279. *Acid–Base Catalysis in Non-aqueous Solvents. Part XII. The Amine-catalysed Decomposition of Nitramide in Anisole Solution.*

By R. P. Bell and A. F. Trotman-Dickenson.

Kinetic measurements have been made on the decomposition of nitramide in anisole solution, catalysed by 24 amine bases. For a given type of amine (primary, secondary, or tertiary aniline derivative, or heterocyclic base) there is a relation between dissociation constants in water and catalytic constants in anisole, but no one relation holds for all four types. The distinction between primary, secondary, and tertiary aniline derivatives is attributed to anomalies in the dissociation constants in water, arising from hydrogen bonding between the amine cation and water molecules. Comparison with data in three other solvents indicates that the amine-catalysed decomposition of nitramide is favoured by an increase in dielectric constant.

In addition to the large amount of work done with aqueous solutions, the kinetics of the decomposition of nitramide have been studied in *iso*amyl alcohol (Brönsted and Vance, *Z. physikal. Chem.*, 1933, *A*, **173**, 240) and in *m*-cresol (Brönsted, Nicholson, and Delbanco, *ibid.*, 1934, **169**, 379). The object of the present work was to extend the range of solvents studied, and to obtain more information about amine catalysts. Brönsted and Duus (*Z. physikal. Chem.*, 1925, **117**, 299) used substituted anilines as catalysts for the nitramide catalysis in water, and found a close relation between catalytic power and basic strength, but the few measurements reported for tertiary bases (Brönsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185; *J. Amer. Chem. Soc.*, 1938, **60**, 1513) do not conform to this relation. It is therefore of interest to investigate a wider range of amine bases, as has already been done for another type of reaction (Bell and Rybicka, *J.*, 1947, 24).

Experimental.

Anisole was dried ($CaCl_2$) and fractionated, the middle fraction boiling over a range of 0·5° being used. Nitramide was prepared by the method of Marlies, LaMer, and Greenspan (*Inorg. Synth.*, Vol. I, p. 68, New York, 1939) and could be stored in an open vessel over potassium hydroxide in a vacuum desiccator. Some samples which had been stored over phosphoric oxide gave low and erratic velocity constants, presumably because of some volatile acidic impurity. It was often more convenient to store the nitramide in the ice-box as an approximately 0·1M. solution in anisole, the half-life being then about 60 days. The bases used as catalysts were (if liquid) dried with potassium hydroxide, and were purified by fractional distillation or recrystallisation. Their physical constants are given in the tables of results.

The reaction was followed by measuring the pressure of nitrous oxide evolved in the apparatus shown in Figure 1, designed by Mr. E. F. Caldin. Its total volume is about 20 c.c. and it holds 3 c.c. of solution. The vertical capillary is of 1-mm. internal diameter, is graduated in millimetres, and is evacuated at the top. With these dimensions, 3 c.c. of a 0·1M-nitramide solution give a pressure change of about 120 mm. of mercury. The whole apparatus is held in a clamp below the surface of a thermostat at 25° ± 0·01°, and agitated by an electrically operated rubber hammer which strikes the bulb about 80 times per minute (cf. Bell and Baughan, *Proc. Roy. Soc.*, 1937, **158**, *A*, 464). To carry out an experiment, the nitramide and catalyst solution are mixed outside the apparatus and then run into the bulb. The apparatus is evacuated through *A* for a few seconds, then sealed off at *B*, and placed in its clamp in the thermostat. It was possible to obtain reliable readings about two minutes after agitation had commenced, *i.e.*, about four minutes after mixing. Readings were then taken at suitable intervals, and the end-point observed after at least eight half-lives. For some of the slower reactions, completion of the reaction was accelerated by immersing the apparatus in a thermostat at 60°, and then returning it to the 25° thermostat to observe the end-point.

The velocity constants were obtained graphically by plotting $\log_{10}(r_0 - r)$ (where r is the manometer reading) against the time, and are defined by $k = \mathrm{d}\log_{10}(r_0 - r)/\mathrm{d}t$ with t in minutes. The plots obtained showed a very slight curvature as the reaction progressed, owing to a displacement of the equilibrium, $H_2N_2O_2 + B \rightleftharpoons (HN_2O_2)^- + BH^+$, where B is the basic catalyst; however, all experiments were carried out with approximately the same nitramide concentration and covered about the first three quarters of the reaction, so that the best straight lines gave comparable values for the velocity constants in different experiments. The existence of this equilibrium also caused the apparent catalytic constant k/c to vary slightly with the base concentration, c, making it necessary to use an extrapolation to obtain the true catalytic constant. Let the concentration of $(B + BH^+)$ be c, and the concentration of $(HN + N^-)$ (N = nitramide) be x; similarly, let the concentrations of both BH^+ and

TABLE I.

c = concentration of base in moles/kg. of solution.
k = first-order velocity constant, decadic logarithms, minutes.

