542. *The Decomposition of Nitramide in Anisole Catalysed by Aniline Derivatives.*

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Decomposition of nitramide catalysed by primary, secondary, and tertiary aniline derivatives in anisole has been investigated between 7° 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

$$\log_{10} k_c\ (25°)\ (\text{mole}^{-1}\ \text{kg. min.}^{-1}) = 23{\cdot}2 - 1{\cdot}63E\ (\text{kcal. mole}^{-1})$$

The catalytic coefficients of a series of acidic or basic catalysts for a reaction are normally related to their respective dissociation constants by the Brönsted relation. In theoretical discussions of this kind of free-energy relation it is generally supposed that the difference in the catalytic power of the various catalysts can be attributed to the different activation energies of the fundamental protolytic reactions.[1] The temperature coefficients of comparatively few reactions catalysed by acids or bases have been measured. Consequently it is difficult to say whether there is any real basis for the supposition. Further, most of the reactions for which temperature coefficients have been measured have been studied in aqueous solution. It is known that ionic processes in aqueous solution frequently do not conform to the simplest types of energy relation. Accordingly it is not surprising that the results obtained with aqueous solutions do not often yield simple relations between the catalytic coefficients and activation energies.

This work was undertaken to obtain results in a solvent which does not readily form hydrogen bonds. The decomposition of nitramide was chosen because it has been very fully investigated and can easily be followed.[1] Anisole is a convenient solvent which can easily be sufficiently purified and in which a considerable amount of work has been done. Substituted anilines were chosen as catalysts because they have also been fairly fully studied.[1-4]

Experimental

Materials.—Anisole was dried ($CaCl_2$) and fractionated on an 18″ column packed with glass helices. Several batches were purified; all behaved similarly. Aniline derivatives were distilled over potassium hydroxide pellets under reduced pressure and stored in sealed containers. Nitramide was prepared by the method of Marlies, LaMer, and Greenspan [5] and stored in a refrigerator as a solution in anisole.

Apparatus and Procedure.—The runs were carried out in reaction vessels similar to those used by Bell and Caldin.[3] The faster runs were carried out in vessels with taps, the slower runs in sealed vessels. The vessels were placed in a glass-fronted thermostat maintained to ±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. Anisole, 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 runs were followed by observing the increase in pressure of the evolved gas. First-order plots were then drawn, based on the pressure of gas after complete reaction. In the slowest runs the reaction vessels were placed in a warm bath to bring the reaction to completion overnight. The rate constants were deduced from the observations taken during the first two half-lives of the reactions, after which some of the plots tailed off. The catalytic coefficients

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

[2] Bell and Caldin, *Trans. Faraday Soc.*, 1951, **47**, 50; Caldin and Peacock, *ibid.*, 1955, **51**, 1217.

[3] Bell and Trotman-Dickenson, *J.*, 1949, 1288.

[4] Bell and Wilson, *Trans. Faraday Soc.*, 1950, **46**, 407.

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

of the bases were found to be a function of the concentration of the solutions. The extrapolations devised by Bell and Trotman-Dickenson [3] were used to obtain the true coefficients.

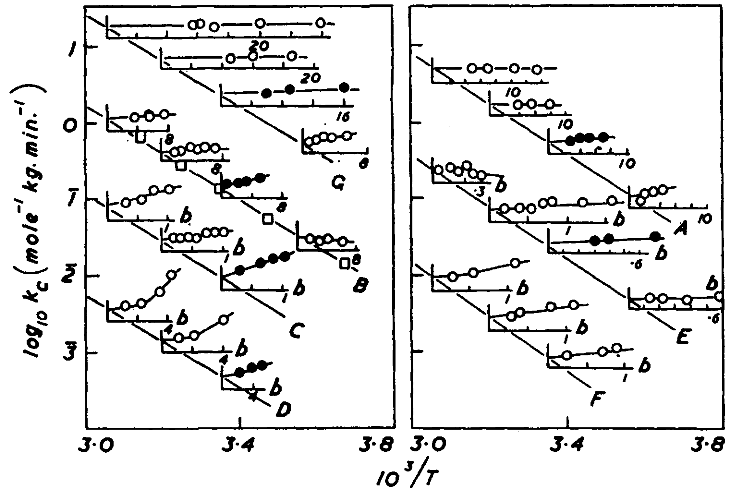
RESULTS

The results of the kinetic measurements are included in Arrhenius plots (Fig. 1*a* and *b*) which show the catalytic coefficients from the individual runs and the extrapolations employed.

