidine as nucleophile) and $4.39 \pm 0.25 \cdot 10^{-5}$ l. mol⁻¹ sec⁻¹ (aniline as nucleophile). When X = F the reaction of aniline is catalyzed by aniline and Dabco with linear dependence of k_A on both bases, indicating $k_{-1} \gg k_2 + \sum k_3 B_i [B_i]$.

Primary and secondary amines react with many 1-substituted 2,4-dinitrobenzenes to form 2,4-dinitrophenylamines. Some of these reactions are strongly accelerated by bases, but others are insensitive to base catalysis.²

These observations found interpretation in Scheme I.



The two-step mechanism was initially proposed by Bunnett.³ The susceptibility of such a reaction to catalysis by bases depends on the frequency of reversion of intermediate complex I to reactants.⁴ According to this mechanism only when expulsion of the leaving group X is at least partially rate determining are reactions of this type subject to catalysis by bases.

Whether or not expulsion of the leaving group is rate limiting depends upon the relative rates of reversion of the intermediate I to reactants and progression to products. Thus base catalysis is observable in those cases where the leaving group is slow to separate from carbon⁵ and/or when the amine moiety is easily expelled from the complex.^{2a}

In particular, numerous reactions where a secondary amine displaces fluorine from a nitro activated aromatic substrate are base catalyzed ($k_2/k_{-1} \ll 1$) while the analogous displacement of chlorine is not subject to base catalysis^{2a} ($k_2/k_{-1} \gg 1$). Even in a nonpolar solvent such as benzene which tends to make all k_2/k_{-1} ratios small compared to more polar solvents, the reaction of piperidine with 1-chloro-4-nitrobenzene⁶ or with 1-chloro-2,4-dinitrobenzene⁷ is not base catalyzed by piperidine, indicating $k_2/k_{-1} \gg 1$.

For these reasons a report by Bamkole, *et al.*,⁸ in which the reaction of piperidine with 1-chloro-2,4-dinitrobenzene

Table I
Reactions of 1-Chloro-2,4-dinitrobenzene with Piperidine and Aniline in Acetone

A. With piperidine at 25.0 \pm 0.1 $^{\circ}$ a, b		
Piperidine, M	k , 10 ³ sec ⁻¹	k_A , l. mol ⁻¹ sec ⁻¹
0.00202	0.869	0.430 \pm 0.010
0.00500	2.23	0.442 \pm 0.012
0.0101	4.40	0.436 \pm 0.012
0.0149	6.55	0.438 \pm 0.010
0.0202	8.89	0.440 \pm 0.010
0.202	84.8	0.419 \pm 0.030
		Av 0.434 \pm 0.011
B. With aniline at 50.0 \pm 0.1 $^{\circ}$ b, c		
Aniline, M	k , 10 ⁶ sec ⁻¹	k_A , 10 ⁵ l. mol ⁻¹ sec ⁻¹
0.099	4.48	4.53 \pm 0.20
0.149	6.67	4.47 \pm 0.10
0.198	8.60	4.34 \pm 0.15
0.295	12.42	4.21 \pm 0.30
		Av 4.39 \pm 0.25

^a Substrate 4.87×10^{-5} M. ^b Rate constants are average of two or three determinations, average deviation is given. ^c Substrate 3.20×10^{-4} M.

is strongly catalyzed by piperidine in the polar solvent acetone, has been regarded with considerable skepticism.^{2a}

We report here a reinvestigation of this and some other reactions studied in the same laboratory. Our results not only fail to confirm the earlier report of piperidine catalysis in the reaction of piperidine with 1-chloro-2,4-dinitrobenzene in acetone, they are also at variance with a similar report on the reaction of aniline with the same substrate and with 1-fluoro-2,4-dinitrobenzene.

