

Kinetics of the Reaction of 2,4-Dinitroanisole with 1,3-Diaminopropane and 1,3-Diamino-2,2-dimethylpropane in Benzene

BO LAMM and INGELA PALMERTZ

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg,
Fack, S-402 20 Göteborg, Sweden

The kinetics of the reaction between 2,4-dinitroanisole and the two diamines 1,3-diaminopropane and 1,3-diamino-2,2-dimethylpropane in benzene has been studied.

The choice of the dimethyl-substituted diamine was expected to favour intramolecular base catalysis of the second step of the reaction. This was not observed, however.

In an earlier publication by the present authors,¹ the kinetics of the reaction between 2,6-dinitroanisole and a series of α, ω -diaminoalkanes $H_2N(CH_2)_nNH_2$, $n = 2 - 5$, was studied in methanol, dioxane, and 60 % dioxane—40 % water. The purpose of that investigation was to demonstrate intramolecular base catalysis for the system concerned. One amino group should act as a nucleophile and the other amino group within the same molecule as a base. The relative importance of this intramolecular effect should depend on the number of methylene groups joining the two amino nitrogens. From the results, however, no definite conclusions could be drawn.

In an NMR study² of some nitro-substituted *N*-alkylanilines, hydrogen exchange in the compound *N*-(2,4-dinitrophenyl)-1,3-diamino-2,2-dimethylpropane was investigated. Evidence was found for intramolecular hydrogen exchange between the two different nitrogen atoms.

In a branched bifunctional compound such as 1,3-diamino-2,2-dimethylpropane, the two geminal methyl groups should favour a spatial arrangement in which the two amino groups come close to each other. This so-called "gem-dimethyl effect" has been utilized in various fields of physical organic chemistry.³

A comparison of the reaction rates of 1,3-diaminopropane and 1,3-diamino-2,2-dimethylpropane with a suitable aromatic compound, *e.g.*, 2,4-dinitroanisole, has therefore now been undertaken. The substrate 2,4-dinitroanisole was chosen instead of the 2,6-dinitro isomer used in a previous study,¹ since the reaction product *N*-(2,4-dinitrophenyl)-1,3-diamino-2,2-dimethylpropane and the similar *N*-(2,4-dinitrophenyl)-1,2-diaminoethane have been used earlier for NMR studies.^{2,4} Methoxy was chosen as the leaving group since it is supposed to be a poor one in nucleophilic aromatic substitution⁵ and should favour a rate-limiting decomposition of the intermediate I in the Scheme. It is in this step that the base catalysis might operate.

The same dimethyl-substituted diamine has also been studied by Pratt and Lawlor,⁶ who found that 1,3-diamino-2,2-dimethylpropane aminolyzed phenyl acetate at about the same rate as butylamine.

The reactions in the present work were studied in benzene at 25°C by the direct spectrophotometric method described earlier.⁷

EXPERIMENTAL

General. The NMR spectra were recorded on a Varian Model A 60 or on a Bruker WH 270 spectrometer and the UV spectra on a Cary Model 15 spectrophotometer. A Perkin-Elmer Model 900 instrument was used for gas chromatography. Melting points were determined on a Kofler Hot Stage microscope. The purity of the chemicals was also checked by TLC.

Synthesis. 1,3-Dinitro-2,2-dimethylpropane was prepared from acetone and nitromethane,

using diethylamine as a catalyst.^{2,6} An almost colourless product was obtained in a 31% yield. B.p. 142–144°C/2.4 kPa, lit.⁸ 130–132°C/1.3 kPa.

1,3-Diamino-2,2-dimethylpropane was obtained by catalytic hydrogenation over Raney Nickel of the above nitro compound according to the method of Lamm and Nordfält.² The crude product was distilled on a spinning band column (Normag, Teflon band, 60 cm). A colourless product with b.p. 153–154°C, lit.² 154°C and lit.⁹ 154–156°C, was obtained in a 29% yield.

N-(2,4-Dinitrophenyl)-1,3-diaminopropane was prepared for spectral comparison by mixing 2,4-dinitroanisole and 1,3-diaminopropane in the molar proportions 1:2 in dry benzene. The reaction mixture was allowed to stand for three days at room temperature. After evaporation of the solvent and recrystallization from isopropyl alcohol, yellow crystals were obtained in a 96% yield. M.p. 87–88°C, lit.⁹ 86–87°C.

