

206. *The Kinetics of the Decomposition of Acetaldehyde-ammonia in Aqueous Acid Solution, and Some Notes on the Aldines.*

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A very pure form of acetaldehyde-ammonia can be prepared by the method of Aschan and Vaskio (*Ber.*, 1915, 48, 883). It decomposes according to the unimolecular law when treated in aqueous solution with hydrochloric acid. The products have a negligible influence on the decomposition rate, though the reaction is complicated by the slow formation in solution of an unstable form, which is instantaneously neutralised by acid. The formation of this form explains the various anomalies observed by previous investigators during molecular-weight determinations and corroborates the view that acetaldehyde-ammonia in solution is not one pure substance.

The rate of the unimolecular reaction is directly proportional to the fraction of stable form present in solution at the commencement of the run.

The preparation of certain aldines is described.

ACETALDEHYDE-AMMONIA decomposes so rapidly in the presence of hydrochloric acid that its purity may be determined by direct titration of known weights of the crystals in aqueous solution with standard acid, methyl-red being the most suitable indicator. It was observed that the neutralisation was not immediate, but that the red colour of the indicator slowly reverted to yellow in the later stages of the titration, becoming permanent only at the theoretical end-point.

Hydrofluosilicic acid and its salts behave similarly (Hudleston and Bassett, *J.*, 1921, 119, 407; Hudleston and Rees, *J.*, 1936, 1334), and though the entire reaction was complete in 1–2 minutes, the former authors investigated the kinetics of this unimolecular change with considerable accuracy by means of a simple apparatus. A similar apparatus was therefore employed to investigate the acetaldehyde-ammonia decomposition.

Two forms of acetaldehyde-ammonia are known, the m. p.'s differing by about 10°. It was therefore necessary to study these two varieties before starting the kinetic work.

Acetaldehyde-ammonia.—(1) Freshly distilled acetaldehyde (b. p. 20·8°) was dissolved in anhydrous ether and saturated with dry ammonia. The white crystals (m. p. 86–87°) were collected, washed with more ether, and kept in a desiccator. Known weights were titrated with standard hydrochloric acid, and the equivalent weight varied between 65 and 67 (Calc. : 61). This variation was consistently observed in more than a dozen determinations despite all precautions to ensure the purity of the initial reagents. It was thought possible that an etherate might be formed, but a preparation in carbon tetrachloride as solvent gave the same compound (m. p. 86°; equiv., 66·25). The crystals obtained from ether become light brown in the course of a few hours and smell distinctly of ammonia. If exposed to the air for a day, they become dark brown and finally volatilise, leaving a slight gummy residue. The rather high equivalent weight is therefore attributed to the instability of this compound, and it is probable that it has a different molecular configuration from the stable form (see below). Estimation of the aldehyde in the unstable form also gave a low result (Found : 65·8. Calc. : 72·2%), so the possibility of aldehyde of crystallisation is excluded.

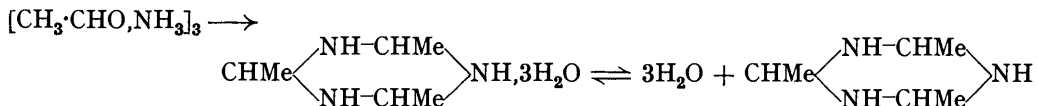
(2) Aschan and Vaskio (*Ber.*, 1915, 48, 883) obtained a form of acetaldehyde-ammonia (m. p. 95–97°) by adding acetaldehyde to ammonia solution (*d* 0·88) cooled in an ice-bath. In the present work, more than 30 freshly prepared samples of these crystals were analysed, the mean equivalent weight being 61·15, in excellent agreement with that calculated; the deviation never exceeded 0·3%. The m. p. was almost consistently 95°, and the crystals were fairly stable in air but went slightly brown after 4 or 5 days. It was therefore decided to use this form in the kinetic investigation.

If either form of acetaldehyde-ammonia is left for 24 hours in a vacuum desiccator containing sulphuric acid, it loses the elements of water, affording white cubes (m. p. 85°), which may be recrystallised from ether and give an equivalent on titration of 43·1 [Calc. for $(\text{CH}_3\text{CH}_2\text{NH})_n$: 43·0]. Occasionally, during the taking of the m. p. of this form, the entire mass liquefied at about 72°, and it was suspected that another form was also being produced. Accordingly, a freshly prepared sample of the anhydrous form was left in a vacuum desiccator for a month.