Results and Discussion

A. 1-Chloro-2,4-dinitrobenzene. In the reaction of piperidine with this substrate (Table I, A) a 1000-fold increase in the concentration of the base causes no increase in the second-order rate constant, k_A . Similar behavior is

Table II
Reactions of 2,4-Dinitrofluorobenzene with Aniline
in Acetone at 50°

A. Catalyzed by Aniline ^a		
Aniline, M	$k_{\text{obs}}, 10^5 \text{ sec}^{-1}$	$k_A, 10^4 \text{ l. mol}^{-1} \text{ sec}^{-1}$
0.010	0.0747	0.747
0.020	0.218	1.09
0.051	1.147	2.25
0.101	4.362	4.319
0.143	8.916	6.235
0.202	16.16	8.500
0.247	23.50	9.513
0.300	38.20	12.73

B. Catalyzed by DABCO ^b		
Dabco, M	$k_{\text{obs}}, 10^6 \text{ sec}^{-1}$	$k_A, 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$
0.00546	2.63	0.537
0.0148	49.45	1.010
0.0292	90.70	1.851
0.0386	125.3	2.556

^a Substrate, $9.14 \times 10^{-5} \text{ M}$. ^b Aniline, 0.049 M, substrate, $9.17 \times 10^{-5} \text{ M}$.

found with aniline as nucleophile (Table I, B), where a threefold increase in the aniline concentration does not change k_A within experimental error.

The kinetic expression derived with reference to the mechanism depicted in Scheme I by means of the usual steady-state approximation, is represented in eq 1, where

$$\frac{\text{rate}}{(\text{ArX})(\text{HNRR}')} = k_A = \frac{k_1(k_2 + \sum k_3^{\text{Bi}}[\text{B}_i])}{k_{-1} + k_2 + \sum k_3^{\text{Bi}}[\text{B}_i]} \quad (1)$$

k_A is the observed second-order rate constant,⁹ and the summation includes all the bases present in the medium including the nucleophile. Independence of k_A on the base concentration means that $k_2 + \sum k_3^{\text{Bi}}[\text{B}_i] \gg k_{-1}$ which simplifies eq 1 to

$$k_A = k_1 \quad (2)$$

According to this equation the rate constants presented in Table I represent the rate of formation of the intermediate I ($\text{X} = \text{Cl}$, $\text{RR}'\text{NH} = \text{aniline or piperidine}$). The reaction of 1-chloro-2,4-dinitrobenzene with piperidine in benzene,⁷ with aniline in ethyl acetate,^{10,11} and with aniline in acetonitrile¹² are not base catalyzed, indicating that eq 2 holds. In acetone, a solvent of dielectric constant close to acetonitrile, and much more polar than benzene, it is not unexpected that the rate-determining step for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine and aniline would be the formation of the intermediate complex I.

B. 1-Fluoro-2,4-dinitrobenzene. Our results in the reaction of aniline with 1-fluoro-2,4-dinitrobenzene in acetone at 50.0° are shown in Table II. This reaction is strongly catalyzed by aniline and by 1,4-diazabicyclo[2.2.2]octane (Dabco). Plots of k_A vs. aniline and Dabco concentration are linear (Figures 1 and 2). Linear dependence of the second-order rate coefficient, k_A , with base concentration means that $k_{-1} \gg k_2 + \sum k_3^{\text{Bi}}[\text{B}_i]$, a condition which simplifies eq 1 to eq 3 (for this particular case $\text{B}_i = \text{aniline and Dabco}$).

$$k_A = \frac{k_1 k_2}{k_{-1}} + \frac{k_1}{k_{-1}} \sum k_3^{\text{Bi}}[\text{B}_i] \quad (3)$$

According to this equation the intercept in Figure 1 is $k_1 k_2 / k_{-1}$ and is reckoned to be *ca.* $0.2 \times 10^{-4} \text{ l. mol}^{-1}$

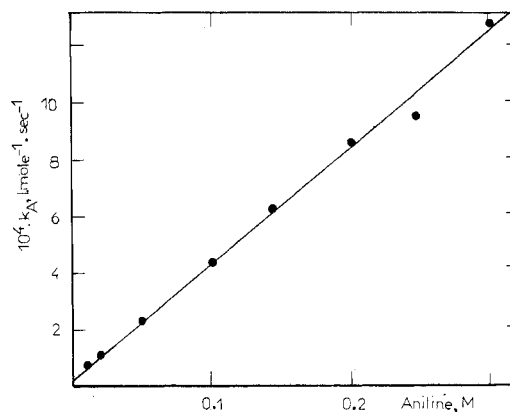


Figure 1. Reactions of 1-fluoro-2,4-dinitrobenzenes with aniline catalyzed by aniline in acetone at 50.0°. Substrate, $9.14 \times 10^{-5} \text{ M}$.