Quinoline, b. p. 231—233°,	10^3c	13·4	27·1	30·1	39·6	62·1
k_c = 0·365.	k/c	0·487	0·440	0·463	0·437	0·442
Pyridine, b. p. 114·6—114·8°,	10^3c	6·12	15·9	19·5	29·7	
k_c = 0·814.	k/c	0·850	0·829	0·832	0·833	
*iso*Quinoline, b. p. 239·4—239·6°,	10^3c	4·18	16·7	24·2	29·3	51·8
m. p. 22·5°, k_c = 1·14.	k/c	1·29	1·23	1·20	1·21	1·17
α-Picoline, b. p. 128·3—128·5°,	10^3c	1·64	2·32	6·50	9·26	
k_c = 2·22.	k/c	2·52	2·44	2·36	2·34	
γ-Picoline, b. p. 144·2—144·6°,	10^3c	1·67	3·38	6·75	10·1	
k_c = 2·30.	k/c	3·19	3·05	2·83	2·60	
β-Picoline, b. p. 141·5—141·8°,	10^3c	3·36	7·37	10·34		
k_c = 2·94.	k/c	2·71	2·82	2·80		
2 : 4-Lutidine, b. p. 155·3—155·4°,	10^3c	1·59	2·91	3·88	5·75	
k_c = 8·00.	k/c	6·40	6·76	6·90	7·22	
s-Collidine, b. p. 172—173°,	10^3c	0·84	1·87	2·64	3·20	
k_c = 13·5.	k/c	9·2	10·2	11·1	11·6	
Dimethylaniline, b. p. 191·0—	10^3c	13·1	70·0	86·8	203	254
191·2°, k_c = 0·065.	k/c	0·100	0·0814	0·0758	0·0745	0·0767
	10^3c	261	396	404	616	
	k/c	0·0754	0·0713	0·0731	0·0692	
Dimethyl-*m*-toluidine, b. p. 208·5—	10^3c	158	252	309		
209·0°, k_c = 0·089.	k/c	0·099	0·096	0·096		
Dimethyl-*o*-toluidine, b. p. 182·4—	10^3c	175	233	643		
182·7°, k_c = 0·115.	k/c	0·125	0·123	0·120		
Dimethyl-*p*-toluidine, b. p. 207·0—	10^3c	20·7	48·8	73·3	103	
207·7°, k_c = 0·260.	k/c	0·291	0·293	0·280	0·257	
Diethylaniline, b. p. 211·1—211·4°,	10^3c	15·3	32·9	58·5	90·1	
k_c = 0·360.	k/c	0·371	0·377	0·370	0·363	
Diethyl-*p*-toluidine, b. p. 102—	10^3c	3·30	6·03	14·5	27·0	
103°/14 mm., k_c = 1·30.	k/c	1·52	1·69	1·47	1·36	
Benzyldiethylamine, b. p. 207·2—	10^3c	0·28	1·23	1·49	2·22	2·82
207·8°, k_N = 7·8.	k/c	8·1	10·6	10·9	12·1	12·8
	10^3c	3·85	4·10	4·30		
	k/c	15·4	16·2	15·7		
Tri-*n*-butylamine, b. p. 209·2—	10^3c	0·83	1·61	2·05	3·10	3·95
210·2°, k_N = 5·5.	k/c	6·4	7·5	8·1	11·9	17·2
Triethylamine, b. p. 88·1—88·4°,	$10^3/c$	0·91	1·44	2·84	4·13	
k_N = 5·1.	k/c	5·19	5·09	4·97	5·20	
Methylaniline, b. p. 193·3—	10^3c	270	376	730		
193·5°, k_c = 0·0122*.	k/c	0·0124	0·0131	0·0133		
Ethyl-*o*-toluidine, b.p . 212·7—	10^3c	202	267	381	650	
212·8°, k_c = 0·0149*.	k/c	0·0150	0·0153	0·0155	0·0157	
Ethylaniline, b. p. 202·0—202·2°,	10^3c	222	346	501	728	
k_c = 0·0230*.	k/c	0·0228	0·0239	0·0232	0·0232	
o-Chloroaniline, b. p. 206·0—	10^3c	624	954	1220		
206·3°, k_c = 0·000230*.	k/c	0·000234	0·000252	0·000270		
m-Chloroaniline, b. p. 103°/14	10^3c	252	513	840		
mm., k_c = 0·00078*.	k/c	0·00076	0·00074	0·00072		
p-Chloroaniline, m. p. 69·2—	10^3c	261	522	742	744	
69·3°, k_c = 0·00147*.	k/c	0·00140	0·00133	0·00126	0·00128	
Aniline, b. p. 181·5—181·9°,	10^3c	381	654	857	1023	
k_c = 0·00350*.	k/c	0·00505	0·00650	0·00693	0·00770	