N-(2,4-Dinitrophenyl)-1,3-diamino-2,2-dimethylpropane was analogously prepared from 2,4-dinitroanisole and 1,3-diamino-2,2-dimethylpropane. Recrystallization from isopropyl alcohol gave yellow crystals in an 88% yield. M.p. 114–115°C, lit.² 108–110°C.

Benzene was dried with Molecular Sieves 4 Å, and then distilled on an effective column.

1,3-Diaminopropane was purified as described earlier.¹

2,4-Dinitroanisole was available from previous work and was recrystallized from methanol. M.p. 87–88°C, lit.¹⁰ 87–88°C (unst.) and 94.5–95.5°C (st.).

Kinetic procedure. The same apparatus as described earlier⁷ was used for the kinetic measurements. The reactions were studied at 25.00 ± 0.05°C in benzene at the wavelength 420 nm. First-order conditions were chosen, with the diamine in large excess over the substrate 2,4-dinitroanisole. The initial substrate concentration in all runs was 1.0 × 10⁻⁴ M.

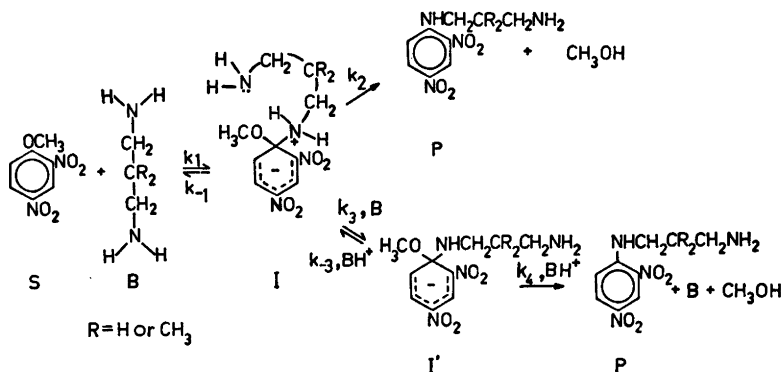
The amine concentration was 0.052 to 0.281 M. For each kinetic run, about 20 points were taken and all runs were made in duplicate or triplicate. To obtain the absorbance infinity value, A_{∞} , a mock infinity solution was prepared,⁷ of the same composition as expected at infinite time in the kinetic runs. The molar absorptivity for the product in the reaction with 1,3-diaminopropane is 4850 and, for the dimethyl-substituted diamine, 5120 at 420 nm.

Bunnett and Garst have reported¹¹ that in the nucleophilic attack of piperidine on the 1-carbon of 2,4-dinitroanisole in methanol at 67.9°C a side reaction may take place to form N-methylpiperidine and 2,4-dinitrophenol via S_N2 displacement on the methyl carbon.

In the present work, the possibility of the same side reaction, *i.e.*, N-methylation of the

Table 1. First- and second-order rate constants in the reactions of 1,3-diaminopropane and 1,3-diamino-2,2-dimethylpropane with 2,4-dinitroanisole at 25°C in benzene. Substrate concentration 1.0 × 10⁻⁴ M.

[Amine]/ M	$k_{\text{obs}}/$ 10 ⁻⁵ s ⁻¹	$(k_{\text{obs}}/[B])/$ 10 ⁻⁴ dm ³ mol ⁻¹ s ⁻¹
1,3-Diaminopropane		
0.052	2.13	4.10
0.104	4.58	4.40
0.156	7.57	4.85
0.208	10.84	5.21
0.260	14.88	5.71
1,3-Diamino-2,2-dimethylpropane		
0.056	1.47	2.62
0.112	3.33	2.98
0.169	5.39	3.20
0.225	7.50	3.34
0.281	10.21	3.63



Scheme 1. Scheme for the reaction between a diamine and 2,4-dinitroanisole.

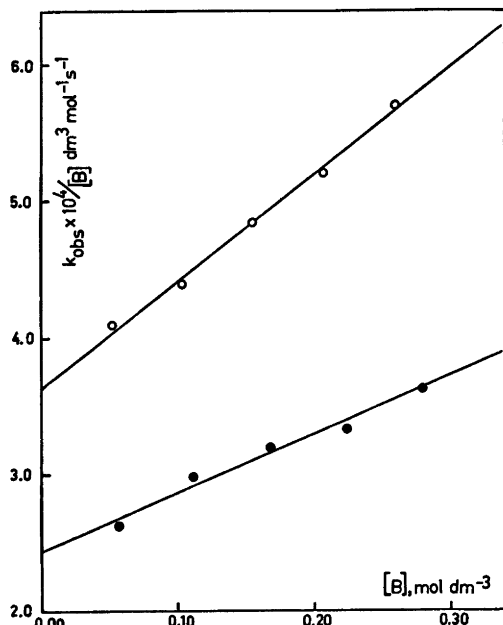


Fig. 1. Plot of the apparent second-order rate constant versus base concentration in the reactions of 1,3-diaminopropane (open circles) and 1,3-diamino-2,2-dimethylpropane (filled circles) with 2,4-dinitroanisole in benzene.