Base	Catalytic coefficients, 10^3k_c (mole^{-1} kg. min.$^{-1}$) (temp. in parentheses)				$\log_{10} A$	E (kcal. mole^{-1})
Diethyl-*p*-toluidine ...	480 (7·6°)	2295 (25·0°)	6760 (39·6°)	17,340 (54·1)°	9·43	13·9
Dimethyl-*p*-toluidine	105 (7·6)	599 (25·0)	1730 (39·6)	4875 (54·1)	9·22	14·5
Dimethylaniline	31 (8·6)	150 (25·0)	425 (40·0)	1230 (54·1)	8·81	14·8
Methylaniline	4·28 (7·7)	27·6 (25·0)	72·3 (40·0)	242 (54·1)	8·17	15·0
Aniline	—	8·07 (25·0)	30·0 (40·0)	80·0 (54·0	8·21	15·5
m-Chloroaniline	—	0·85 (25·0)	2·90 (39·6)	9·5 (54·1)	7·44	16·1
o-Chloroaniline	—	0·20 (25·0)	1·43 (40·0)	3·80 (54·1)	5·87	14·1

The results are summarized in the Table. Generally they agree very well with those of Bell and Trotman-Dickenson [3] and Bell and Caldin,[2] those for *m*-chloroaniline being the only exceptions (we can suggest no reason for the discrepancy; the identity of the present material was confirmed by measurement of its refractive index and of the m. p. of its benzoyl derivative). The accuracy of the determination of the activation energies cannot be readily assessed because of the need for the extrapolation. An error of ±0·3 kcal. mole^{-1} may reasonably be assigned.

FIG. 1*a and b. Arrhenius plots for the decomposition of nitramide in anisole catalysed by aniline derivatives. The individual points and the extrapolations are shown.* ○, *This work*; ●, *Bell and Trotman-Dickenson* [3]; □, *Bell and Caldin.*[2] *Concentrations are in moles kg.*$^{-1}$. *Except where the scale is marked b when the second method of extrapolation was used, the concentration scale on the abscissæ is for* $1/\sqrt{b}$ *corresponding to the first method of extrapolation. A, Dimethyl-*p*-toluidine; B, dimethyls aniline; C, aniline; D,* o*-chloroaniline; E, methylaniline; F,* m*-chloroaniline; G, diethyl-*p*-toluidine.*



DISCUSSION

The activation energies of the catalytic coefficients are plotted against the catalytic coefficients of the various bases at 25° in Fig. 2. All except that for *o*-chloroaniline lie on a straight line given by $\log_{10} k_c$ (25°) $= 23{\cdot}2 - 1{\cdot}63E$. The deviation of the *ortho*-substituted compound is not surprising; many free-energy relations break down for *ortho*-compounds. The slope of the line in Fig. 2 differs markedly from that which would be obtained (broken line) if all the differences between the catalytic coefficients could be attributed to variations in activation energy. The line representing the variation of $\log_{10} k_c$ with E deviates from the " theoretical " slope, which corresponds to a constant value of A, for many series of reactions. Usually the slope is too great, *i.e.*, systematic changes in A compensate for the variations in E. In the present reaction the reverse occurs; A is not constant; it varies so as to reinforce the changes in E.

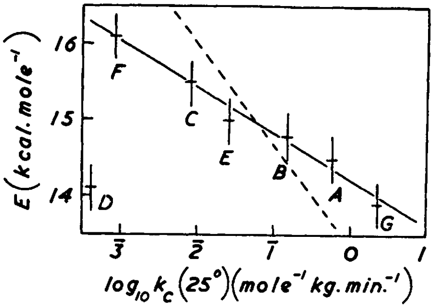


FIG. 2. *Relation between activation energies and catalytic coefficients for the aniline-catalysed decomposition of nitramide. A—G, see Fig. 1. Slope of broken line* = $2{\cdot}303\mathbf{R}T$.

The fact that the activation energies of the primary, secondary, and tertiary bases (except *o*-chloroaniline) obey the same relation supports the interpretation of the basic strength of amines, as measured in aqueous solutions, which has been suggested by Bell and Trotman-Dickenson.[3, 6]

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[6] Trotman-Dickenson, *J.*, 1949, 1293.