N^- be y. Then, if k_c and k_N are the catalytic constants of B and N^-, respectively, in decadic logarithms, the actual reaction velocity is given by

$$0{\cdot}434v = k_c(x - y)(c - y) + k_N y(x - y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Most of the bases used are considerably weaker than the nitramide ion, and it can therefore be assumed that y is much smaller than c or x, and terms in y^2 can be neglected. Under the same conditions, we can write $y = (K'cx)^{\frac{1}{2}}$, where K' is the equilibrium constant for the reaction, $HN + B \rightleftharpoons N^- + BH^+$. The observed value of k/c is then given by

$$k/c = 0{\cdot}434v/cx = k_c + \{k_N - k_c(1 + c/x)\}(K'x/c)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since the variation of k/c with c is small, and the initial nitramide concentration was kept approximately the same throughout, equation (2) can be applied to the mean velocity constants obtained graphically. For most purposes, k_c can be obtained by plotting k/c against $c^{-\frac{1}{2}}$ and extrapolating to $c^{-\frac{1}{2}} = 0$, since for the stronger bases $c \ll x$ throughout, whilst for the weaker bases $k_N \gg k_c$; in either case, the expression inside the first bracket is effectively independent of c. This method of extrapolation was used for the majority of the bases studied. For the weakest bases used, the extent of reaction with nitramide will be very small, but the high concentrations of base may well involve an appreciable medium effect. Equation (2) would not then be applicable, and in fact, for some of these bases, k/c increases slightly with increasing c, which is the opposite change to that predicted by the equation. In such cases we have allowed for the medium effect by plotting k/c against c and extrapolating to $c = 0$; catalytic constants obtained by this method are marked with an asterisk in Table I. The general conclusions drawn from the catalytic constants would not be modified by any reasonable change in the method of extrapolation.

The data for the three bases benzyldiethylamine, tri-*n*-butylamine, and triethylamine cannot be treated in this way, since they are strong enough to react with nitramide to a considerable extent, so that the observed catalysis is largely due to the nitramide ion, especially in dilute solutions of the bases. In equation (1) we can now put $y \sim c$, giving

$$k/c = k_N + (k_c/K' - k_N)c/x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It should thus be possible to obtain k_N by plotting k/c against c and extrapolating to $c = 0$. The resulting values are given in Table I; those from the data for tri-*n*-butylamine and triethylamine agree well, whilst benzyldiethylamine gives a somewhat higher value, probably because it is not a strong enough base for the successful application of equation (3). It is not possible to derive values of k_c for these bases without a knowledge of the equilibrium constants K' in anisole solution.

Nitramide decomposes slowly in pure anisole, the velocity constant being about 5×10^{-6}. This rate could be neglected in most of the amine solutions, but a small correction was made in the experiments with *o*- and *m*-chloroaniline. It was thought possible that the water produced in the reaction might catalyse the reaction; however, the spontaneous rate was not appreciably increased by using anisole saturated with water, and three experiments with diethyl-*p*-toluidine solutions containing 0·04 mol. of water per l. gave normal velocity constants.

Results.—The results of the kinetic measurements are collected in Table I.

DISCUSSION.

The measurements given above show that the decomposition of nitramide in anisole solution is a first-order reaction catalysed by bases, as in the other solvents previously investigated. It is of interest to compare the catalytic powers of the bases studied with their basic strengths in water, and the latter are most conveniently expressed by pK_a, the acid dissociation exponent of the conjugate acid cations, BH^+. This quantity is more convenient than the conventional basic dissociation constant K_b, since K_a is normally the quantity which is measured experimentally, K_b being derived from it by using the ionic product K_w, which varies considerably with temperature and salt concentration. Table II contains the collected values of the catalytic constants, k_c, together with pK_a and the sources of the latter.