diamines by 2,4-dinitroanisole, was regarded. The entire UV spectrum was therefore recorded in a few runs during the reaction and after completion. The UV spectra of the mock infinity solutions were identical with those obtained from the kinetic runs. The conclusion was therefore drawn that this side reaction is unimportant in the present work, in which the rates were determined at 25 °C.

Treatment of data. The same treatment of data as described earlier⁷ was used. The standard deviation in each separate run, typically less than 1 %, equals the deviations between the different runs.

RESULTS AND DISCUSSION

If intramolecular base catalysis is to be kinetically observable, it requires that the second step of the reaction, *i.e.*, the decomposition of the intermediate I, is rate-limiting. Using the symbols given in Scheme 1 and the same deduction as in a previous paper,¹ we can then express the observed first-order rate constant as a sum of two terms

$$k_{\text{obs}} = k_2'[\text{B}] + k_3'[\text{B}]^2 \quad (1)$$

The second- and third-order rate constants k_2' and k_3' can be obtained from the values in

Table 1 as the intercept and the slope, respectively, from a plot of $k_{\text{obs}}/[\text{B}]$ versus $[\text{B}]$ as in Fig. 1.

For the reaction with 1,3-diaminopropane, k_2' and k_3' are found to be $(3.64 \pm 0.06) \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(7.8 \pm 0.4) \times 10^{-4} (\text{dm}^3)^2 \text{ mol}^{-2} \text{ s}^{-1}$, respectively, and in the reaction with 1,3-diamino-2,2-dimethylpropane, $(2.44 \pm 0.07) \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(4.2 \pm 0.4) \times 10^{-4} (\text{dm}^3)^2 \text{ mol}^{-2} \text{ s}^{-1}$.

The ratio k_2'/k_3' is, for the former diamine, 0.47 mol dm^{-3} and, for the latter, 0.58 mol dm^{-3} . Our expectation was that this ratio should be larger for the dimethyl-substituted diamine, where the "gem-dimethyl effect" might favour intramolecular base catalysis. The ratio is in fact somewhat larger for the branched compound, but the difference is too small to allow any conclusions to be drawn whether intramolecular base catalysis is operating or not. The constant k_2' accounts for all kinds of catalysis except for that by B and even for the possibility that the proton is removed from nitrogen in a rapid third step.

We must also consider the possibility that the first step in the reaction is rate-limiting and that the observed dependence of k_{obs} on $[\text{B}]$ is merely a medium effect. At any given amine concentration $[\text{B}]$, the rate constants for the unsubstituted and the branched diamine differ by a factor of about 1.6 (see Fig. 1). This would mean that the medium effect on the rate of the addition step is unaffected by the dimethyl-substitution in the diamine.

Acknowledgement. We wish to thank Professor Lars Melander for constructive criticism and helpful discussions.

REFERENCES

1. Palmertz, I. and Lamm, B. *Acta Chem. Scand.* **23** (1969) 3361.
2. Lamm, B. and Nordfält, K. *Acta Chem. Scand.* **24** (1970) 1241.
3. Newman, M. S. *Steric Effects in Organic Chemistry*, Wiley, New York 1963.
4. Lamm, B. *Acta Chem. Scand.* **19** (1965) 1492.
5. Miller, J. *Aromatic Nucleophilic Substitution*, Elsevier, Amsterdam 1968.
6. Pratt, R. F. and Lawlor, J. M. *Chem. Commun.* (1968) 522.
7. Lamm, B. and Palmertz, I. *Acta Chem. Scand. B* **30** (1976) 15.
8. Lambert, A. and Lowe, A. *J. Chem. Soc.* (1947) 1517.
9. *Brit. Patent* 1,150,445 (1969) in *Chem. Abstr.* **71** (1969) 92641 b.
10. *Beilsteins Handbuch der Organischen Chemie*, **E III** 6 853.
11. Bunnett, J. F. and Garst, R. H. *J. Org. Chem.* **33** (1968) 2320.

Received June 2, 1975.