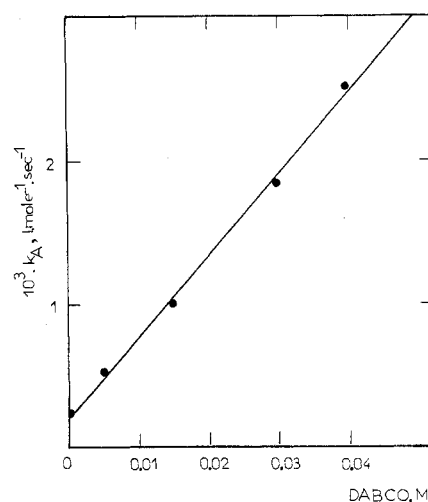


Figure 2. Reactions of 1-fluoro-2,4-dinitrobenzene with aniline catalyzed by Dabco in acetone at 50.0°. Aniline, 0.049 M, substrate, $9.17 \times 10^{-5} \text{ M}$.

sec^{-1} . This value represents a very small intercept and therefore can only be regarded as an approximate value. From the slope of the same plot $k_1 k_3^{\text{An}} / k_{-1}$ is reckoned to be $4.15 \times 10^{-3} \text{ l.}^2 \text{ mol}^{-2} \text{ sec}^{-1}$. Combining these two values the ratio of the catalyzed to the uncatalyzed pathway k_3^{An} / k_2 for the decomposition of the intermediate I is calculated as 200.

For the reaction of 1-fluoro-2,4-dinitrobenzene catalyzed by Dabco from the slope of the plot of k_A vs. Dabco concentration (Figure 2) $k_1 k_3^{\text{Dabco}} / k_{-1}$ is reckoned to be $5.95 \times 10^{-2} \text{ l.}^2 \text{ mol}^{-2} \text{ sec}^{-1}$. From the ratio of the slope of Figures 1 and 2 we calculated $k_3^{\text{Dabco}} / k_3^{\text{aniline}} = 14$, the ratio of the catalytic effectiveness of both bases.

Bamkole, *et al.*,⁸ reported that the reaction of 1-fluoro-2,4-dinitrobenzene with aniline is catalyzed by aniline with curvilinear dependence of k_A vs. base concentration. With reference to eq 1 it means that $k_{-1} \approx k_2 + \sum k_3^{\text{Bi}}[\text{B}_i]$; however, we could not reproduce that report (Figure 1).

As a means to demonstrate absolutely that $k_{-1} \gg k_2 + \sum k_3^{\text{Bi}}[\text{B}_i]$ we turned our attention to Dabco because it is much stronger base than aniline, and it could bring $k_2 + \sum k_3^{\text{Bi}}[\text{B}_i]$ closer to k_{-1} . In this case we also obtained a straight line in the plot of k_A vs. base concentration (Figure 2), which means that even with Dabco the relationship $k_{-1} \gg k_2 + \sum k_3^{\text{Bi}}[\text{B}_i]$ still holds.

Experimental Section

Materials. Acetone (BPC Erba) was stored over K_2CO_3 and distilled as needed. Piperidine (Fluka pa) was heated for 12 hr at re-

flux with sodium metal and then distilled; the fraction of boiling point 104° was taken and stored under nitrogen and in the dark. Aniline (Mallinckrodt) was dried with KOH and twice distilled from Zn dust. 1-Fluoro-2,4-dinitrobenzene (Aldrich) and 1-chloro-2,4-dinitrobenzene (Merck pa) were used without further purification. *N*-(2,4-Dinitrophenyl)piperidine, mp 92–92.5°,¹³ and 2,4-dinitrodiphenylamine, mp 156–157°,¹⁴ were prepared and purified by standard methods. A commercial sample of Dabco was purified by fractionated sublimation. The fraction of mp 154–156° was employed.