Figure 2 shows a plot of $\log_{10} K_c$ against pK_a for all the amines considered above. It is clear that there is no single relation between basic strength and catalytic power which covers all the catalysts studied, but that such a relation is satisfied (probably within the uncertainty of the experimental values) for each of the four classes of amines given in Table II. The equations of the four lines drawn in Figure 1 are as follows :

Primary aromatic amines	$K_c = 4{\cdot}1 \times 10^{-6}(1/K_a)^{0{\cdot}64}$
Secondary ,,	$K_c = 1{\cdot}1 \times 10^{-5}(1/K_a)^{0{\cdot}64}$
Tertiary ,,	$K_c = 3{\cdot}8 \times 10^{-5}(1/K_a)^{0{\cdot}64}$
,, heterocyclic amines	$K_c = 3{\cdot}2 \times 10^{-4}(1/K_a)^{0{\cdot}64}$

The separation of the amines into four distinct classes seems too marked to be ascribed entirely to modifications in the shape of the potential energy curves (cf. Horiuti and Polanyi, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 505; Bell, *Proc. Roy. Soc.*, 1936, *A*, **154**, 414), since the differences are comparable with those caused by a change in the charge-type of the catalyst, and the slopes of the four lines are identical. A similar distinction between primary, secondary, and tertiary amines has been observed in this laboratory in catalysed keto–enol transformations,

TABLE II.

	$\log_{10}k_c$.	pK_a.	Source.
Pyridine and quinoline bases.			
Quinoline	$\bar{1}$·56	4·80	(1)
Pyridine	$\bar{1}$·91	5·27	(2)—(7)
*iso*Quinoline	0·11	5·36	(8)
α-Picoline	0·35	6·02	(7)
γ-Picoline	0·36	6·00	(9)
β-Picoline	0·47	6·00	(9)
2 : 4-Lutidine	0·90	6·65	(8)
s-Collidine	1·13	7·34	(2), (4)
Tertiary aromatic amines.			
Dimethylaniline	$\bar{2}$·81	5·06	(10)
Dimethyl-*m*-toluidine	$\bar{2}$·95	5·34	,,
Dimethyl-*o*-toluidine	$\bar{1}$·06	5·50	,,
Dimethyl-*p*-toluidine	$\bar{1}$·42	5·86	,,
Diethylaniline	$\bar{1}$·56	6·56	,,
Diethyl-*p*-toluidine	0·11	7·90	,,
Secondary aromatic amines.			
Methylaniline	$\bar{2}$·08	4·78	,,
Ethyl-*o*-toluidine	$\bar{2}$·17	4·92	,,
Ethylaniline	$\bar{2}$·36	5·11	,,
Primary aromatic amines.			
o-Chloroaniline	$\bar{4}$·30	2·77	,,
m-Chloroaniline	$\bar{4}$·89	3·52	,,
p-Chloroaniline	$\bar{3}$·17	4·00	,,
Aniline	$\bar{3}$·54	4·58	,,

References for pK_a *values.* (1) Felsing and Biggs, *J. Amer. Chem. Soc.*, 1933, **55**, 3624. (2) Goldschmidt and Salcher, *Z. physikal. Chem.*, 1899, **29**, 89. (3) Hahn and Klockmann, *ibid.*, 1904, **48**, 435. (4) Lunden, *J. Chim. physique*, 1907, **5**, 574. (5) Mizutani, *Z. physikal. Chem.*, 1926, **118**, 327. (6) Hall, *J. Amer. Chem. Soc.*, 1930, **52**, 5115. (7) Guzman-Barron, *J. Biol. Chem.*, 1937, **121**, 313. (8) Karrer and Schmid, *Helv. Chim. Acta*, 1946, **29**, 1853. (9) Constam and White, *Amer. Chem. J.*, 1903, **29**, 36. (10) Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

FIG. 1.

