655. *The Decomposition of Nitramide in* m-*Cresol catalysed by Aniline Derivatives.*

By W. W. CARNIE, P. M. DUNCAN, J. A. KERR, KATHLEEN SHANNON, A. F. TROTMAN-DICKENSON, and J. A. WHITE.

Decomposition of nitramide catalysed by primary, secondary, and tertiary aniline derivatives in *m*-cresol has been investigated between 9° and 55°. Activation energies for the catalytic coefficients have been determined. The catalytic coefficients at 25° are related to the activation energies by the expression E (kcal. mole^{-1}) $= 15{\cdot}0 - 0{\cdot}135 \log_{10} k_c$ (25°) (mole^{-1} kg. min.$^{-1}$). The significance of the findings is discussed.

REACTIONS that are catalysed by acids and bases are among the simplest of all chemical processes, at least in so far as their formal representation is concerned. The rate-determining steps of many of them consist solely of the transfer of a proton from one compound to another. In view of their simplicity, it is not surprising that they were the subject of one of the first generalisations of chemical kinetics, the Brönsted relation, which relates the catalytic coefficients of acids or bases to their dissociation constants.[1] The attempts that have been made to understand this free-energy relation have usually depended upon the assumption that the differences in the catalytic coefficients of different members of a class of compound are determined by the different heats of activation. The variations in the heats of activation were then explained in terms of potential-energy curves. Few attempts have been made to confirm this plausible interpretation by measurements of activation energies. Most activation energies have been measured in aqueous solution. It is not surprising that no simple relation has been found between the activation energies and catalytic coefficients in water. Ionic processes in water frequently fail to conform to the simplest types of energy relation.

This work was undertaken to extend that previously carried out on the decomposition of nitramide by aniline derivatives in anisole solution.[2] Anisole was chosen because it is a convenient solvent with which a considerable amount of work had been done. *m*-Cresol was chosen for the same reason, and had the further advantage that the value of the Brönsted coefficient, α, 0·84 for amines in *m*-cresol is considerably different from the corresponding value 0·64 for anisole. A marked difference in behaviour might therefore be expected. Caldin and Peacock [3] have, moreover, argued that there is some difference between hydroxylic and other solvents.

EXPERIMENTAL

Materials.—Some batches of the *m*-cresol (B.D.H.) were dried (P_2O_5–KOH) and fractionated on an 18″ column packed with glass helices; some were simply fractionated, and other used as they were supplied. No difference in kinetic behaviour was detected. Aniline derivatives were usually distilled over potassium hydroxide under reduced pressure and stored in sealed containers. 3,4-Dichloroaniline was recrystallised from methanol. Nitramide was prepared by the method of Marlies, LaMer, and Greenspan.[4] As recommended by Ray and Ogg [5] the ethyl carbamate was, in the last two preparations, recrystallised from benzene, and the ammonium nitrourethane from methanol. The nitramide was dissolved in ether and precipitated with isopentane four times. If these precautions were not followed trouble was caused by an unknown catalytic impurity.

Apparatus and Procedure.—The runs were carried out in reaction vessels similar to Bell and Caldin's,[6] fitted with taps. Reaction mixtures were made up by weight. First, a convenient

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[1] Bell, "Acid-Base Catalysis," Oxford, 1941.

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

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

[4] Marlies, LaMer, and Greenspan, *Inorg. Synth.*, 1939, **1**, 68.

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

[6] Bell and Caldin, *Trans. Faraday Soc.*, 1951, **47**, 50; Bell and Trotman-Dickenson, *J.*, 1949, 1288.

quantity of catalyst or catalyst solution was weighed in a weighing bottle. Sufficient hydrochloric acid was added to convert 5—10% of the base into its hydrochloride, to form a buffer solution. *m*-Cresol, to make approximately 2 g. of mixture, was then added. Finally, 2 c.c. of nitramide solution were added immediately before the mixture was introduced into the reaction vessel.

The increase in pressure of the evolved gas was observed. First-order plots were drawn, based on the pressure of gas after complete reaction. The lines obtained were usually very good. They remained straight for 3—4 times as long as the half-life, after which the points were scattered because it was difficult to measure accurately the small changes in pressure; but there was no consistent trend.

RESULTS AND DISCUSSION

The results are summarised in the Table. The values for the rate constants at 20° found by Brönsted, Nicholson, and Delbanco[7] are in reasonably good agreement with those found by interpolation from the present work in so far as the bases were common to the two investigations. The present value of k_c for dimethylaniline at 25° fits well on the Arrhenius plot found by Caldin and Peacock. The Arrhenius parameters for all except the first two bases were found by the method of least squares. The errors are probable errors. The same treatment could not be applied to *NN*-diethylaniline or *NN*-diethyl-*p*-toluidine because at the highest temperature k_c for both these bases increased with the base concentration. The value of k_c used in the calculation of the activation energy was for an infinite concentration of base and was found by an extrapolation of the straight line obtained by plotting $1/k$ against 1/[Base]. This is an empirical correction with no basis in theory. The Arrhenius parameters obtained in this way are therefore doubtful. It did not seem that the effect could be simply ascribed to the presence of an acidic impurity.