Rate Measurements. The kinetics were determined under conditions of excess nucleophile over substrate by measuring the increase in absorbance at the absorption maximum of the 2,4-dinitroaniline produced (370 nm for aniline and 390 nm for piperidine). For the reaction of 1-chloro-2,4-dinitrobenzene with piperidine, 10 μ l of the substrate solution were added to 3 ml of piperidine solution contained in a 10-mm stoppered quartz cuvette placed into the thermostated cell compartment of the spectrophotometer.¹⁵ In all cases excellent pseudo-first-order plots were obtained up to 90% reaction and the absorption spectrum of the reaction mixture at infinite time corresponded within 2% to the "mock" infinity prepared by the appropriate materials.¹⁶ For the reactions of 1-chloro- and 1-fluoro-2,4-dinitrobenzenes with aniline reaction solutions were prepared in a volumetric flask at 0°; 5 ml of the solution was placed in eight or nine volumetric flasks (10 ml) and then the flasks were placed all at once in the thermostat at 50 \pm 0.1°. The flasks were removed at measured times and quenched with a 2 M hydrochloric acid in 50% ethanol–50% water solution. In the runs with 1-chloro-2,4-dinitrobenzene and those at low concentration with 1-fluoro-2,4-dinitrobenzene the reaction was followed only until 10% of reaction and the infinity value was calculated with the known extinction coefficient of the product in the same solvent.

The symbols for the different rate coefficient used in this work are as follows: k_{ψ} is the pseudo-first-order coefficient for the disappearance of the substrate as determined graphically from a log ($A_{\infty} - A_t$) vs. time plot, k_A , second-order rate coefficient, equal to $k_{\psi}/(\text{amine})$.

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Registry No.—1-Chloro-2,4-dinitrobenzene, 97-00-7; piperidine, 110-89-4; aniline, 62-53-3; 2,4-dinitrofluorobenzene, 70-34-8.

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- (15) A Shimadzu Type QV 50 spectrophotometer equipped with a thermostated cell compartment was used.
- (16) With reference to a comment made by a Reviewer about possible complication arising from reaction of the amines with acetone,¹⁷ it might be worth mentioning that when the kinetic measurements were made with solutions about 24 hr old the rate constants for the reactions of piperidine with 1-chloro-2,4-dinitrobenzene were about 20% lower than with solutions freshly prepared. However, we got reproducible results working with solutions freshly prepared (no more than 1 or 2 hr old), and so we did every experiment in this study. Moreover the fact that the spectrum of the reaction products matches that of a "mock" infinite solution is a good indication that products arising from side reactions are not important.
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Electrochemical Oxidation of Some Phenethylamines¹

Louis C. Portis, Jacob T. Klug, and Charles K. Mann*

Department of Chemistry, Florida State University,
Tallahassee, Florida 32306

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The anodic reactions of a number of substituted phenethylamines have been examined. Compounds selected include *N*-methylated phenethylamines which were substituted with hydroxyl and methoxyl on the ring and with hydroxyl and methyl on the side chain. Presence of the phenyl ring with or without substituents may affect certain aspects of anodic behavior, such as voltammetric peak potentials, but the course of the overall reaction is apparently unaffected unless the substituents are themselves reactive. Substitution of hydroxyl on the side chain does alter the course of the reaction by causing cleavage of a carbon–carbon bond in the side chain, rather than dealkylation. Some parallels between electrochemical and metabolic processes are cited.

It has been shown previously that anodic oxidation of aliphatic amines causes dealkylation owing to hydrolytic cleavage of an intermediate.² The reaction scheme suggested is shown in eq 1–6. The sequence 1–3 represents a two-electron process forming the iminium ion 3, which would be hydrolyzed as shown in eq 5. The one-electron sequence 1, 2, 4 produces the enamine 4 which could also be hydrolyzed as shown in eq 6. Both sequences would give the same products and show the same stoichiometry and coulometry.

When unsymmetrically substituted amines are oxidized, it becomes apparent that the process is not random. Two factors were suggested that could account for the relative importance of these two sequences. If the radical interme-

