760. *The Decomposition of Nitramide in Nitrobenzene catalysed by Aniline Derivatives.*

By D. D. CALLANDER, W. D. FERGUSON, G. C. FETTIS,
and A. F. TROTMAN-DICKENSON.

Decomposition of nitramide catalysed by primary, secondary, and tertiary aniline derivatives in nitrobenzene has been investigated between 10° and 56°. Activation energies for the catalytic coefficients have been determined. The catalytic coefficients at 25° are not simply related to the activation energies, but are given by $\log_{10} k_c$ (25°) (mole^{-1} kg. min.$^{-1}$) $= -3{\cdot}84 + 0{\cdot}67 \log_{10} K_a$ (25°) (mole^{-1} l.) where K_a is the corrected dissociation constant of an aniline derivative.

THE decomposition of nitramide catalysed by aniline derivatives has been studied over a range of temperature in several solvents.[1-4] The most detailed studies with several bases in anisole[3] and *m*-cresol[4] yielded linear relations of the form $E = W + X \log k_c$ and $\log A = Y + Z \log k_c$ between the Arrhenius parameters for the catalytic coefficients of the bases and the coefficients themselves. The values of X and Z were $-0{\cdot}135$ and $+0{\cdot}90$ (*m*-cresol), and $-0{\cdot}62$ and $0{\cdot}55$ (anisole) respectively.* When these points were plotted

---

* The unit of time is incorrectly stated at several points in ref. 4; the rate constants are in mole^{-1} kg. min.$^{-1}$ throughout.

[1] Bell and Caldin, *Trans. Faraday Soc.*, 1951, **47**, 50.

[2] Caldin and Peacock, *Trans. Faraday Soc.*, 1955, **51**, 1217.

[3] Fettis, Kerr, McClure, Slater, Steel, and Trotman-Dickenson, *J.*, 1957, 2811.

[4] Carnie, Duncan, Kerr, Shannon, Trotman-Dickenson, and White, *J.*, 1959, 3231.

against the logarithms of the dielectric constant (D) of the solvents, lines were obtained which at unit dielectric constant gave $X = -1{\cdot}36$ and $Z = 0$. These are the values that would be expected for a series of reactions with constant A factors. Such series in which changes in activation energy are solely responsible for changes in rate constants are usually cited in support of theories that interpret free-energy relations in terms of potential-energy curves. The principal object of the present work was to obtain values of X and Z for a solvent of high dielectric constant. Nitrobenzene was selected because it had the highest dielectric constant of any solvent, apart from water, in which the decomposition of nitramide had been studied.[2] Water was unsuitable because the simplest types of energy relation rarely hold for ionic processes in aqueous solution.

EXPERIMENTAL

Materials.—Nitrobenzene was dried (P_2O_5–KOH) and fractionated by distillation at 24 mm. from potassium hydroxide. Aniline derivatives were distilled over potassium hydroxide under reduced pressure and stored in sealed containers. Nitramide was prepared by the method of Marlies, La Mer, and Greenspan.[5] Ethyl carbamate was recrystallised once from benzene to remove catalytic impurities of unknown composition.[6] Ethyl nitrate in a 60% w/w solution in ethanol was added during 2 hr. in the preparation of the nitrourethane. The nitramide was pure white at the first precipitation. It was not purified further but showed none of the irregular behaviour frequently encountered.

Apparatus and Procedure.—The runs were carried out in reaction vessels similar to Bell and Caldin's,[1,7] the faster in vessels with taps, the slower in sealed vessels. The vessels were placed in a glass-fronted thermostat maintained within 0·02° and were agitated by percussion. Reaction mixtures were made up by weight. First, a convenient quantity of catalyst (or catalyst solution for the stronger bases) was weighed in a weighing bottle. Nitrobenzene, to make approx. 2 g. of mixture, was then added. Finally, either 1 or 2 c.c. of 0·08M-nitramide solution was added immediately before the mixture was introduced into the reaction vessel.

The runs were followed by observing the increase in pressure of the evolved gas. First-order plots were drawn, based on the pressure of gas after complete reaction. The lines obtained were usually good. They remained straight for about three half-lives, after which the points were scattered and tended to indicate too little reaction.

RESULTS AND DISCUSSION

The results are summarised in Table 1. The present value of k_c for dimethylaniline at 25° fits well on the Arrhenius plot found by Caldin and Peacock.[2] The probable errors for the activation energies are $\pm 0{\cdot}3$ kcal. mole^{-1} or less. An attempt to study catalysis by 3,4-dichloroaniline was unsuccessful. At the lower temperature the reactions were very slow, possibly because all the base did not go into solution. Three concordant

TABLE 1. *Catalytic coefficients,* 10^3k_c (mole^{-1} kg. min.$^{-1}$) (*temp. in parentheses*).