The cubes crumbled to a white, neutral powder which, on exposure to air, vanished completely in a few seconds.

The very unstable hydrochloride of acetaldehyde-ammonia was prepared by saturating an ethereal solution of the imine with hydrogen chloride; the excess of ether and hydrogen chloride were removed in a vacuum, the desiccator filled with dry nitrogen, and a sample removed for analysis in a stoppered bottle (Found: Cl, 42.3, 44.7. Calc. for $\text{CH}_3\cdot\text{CHO}\cdot\text{NH}_4\text{Cl}$: Cl, 44.7%). The existence of this compound indicates that the presence of water is essential before the acid can break up the acetaldehyde-ammonia molecule, for the decomposition is obviously non-existent in dry ether as solvent, even in the presence of excess acid.

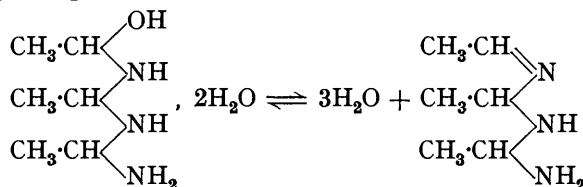
It has been suggested by Delépine (*Ann. Reports*, 1915, 83; see *Abs.*, 1898, i, 462), and by Moerman (*Z. Krist.*, 1938, 98, 447) from X-ray evidence, that acetaldehyde-ammonia is the trihydrate of trimethylhexahydrotriazine, the anhydrous form being formed as shown:



This structure has much to commend it. For instance, Delépine obtained a trinitroso-derivative, and Wöhler (*Annalen*, 1846, 61, 11), by passing hydrogen sulphide and selenide into solutions of acetaldehyde-ammonia, obtained the ether-soluble derivatives, thialdine and selenaldine, which have a ring structure corresponding to the Delépine formulation. Both these compounds were prepared during the present work, but the analogous telluraldine could not be prepared: it decomposed immediately, though the onion smell characterising the aldimines was immediately discernible. Selenaldine (m. p. 108°) also decomposes slowly, depositing red selenium.

The compound from propaldehyde-ammonia was also made; it was a colourless liquid with a pungent onion smell, immiscible with water but readily soluble in ether. Attempts to purify it by distillation at 20 mm., after drying over sodium sulphate, were unsuccessful, as it decomposed at 90° even under reduced pressure.

All these aldimines are readily decomposed by acids, giving free sulphur or its analogue, and many metallic salts (*e.g.*, silver nitrate) in aqueous alcohol give precipitates of the sulphides or selenides. The ring structure is thus not particularly stable, though it has been verified for the analogous paraldehyde by parachor measurements (Sugden, "The Parachor and Valency," p. 45). Aschan and Vaskio (*loc. cit.*), on the grounds that acetaldehyde-ammonia should be a fairly stable substance if it possessed the ring formulation, suggested the following alternative scheme, their cryoscopic determinations corroborating the trimeride initially proposed by Delépine:



The doubt which thus exists regarding the true nature of this compound renders difficult the exact interpretation of the kinetic results, though these show clearly the cause of anomalies observed by previous authors who have worked with this substance.

Kinetic Experiments.—Aldehyde-ammonia crystals (m. p. 95°) were prepared as previously described, washed with ether, and dried on the filter. Fresh samples were prepared for practically every run, and 0.1—0.2N-solutions were used for the experiments; 10 c.c. were placed in lightly-blown, glass bulbs, and these were placed in stout boiling-tubes containing various amounts of standard acid. The burette used to deliver the acid had its jet drawn out to a capillary. Owing to the well-known effect of acetaldehyde on rubber, the tubes were sealed with good-quality compressed corks, through which passed glass rods which practically touched the fragile bulbs. The bulbs were thus instantaneously shattered when the tubes were shaken.

One drop of indicator (methyl-red, light-filtered with methylene-blue) was placed in each tube, all solutions being made up with freshly distilled water as this indicator is very susceptible to traces of bicarbonate. The reaction time was taken by means of a stop-watch. With times of the order of 60 secs., the intermediate colourless transition stage of the indicator was taken as the end-point, but with shorter times the colourless phase passed so rapidly as to escape observation, the green colour following almost immediately on the disappearance of the purple tinge characterising the acid solution. For work at 0°, the tubes were covered with finely crushed ice, equilibrium being reached in 2—3 hours; at higher temperatures, they were clipped in a vertical position in a thermostat maintained at the desired temperature. Duplicate tubes were used in each case, and the mean times assumed correct. With practice, it was possible to obtain timings agreeing to 0.2 sec., though with the longer runs, when the reactants were present in almost equivalent proportion, differences of seconds were observed in the duplicate tubes. For this reason, it was not deemed advisable to approach nearer than 10% from the end-point.

