690. *Rates of Ionization of* ·O–H *and* :N–H *Bonds.*

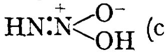
By R. P. Bell and R. G. Pearson.

It has been shown that the reaction of hydrogen ions with the anions of *p*-nitrophenol and 2 : 6-dinitrophenol reaches equilibrium in less than one millisecond, thus disproving earlier reports of a slow reaction. The reaction of ethylenedinitramine with aqueous ammonia has been studied by a flow method and shows a measurable rate during a few milliseconds. Ethylenedinitramine has also been investigated as a catalyst in the dehydration of acetaldehyde hydrate; it has an abnormally low catalytic power, thus resembling the nitroparaffins and other pseudo-acids. It is concluded that proton transfers to or from oxygen and nitrogen atoms will normally be too fast for direct observation.

Recorded examples of proton transfers which take place at a measurable rate are confined almost entirely to reactions involving a carbon–hydrogen bond, and it is generally considered that the transfer of a proton to or from an oxygen atom takes place too rapidly to be directly observed. There is however a report (Branch and Jaxon-Deelman, *J. Amer. Chem. Soc.*, 1927, **49**, 1765) that the ion of *p*-nitrophenol reacts at a measurable rate with hydrogen ions; the reaction was followed by conductivity measurements in 50% aqueous methanol, and with concentrations of about 0·005M half-times of several minutes were observed at −10°. A measurable rate seems not impossible for this type of proton transfer, since the anion and the acid differ considerably in charge distribution (cf. Bell, *J. Phys. Chem.*, 1951, **55**, 885), and the initial object of this work was to obtain further kinetic data with nitrophenols, by using modern methods for following fast reactions.

The first method employed was the thermal one developed by Bell and Clunie (*Proc. Roy. Soc.*, 1952, *A*, **212**, 16) which is suitable for the quantitative study of reactions with half-times down to about 3 seconds. The ions of *p*-nitrophenol and of 2 : 6-dinitrophenol were allowed to react with solutions of hydrochloric acid or with buffer solutions prepared from acetic or dichloroacetic acid. Concentrations were about 0·01M, and experiments were carried out at 0° and 25° in water and in 50% aqueous methanol. In every case the reaction was too fast to enable any estimate of its velocity to be made, which means that it must have been effectively complete in less than one second.

Similar results were obtained when the range of measurement was extended by using a flow method, in which the pH of the solution is determined spectrophotometrically very soon after mixing.* When the anions of *p*-nitrophenol and 2 : 6-dinitrophenol reacted at room temperature with hydrochloric acid, reaction was complete in less than one millisecond. These results are in direct conflict with Branch and Jaxon-Deelman's observations (*loc. cit.*), and agree with the usual view that proton transfers to and from oxygen atoms are extremely fast.

It seemed more probable that measurable rates could be obtained for proton-transfers to or from nitrogen atoms, and the acidic system chosen for study was $\cdot NH \cdot NO_2$. The decomposition of nitramine probably has a rate-determining step involving the removal of a proton from the nitrogen of  $HN{:}\overset{+}{N}{<}^{O^-}_{OH}$ (cf. Pedersen, *J. Phys. Chem.*, 1934, **38**, 581; Bell and Trotman-Dickenson, *J.*, 1949, 1288), and the simple nitroparaffins have a much lower rate of ionization than any other compounds containing a CH group of measurable acidity. Measurements were carried out on the reaction of ethylenedinitramine with aqueous ammonia: this reaction goes almost to completion, since the nitramine has $pK_1 = 5{\cdot}35$, $pK_2 = 6{\cdot}66$ (Lindley and Speakman, *J.*, 1949, 1657).

A sample of ethylenedinitramine was kindly given to us by Dr. A. H. Lamberton (Sheffield University) and was recrystallised from water. Its reaction with ammonia proved too fast to observe by the thermal method, but a measurable rate was recorded by using the flow method, with bromophenol-blue as indicator. (Independent experiments show that the response of this indicator to changes in acidity is effectively instantaneous.) By using 0·02M-ethylenedinitramine and 0·03M-ammonia solution at room temperature a pH change of 0·21 units was recorded in the time interval 0·7—4 milliseconds. This corresponds to the second stage of the reaction, *i.e.* if the nitramine is written as AH_2, the rate-determining process may be either or both of the two following reactions:

$$HA^- + NH_3 \longrightarrow A^= + NH_4^+ \quad \text{. . . . .} \quad (1a)$$

$$HA^- + OH^- \longrightarrow A^= + H_2O \quad \text{. . . . .} \quad (1b)$$

In any case the integration of the rate equation gives

$$\log \{[NH_3] - [NH_3]_\infty\} = -0{\cdot}01kt + \text{constant} \quad \text{. . . . . . .} \quad (2)$$

where $[NH_3]_\infty$ is the equilibrium ammonia concentration. This assumes that the equilibrium between NH_3 and NH_4^+ is effectively instantaneous, and also that the concentration of HA^- is almost constant at 0·01M: the latter assumption is valid for the part of the reaction studied. k is strictly speaking a composite constant involving both the forward and reverse constants of reactions (1*a*) and (1*b*), but the reverse reactions can be neglected under our experimental conditions. In the pH range observed ($\simeq 7$) almost all the ammonia present is in the form of NH_4^+, so that $[NH_3]$ is inversely proportional to $[H^+]$. The values of $[H^+]$ in the time interval 0·7—4 milliseconds can be estimated from the photographic record of the light absorption, and a plot of $\log \left\{\frac{1}{[H^+]} - \frac{1}{[H^+]_\infty}\right\}$ against time gives a straight line of slope $-0{\cdot}01k$.

The value thus obtained is $k = 1{\cdot}5 \times 10^5$ l./mole-sec., which may be compared with the value of about 0·007 l./mole-sec. obtained for the same composite constant in the reaction of nitroethane ($pK \simeq 9$) with aqueous ammonia (Pearson, *J. Amer. Chem. Soc.*, 1948, **70**, 204). If reaction (1*a*) is the rate-determining step, k is the second-order velocity constant for the reaction between HA^- and NH_3, but if the data are interpreted in terms of reaction (1*b*) as the rate-determining reaction the velocity constant for the reaction between AH^- and OH^- is about 10^8 l./mole-sec. This seems improbably high for a reaction between two ions of like charge, and we may conclude that reaction (1*a*) is more probable.

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* The apparatus used resembled that of Dubois (*J. Biol. Chem.*, 1941, **137**, 123) and its construction will shortly be described by E. F. Caldin and F. W. Trowse. The measurements were made for us in the Chemistry Department of Manchester University by Dr. F. W. Trowse, to whom our best thanks are due.

The measurable rate of reaction of ethylenedinitramine with ammonia should be paralleled by a low activity as an acid catalyst. A convenient reaction for investigating this point is the dehydration of acetaldehyde hydrate, previously investigated by Bell and Higginson (*Proc. Roy. Soc.*, 1949, *A*, **198**, 141). These workers found that a large number of carboxylic acids and phenols (including nitrophenols) obeyed the relation

$$\log_{10} k_e/p = 0{\cdot}54 \log_{10} (qK_A/p) + 3{\cdot}75 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where k_c is the catalytic constant of the acid (in $\log_{10}$, min.$^{-1}$, l., moles^{-1}), K_A its dissociation constant in water, and p and q statistical factors, while a number of pseudo-acids, such as benzoylacetone and the nitroparaffins, gave catalytic constants 1 or 2 powers of ten lower than those predicted by equation (3). Experiments were therefore carried out with ethylenedinitramine as a catalyst for the above reaction, using the same procedure as Bell and Higginson (*loc. cit.*) ; the results are given in the Table.

Dehydration of acetaldehyde hydrate at 25° catalysed by ethylenedinitramine.

[Catalyst]	$[CH_3{\cdot}CO_2H]$	k	k_e
0·0099	0·00033	0·0142	0·76
0·0149	0·00033	0·0174	0·73
0·0149	0·00245	0·0610	0·80
0·0161	0·00145	0·0371	0·50
0·0224	0·00245	0·0646	0·70
		Mean	0·70

All the solutions contained some acetic acid (formed by oxidation of acetaldehyde), the catalytic effect of which was allowed for in calculating k_c. The value calculated from equation (3), the first dissociation constant of the nitramine being used, is $k_c = 10$, so that the observed value is low by a factor of 14. This effect resembles that found by Bell and Higginson for the nitroparaffins, and justifies the describing of the nitramine as a pseudo-acid.

In view of the above results it seems likely that proton transfers to or from oxygen or nitrogen atoms can only be observed directly either by using special techniques for very fast reactions, or by using isotope-exchange methods for reactions which are thermodynamically very unfavourable.

Physical Chemistry Laboratory, Oxford.

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