80. *The Hydrolysis of Acetoxime.*

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The velocity of formation of acetoxime was studied by Barrett and Lapworth (J., 1908, **93**, 85), and Acree and Johnson (*Amer. Chem. J.*, 1907, **38**, 258; 1908, **39**, 300) investigated, not only this velocity, but also the equilibrium between acetone, hydroxylamine, hydrochloric acid, acetoxime, and water. The latter authors use this reaction as an important piece of evidence in favour of their theory of the rôle of the hydrogen ion in catalysis, according to which the hydrogen-ion concentration appears in the expression for the equilibrium constant for the reaction: $[(CH_3)_2CO][NH_3OH^\cdot]/[(CH_3)_2C{:}NOH][H^\cdot] = K$. Further, they assert that hydroxylamine is such a strong base that its salts are not hydrolysed, and replace $[NH_3OH^\cdot]$ by the total concentration of free hydroxylamine, obtaining $[(CH_3)_2CO][NH_2OH]/[(CH_3)_2C{:}NOH] = K[H^\cdot] = K_h$, in which K_h, instead of being a constant, is made to vary directly as $[H^\cdot]$. Acree and Johnson's experimental results are open to criticism on two grounds: (1) they measured only the hydroxylamine and disregarded the possible escape of the volatile acetone from their solutions, and (2) they assumed that the concentration of the hydrogen ion was equal to that of the hydrochloric acid used, accurate methods of measuring it not being then in general use.

It was thought that the author's method for the hydrolysis of acetonesemicarbazone (J., 1933, 204) might be applied to the hydrolysis of acetoxime. Difficulty was at first experienced in obtaining a constant value for K_h, the experimental values fluctuating and being much greater when obtained from acetone–hydroxylamine mixtures than from pure acetoxime; the explanation was found to depend on the fact that the reaction is catalysed by both acids and alkalis and is slow in their absence (Barrett and Lapworth, *loc. cit.*). Further, both products of the reaction are fugitive, acetone volatilising and hydroxylamine decomposing readily in the free state at the temperature chosen (50°). The latter effect can be very largely suppressed by the addition of hydrochloric acid, but this is a catalyst for the reaction, and it was desirable to obtain equilibria in neutral and uncatalysed, as well as in acid-catalysed, solutions. By combining the author's method (estimation of free acetone by means of its partial vapour pressure) with that of the above investigators (estimation of free hydroxylamine by titration with iodine), the total hydroxylamine (including that present as acetoxime) being determined by reaction with ferric sulphate, followed by titration with permanganate, it became possible to study the equilibria and obtain the hydrolytic constant even after 200 hours' heating.

It was necessary to work with buffered solutions, because acetoxime is a weak acid and hydroxylamine is a weak base. The volatilisation of the acetone was avoided by heating the solution in sealed glass tubes until equilibrium had been established, and then breaking the seal and discharging the solution into the vapour-pressure apparatus. As the reaction was slow, this operation could be carried out without risk outside the thermostat: in any case it only took a few seconds, during which the cooling would be slight. It was later established experimentally that equilibrium could be attained in a few hours (as stated by Acree and Johnson) and sealed tubes were no longer used.

Experimental.

The acetoxime was prepared in small batches from pure acetone and hydroxylamine hydrochloride, and recrystallised from warm light petroleum. Its purity was checked by analysis. The estimation of the free acetone was carried out as in the determination of the hydrolysis of its semicarbazone, and the free hydroxylamine by titration with $N/100$-iodine in presence of an acetate or phosphate buffer. The sealed tubes were of glass, about **2** cm. in diameter and of 50 c.c. capacity, each end being drawn out into a capillary and turned up at right angles to facilitate emptying and filling.