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

Base					$\log_{10} A$	E (kcal. mole^{-1})
p-$C_6H_4Me{\cdot}NEt_2$	377 (8·9°)	1960 (24·5°)	—	19,700 (54·7°)	13·3	14·9
$NPhEt_2$	297 (8·9)	1125 (24·5)	—	10,530 (54·7)	12·7	14·4
p-$C_6H_4Me{\cdot}NMe_2$	124 (9·1)	400 (25·0)	1030 (40·0)	240 (53·0)	10·26	11·77 ± 0·1
$NPhMe_2$	—	168 (25·0)	—	—	12·1 *	14·8 ± 0·4 *
NHPhMe	6·01 (9·1)	24·3 (25·0)	91·5 (40·0)	234 (53·0)	11·69	15·3 ± 0·1
NH_2Ph	1·20 (9·1)	5·43 (25·0)	18·3 (40·0)	45·7 (53·0)	10·76	15·0 ± 0·1
m-$C_6H_4Cl{\cdot}NH_2$	0·198 (9·1)	0·820 (25·0)	2·71 (40·0)	6·68 (53·0)	9·62	14·6 ± 0·1
3,4-$C_6H_3Cl_2{\cdot}NH_2$	0·070 (8·9)	0·247 (24·5)	—	3·35 (54·7)	9·94	15·6 ± 0·3

* Result of Caldin and Peacock.[3]

In comparing this table with that for the similar quantities in anisole, it should be noted that *A* factors quoted in ref. 2 are erroneously low by one power of ten.

The results of the present work are shown in Fig. 1 in which the activation energies of the catalytic coefficients are plotted against the catalytic coefficients of the various bases at 25°; they are related by the equation:

$$E \text{ (kcal. mole}^{-1}) = 15{\cdot}0 - 0{\cdot}135 \log k_c \text{ (25°) (mole}^{-1}\text{ kg. min.}^{-1})$$

This equation was obtained by the method of least squares, with the values for *NN*-dimethyl-*p*-toluidine omitted. No reason can be suggested for the anomalous behaviour of this base, which was amply confirmed by independent experiments. The equation may be compared with that found for anisole:

$$E \text{ (kcal. mole}^{-1}) = 14{\cdot}2 - 0{\cdot}62 \log k_c \text{ (25°) (mole}^{-1}\text{ kg. sec.}^{-1})$$

This line and the points from which it is derived are also shown in Fig. 1 as is the slope of the line which would be found if variations in log k_c were entirely determined by changes

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[7] Brönsted, Nicholson, and Delbanco, *Z. phys. Chem.*, 1934, *A*, **167**, 379.

in E, an ideal behaviour which corresponds to a coefficient of log k_c of 1·36. The corresponding equations relating log k_c and A are:

$$m\text{-Cresol: } \log_{10} A \text{ (mole}^{-1}\text{ kg. sec.}^{-1}) = 11{\cdot}0 + 0{\cdot}90 \log k_c \text{ (25°) (mole}^{-1}\text{ kg. sec.}^{-1})$$
$$\text{Anisole: } \log_{10} A \text{ (mole}^{-1}\text{ kg. sec.}^{-1}) = 10{\cdot}4 + 0{\cdot}55 \log_{10} k_c \text{ (25°) (mole}^{-1}\text{ kg. sec.}^{-1})$$

the ideal coefficient of $\log_{10} k_c$ is, of course, zero.

These results confirm, as has been argued by other authors,[3] that the comparison of rate constants measured in different solvents will be misleading because the relation found will depend heavily upon the arbitrarily chosen temperature at which the comparison is made. Clearly it is more satisfactory to compare values of A and E. This was done by Caldin and Peacock [3] for the decomposition of nitramide catalysed by dimethyaniline in nine different solvents. This procedure is little less arbitrary, for whether, for example, E_{anisole} is greater or less than $E_{m\text{-cresol}}$ depends solely upon the base chosen for comparison, as can be seen in Fig. 1. Dimethylaniline is not peculiarly fitted for the purpose.

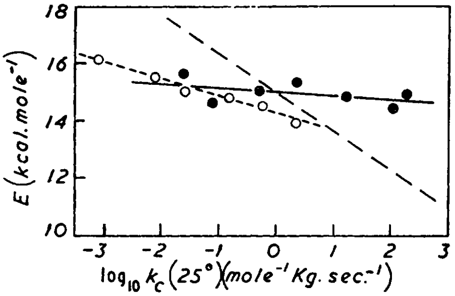

FIG. 1. *Relation between activation energies and catalytic coefficients for the aniline-catalysed decomposition of nitramide.*

● and solid line: in *m*-cresol.
○ and short dashes: in anisole.
Long dashes: slope = 2·303*RT*.

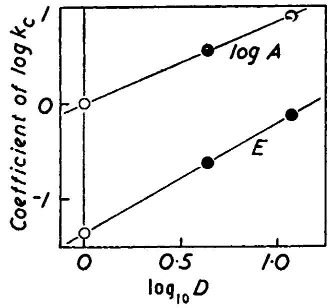

FIG. 2. *Relation between the dependence of A and E on* log k_c *and the dielectric constant of the solvent.*

An interesting empirical correlation has been found between the coefficients of log k_c in the expressions for A and E given above and the dielectric constant of the solvent in which the measurements were made. This is shown in Fig. 2. The striking feature of this figure is the fact that the intercepts (corresponding to a solvent of unit dielectric constant) yield coefficients of zero for A and $-1{\cdot}36$ for E. These are the precise values that would be expected if the differences of the catalytic coefficients for different bases were solely due to changes of activation energy, as is postulated in the simple theoretical treatment of free-energy relations. It will not be possible to say for certain whether this finding has any general significance until these reactions in other solvents and also other types of reaction have been studied.

The principal conclusion of this work is that the effect of solvents on reaction velocity cannot usefully be investigated by experiments at one temperature. Even determinations of the activation energies of a single reaction in several solvents are likely to be misleading. Much more work is required on series of related reactions.

THE UNIVERSITY, EDINBURGH.

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