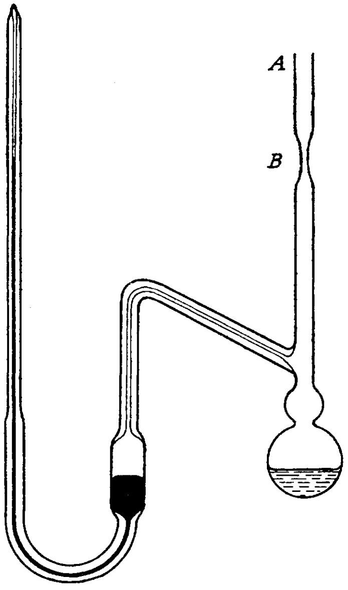
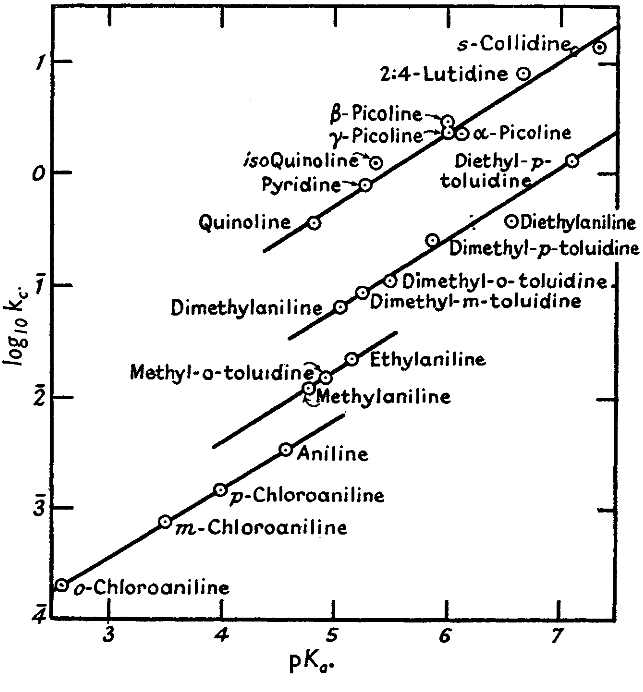


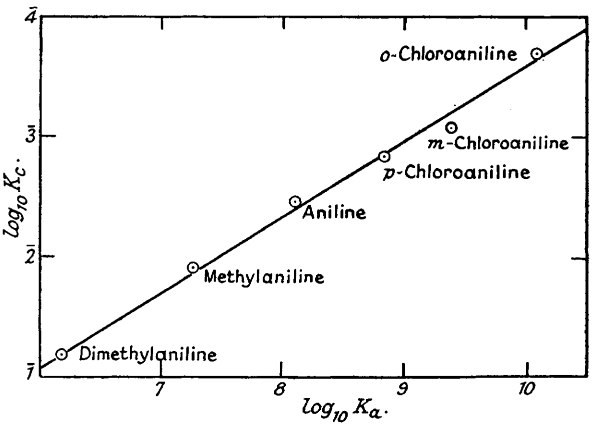
FIG. 2.



and the data of Brönsted, Nicholson, and Delbanco (*Z. physikal. Chem.*, 1934, **169**, 379) on the decomposition of nitramide in *m*-cresol solution show that mono- and di-methylaniline diverge considerably from the relation which holds for primary aniline derivatives when dissociation constants in water are used as the basis of comparison. A part of the differences between primary, secondary, and tertiary amines might be statistical in character, arising from the different numbers of hydrogen atoms on their cations; however, calculation shows that not more than a 50% difference between primary and tertiary amines could be accounted for on this basis, and it is in any case doubtful whether hydrogen atoms attached to the same central atom should be considered statistically independent (cf. Brönsted, *Chem. Reviews*, 1928, **5**, 322).

In our opinion, the failure of primary, secondary, and tertiary bases to conform to the same relation between K_c and K_a can be attributed to anomalies in the dissociation constants in water, which may not represent correctly the proton-accepting powers of the three classes of base. It has long been realised that the dissociation constants of the aliphatic amines are not simply related to their structures, and attempts have been made to explain these anomalies in terms of differing degrees of hydration of the amine molecules (cf. Moore and Winmill, *J.*, 1907, 1373; 1912, 1635) by hydrogen bonding with water molecules. However, it seems likely that such hydrogen bonding would be more important in the cations, where the hydrogen atoms have a greater positive charge, and if this is the case the cations of the amines will be stabilised in aqueous solution to an extent depending on the number of hydrogen atoms which they carry. Everett and Wynne-Jones (*Proc. Roy. Soc.*, 1941, *A*, **177**, 499) invoke the hydrophobic nature of the undissociated molecules to explain the thermodynamic properties of the methylamines, but this is not likely to vary much in a series such as the anilines. In such a series, the hydrogen-bonding power of the cations will be the dominant factor, so that if we are comparing a number of amines having the same proton-accepting power, their dissociation constants in water will increase in the order tertiary < secondary < primary, and their K_a values in the reverse order. This would account for the separation of the three classes, as in Figure 2.

FIG. 3.