In experiments starting from hydroxylamine and acetone, it was necessary to neutralise the hydrogen chloride combined with the former by means of caustic soda. To ascertain whether the sodium chloride thus produced had any effect on the reaction, duplicate experiments on the hydrolysis of hydroxylamine were performed with and without the addition of the calculated amount of sodium chloride, but the results were unaffected. In experiments starting from hydroxylamine there was naturally much greater loss of hydroxylamine by decomposition than in those starting from acetoxime; *e.g.*, in 340 hours at 50°, the loss by decomposition in a sealed tube was 34%, whilst in the reverse direction in 197 hours at the same temperature the loss was only 3·8%. The addition of hydrochloric acid sufficient to bring the acidity to 0·004N (about p_H 2·4) reduced these figures to 0·7% for runs of a similar duration in both cases.

The concentration of acetoxime in the later experiments was about 1% (0·137 g.-mol./litre), and that of the hydroxylamine was equivalent. Owing to the slight hydrolysis very dilute solutions could not be used, and the degree of accuracy obtainable was not as high as in the case of acetonesemicarbazone. The p_H was measured by means of the Universal Indicator, and the buffer solutions were calculated from the data given by Clark (" Determination of Hydrogen Ions ").

In the table of results, col. 1 denotes the number of the experiment and also whether it was hydrolytic (H) or synthetic (S) in direction; col. 2 denotes the number of hours of heating; d, e, and f are the concentrations of hydroxylamine, acetone, and acetoxime respectively at equilibrium, and g is the percentage hydrolysis of the oxime.

Equilibrium between acetone, hydroxylamine, and acetoxime at 49·7°.

Expt.	Hours.	p_H.	$d \times 10^5$.	$e \times 10^5$.	f.	g, %.	$K_h \times 10^6$.
1 H	7	2·4	349	349	0·2490	1·4	48·9
2 H	149	2·4	234	330	0·1274	1·84	60·6
3 H	18	4·6	140	140	0·1356	1·03	14·5
4 S	6	4·6	300	613	0·1189		15·5
5 S	7*	5·5	20	825	0·0983		16·9
6 H	24	6·8	140	157	0·1354	1·15	16·15
7 S	4	9·5	850	511	0·1285		33·9
8 H	5	6·2	121	121	0·1358	0·90	10·85
9 H	197†	6·2†	162	162	0·1302	1·25	20·1

* Solution had been standing for a month at room temperature, hence large loss of hydroxylamine.

† Free hydroxylamine calculated by estimating total hydroxylamine and acetone, the iodine titration not having been adopted then. A small loss of hydroxylamine would not be detectable, but would suffice to make the calculated value of K_h unduly high.

In Expts. 8 and 9 there was no buffer, the p_H being determined solely by the reactants. In Expts. 1, 3, 8, and 9, *free* hydroxylamine was not estimated, but was assumed to be equal to the free acetone. The error thus involved can be seen by comparing Nos. 8 and 9 : the average value of K_h for these two, *viz.*, 15·5 × 10^{-6}, is close to the average of Nos. 3, 4, and 5, *viz.*, 16·2 × 10^{-6}.

DISCUSSION.

The above results show that from p_H 9·5 to p_H 4·6 the change in the value of K_h is small, whilst on Acree and Johnson's theory it ought to have increased 100,000-fold; even at p_H 2·4 it has only risen to four times its minimum value. The discrepancy between the results of those workers and of the author is probably due to the two causes outlined on p. 323 and to the fact that they ignored the possible decomposition of hydroxylamine. Their distinction between the various alternative mechanisms for the formation of acetoxime is therefore not justified. Acetoxime ($p_H = 6·24$ in 1% solution) may be considered a weak acid, and the small changes observed in the value of the equilibrium constant of the reaction are probably connected with changes in the activities of the reactants with p_H.

SUMMARY.

The equilibria between hydroxylamine, acetone, and acetoxime in dilute aqueous solution at 49·7° have been investigated by measuring the concentrations of all three substances at equilibrium. The value of K_h is about 16 × 10^{-6} in neutral solution, but

increases somewhat when the solution becomes very acid. It is concluded that hydrion is not involved in the equilibrium constant of the reaction, but may have a small influence in determining the active masses of the reactants.

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