Base	(10·0°)	(25·0°)	(40·0°)	(55·4°)	$\log_{10} A$	E (kcal. mole^{-1})
p-$C_6H_4Me{\cdot}NEt_2$	1070	3850	—	31,300	10·7	13·8
p-$C_6H_4Me{\cdot}NMe_2$	308	1150	—	12,300	11·0	14·9
$NPhMe_2$	—	269	—	—	10·3 *	14·9 *
NHPhMe	13·3	57·1	—	641	10·3	15·7
NH_2Ph	—	22·1	81·3	239	9·6	15·3
m-$C_6H_4Cl{\cdot}NH_2$	—	3·14	11·8	23·4	6·4	13·3

All values of k_c are means of three or four determinations at base concentrations that differed by a factor of at least two and usually considerably more. No dependence of k_c on concentration was found for any base.

* Result of Caldin and Peacock [2] who found $10^3k_c = 258$ at 25°.

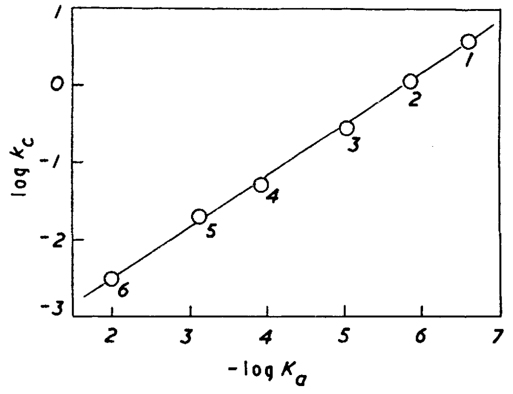
[5] Marlies, La Mer, and Greenspan, *Inorg. Synth.*, 1939, **1**, 68.

[6] Ray and Ogg, *J. Phys. Chem.*, 1956, **60**, 1460.

[7] (*a*) Bell and Trotman-Dickenson, *J.*, 1949, 1288; (*b*) Trotman-Dickenson, *J.*, 1949, 1293.

determinations of $k_c = 0{\cdot}00217$ mole^{-1} kg. min.$^{-1}$ were made at 55·4°. This value is far too low in comparison with the other bases, in view of their relative dissociation constants.

The catalytic coefficients at 25° obey the Brönsted relation, as can be seen from the Figure in which their logarithms are plotted against the logarithms of the dissociation constants of the bases in water at 25°[8] adjusted with the corrections suggested by Trotman-Dickenson.[7b, 9] These corrections had to be applied because no measurements of the strengths of some of the bases in non-aqueous solvents are recorded. The line corresponds to the equation: k_c (mole^{-1} kg. min.$^{-1}$) = $0{\cdot}000145K_a^{-0{\cdot}67}$. These values of G and α are compared with those in other solvents in Table 2. There is no correlation with either dielectric constant or catalytic coefficient.



Plot of —log K_a *against* log k_c.

1, *Diethyl-*p*-toluidine.* 2, *Dimethyl-*p*-toluidine.* 3, *Dimethylaniline.* 4, *Methylaniline.* 5, *Aniline.* 6, m*-Chloroaniline.*

No simple relation exists between log k_c (25°) and the log A's or the activation energies for the different bases in nitrobenzene. Apart from the value for *m*-chloroaniline the values of log A are approximately constant but their scatter is too great for significance to be attributed to this fact.

Nitrobenzene may behave differently from anisole and *m*-cresol as a solvent because the reactants are very strongly solvated. Marked colour changes occurred when the stronger bases were dissolved in nitrobenzene. The colour of nitramide solutions changed as the decomposition progressed. Similar effects were noted by Caldin and Peacock.[2] It appears worthwhile to continue the study of the decomposition of nitramide in solvents that are less likely to form complexes.

TABLE 2. *Brönsted coefficients for the decomposition of nitramide in various solvents at* 25°.

Solvent	Dielectric constant	α	10^6G	10^3k_c
			(mole^{-1} l. sec.$^{-1}$)	
Water [a]	78·5	−0·75	36	230
Nitrobenzene	34·8	−0·67	2·9	3·6
m-Cresol [b]	11·8	−0·84	17	310
Isopentyl alcohol [c]	5·7	−0·92	0·80	36
Anisole [7]	4·3	−0·64	1·1	2·3
Benzene [2]	2·3	−0·7	1·3	4·6

The calculation of G is based on pK_a (25°) = 5·06 for dimethylaniline in water.

k_c is the catalytic coefficient for dimethylaniline.

[a] Brönsted and Pedersen, *Z. phys. Chem.*, 1924, **108**, 185; Bell and Wilson, *Trans. Faraday Soc.*, 1950, **46**, 407. [b] Brönsted, Nicholson, and Delbanco, *Z. phys. Chem.*, 1934, *A*, **169**, 379. [c] Brönsted and Vance, *Z. phys. Chem.*, 1933, *A*, **163**, 240. The value of k_c is taken as 17 times that for aniline. This factor is derived from the present results and the values of α for the two solvents.

THE UNIVERSITY, EDINBURGH. [*Received, March* 15*th*, 1960.]

---

[8] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.
[9] Bell and Bayles, *J.*, 1952, 1518.