If the above view is correct, a better measure of the true basic strengths would be provided by dissociation constants in a solvent having less tendency to accept a hydrogen bond. It was in fact found by Brönsted, Nicholson, and Delbanco (*loc. cit.*) that, if basicity constants determined in *m*-cresol are used, no discrepancy is found for mono- and di-methylaniline in the decomposition of nitramide in that solvent. In the present instance, no data are available for acid–base equilibria in anisole solution, but the protolysis constants of six of the amines which we have used have been determined in *m*-cresol by Brönsted, Delbanco, and Tovborg-Jensen (*Z. physikal. Chem.*, 1934, **167**, 207). Figure 3 shows the relation between these constants (defined by $K_A = [B][C_7H_7OH]/[BH^+][C_7H_7O^-]$) and the catalytic constants in anisole. It is noteworthy that the points for mono- and di-methylaniline now lie on the same line as the primary anilines, thus supporting the view that the separation into three classes shown by Figure 2 is a peculiarity of the dissociation constants in water, and not of the kinetic data. The bearing of this conclusion on structural effects in basic dissociation constants will be discussed elsewhere.

The general features of the nitramide decomposition in anisole resemble those in other solvents, though the slope of the plots in Figure 2 (0·64) is lower than for aniline bases in water

(0·80), *iso*amyl alcohol (0·92) and *m*-cresol (0·84). It is of interest to compare the absolute rates of the reaction in different solvents. Table III gives the catalytic constants for aniline in the four solvents, the values in water and anisole being converted into those for 20°, assuming an activation energy of 20 k.-cals./mole (cf. Bell and Baughan, *Proc. Roy. Soc.*, 1937, *A*, **158**, 464).

TABLE III.

Catalytic constants for aniline at 20° (*log*$_{10}$, *minutes*).

Solvent.	Water.	*m*-Cresol.	*iso*Amyl alcohol.	Anisole.
K_c	0·97	0·15	0·033	0·0019
Dielectric constant	80	13	5·7	4·4

It will be seen that the rate decreases with decreasing dielectric constant, as would be expected for a reaction between two uncharged molecules, in which the transition state presumably involves a considerable charge separation.

The approximate value of 6 obtained for the catalytic constant of the nitramide ion in anisole is about 100 times as great as that of a primary aromatic amine having the same dissociation constant in water. The data for other solvents suggest (cf. Bell, "Acid–Base Catalysis," Oxford, 1941, p. 112) that this ratio would be at least 2000 for a carboxylate ion of similar strength. The nitramide ion thus has an abnormally small catalytic effect, just as in aqueous solution, in which its catalytic constant was found by Tong and Olson (*J. Amer. Chem. Soc.*, 1941, **63**, 3406) to be about 30 times smaller than that of a carboxylate ion of the same dissociation constant. The values given represent upper limits, since in each case a possible decomposition of the nitramide ion itself has been neglected.

These considerations have some bearing on the structure of the nitramide molecule, about which there is still some doubt. It is usually written $NH_2\cdot NO_2$, as originally suggested by Thiele and Lachmann (*Annalen*, 1895, **288**, 267). However, Hantzsch (*ibid.*, 1896, **292**, 340) maintained for many years that it was a stereoisomer of hyponitrous acid, HON:NOH, but eventually abandoned this structure in favour of NH:NO·OH (*Ber.*, 1930, **63**, 1270) in view of optical evidence on the structure of the ion of phenylnitroamine (Cambi and Szego, *ibid.*, 1928, **61**, 2081). The structure of the ion does not necessarily correspond with that of the undissociated molecule, and Pedersen (*J. Physical Chem.*, 1934, **38**, 581) interpreted the mechanism of decomposition by supposing that the equilibrium, $NH_2\cdot NO_2 \rightleftharpoons HN{:}NO\cdot OH$, is set up in aqueous solution, with $NH_2\cdot NO_2$ predominating; on the other hand, Kortüm and Finckh (*Z. physikal. Chem.*, 1940, **48**, *B*, 32) concluded from optical evidence that the equilibrium favoured the form, HN:NO·OH. Measurements of dipole moments by Hunter and Partington (*J.*, 1933, 309) were inconclusive, and these authors favoured the structure, $\overset{-}{N}{=}\overset{+}{N}(OH)_2$, which is not supported by any other evidence. The kinetic evidence mentioned above favours the view that nitramide exists predominantly as $NH_2\cdot NO_2$ in aqueous solution, since the low catalytic effect of the nitramide ion suggests that its formation is accompanied by a considerable electronic rearrangement. However, it would be desirable to obtain more direct evidence on this point.

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