The temperature rise that occurs on mixing remains practically constant in each run, and the temperatures given are the means within the tubes during the run. For instance, runs at 0° showed rises of 0.7—1.0° according to the concentrations employed. The following tables give examples of runs performed at low and at higher temperatures, N being the volume of hydrochloric acid, in c.c., required by 10 c.c. of the aldehyde-ammonia solution for complete neutralisation, and n the volume of acid actually used in the reaction vessel.

CH ₃ ·CHO, NH ₃ = 0.07838 <i>N</i> ; temp. 0.9°; log $N/(N - a) = 0.165$.					CH ₃ ·CHO, NH ₃ = 0.05954 <i>N</i> ; temp. 17.8°; log $N/(N - a) = 0.335$.				
<i>N</i> .	<i>n</i> .	log $N/(N - n)$.	Time, secs.	$k \times 10^5$.	<i>N</i> .	<i>n</i> .	log $N/(N - n)$.	Time, secs.	$k \times 10^5$.
19.33	12.02	0.4224	18.2	1415	21.72	21.00	1.4796	13.0	8800
	13.03	0.4870	21.7	1484		20.00	1.1014	8.8	8710
	14.04	0.5628	27.6	1442		19.50	0.9905	7.5	8738
	15.05	0.6529	33.5	1462		19.00	0.9023	6.5	8730
	16.06	0.7704	41.2	1470		18.50	0.8290	5.8	8520
	17.05	0.9284	51.5	1463		18.02	0.7665	4.8	8989
	18.05	1.1791	75.0	1352				Mean	8748
			Mean	1441					

An attempt was also made to study the reaction by breaking bulbs of solid acetaldehyde-ammonia under acid to see whether a (see below) in this case would be zero. Despite the great rapidity of dissolution of the solid, the results obtained were generally anomalous and led to no definite conclusions. This work, however, gave good reason for believing that even the solid form is considerably changed in properties after 4 or 5 days.

From aqueous solutions of both the aldehyde-ammonia forms, all attempts to isolate the dimeride have proved fruitless, the only products obtained by evaporation on a water-bath being oxyptaldin and oxytetaldin, which have been described by Wislicenus (*J. pr. Chem.*, 1858, 347) and von Babo (*ibid.*, 1897, 72).

DISCUSSION OF RESULTS.

In the foregoing tables, the velocity constants, k , have been computed as follows. It is assumed that in an equivalent of N c.c. of aldehyde-ammonia, a quantity a c.c. is instantaneously neutralised, leaving a quantity equivalent to $(N - a)$ c.c. of a slowly decomposing entity, the reaction then proceeding according to the equation

$$- dx/dt = k(N - a - x)$$

$$i.e., \quad kt = \log(N - a)/(N - n) = \log N/(N - n) - \log N/(N - a)$$

The plot of $\log N/(N - n)$ against t is thus linear, and the intercept $\log N/(N - a)$ will afford a measure of the fraction of total concentration which is neutralised instantaneously, *i.e.*, the concentration of the unstable form. The kinetic work thus establishes the existence of at least two forms in solution, which explains the low values obtained by Delépine and by Aschan and Vaskio for the trimeride molecular weight determined cryoscopically in aqueous solution. The latter authors also found that if their solutions were left for a day or so, the experimental molecular weight slowly fell, and they suggested a gradual change

to dimeride. The accompanying graph shows runs which were performed with the same aldehyde-ammonia solution on three successive days. The intercept is seen to increase gradually to an equilibrium value showing that at 0° about 50% of the aldehyde-ammonia is in the unstable form. The slope k is seen to decrease simultaneously. For this reason, it was not possible, except by chance, to duplicate any run; but the relation between the intercept and the slope was found to be perfectly general over a varied range of concentrations. This is revealed by the collected data (below), where X represents the normality of the aldehyde-ammonia solution used.

It will be seen that the velocity constant rises regularly as the intercept falls. Runs 7 and 8 were carried out in the presence of $N/10$ -ammonium chloride and 1% acetaldehyde respectively, and the results are so consistent with the others that it must be concluded that the products of the reaction exert a minor effect on the rate. Runs 14–18 were at higher temperatures, where the difficulties of working are much increased.

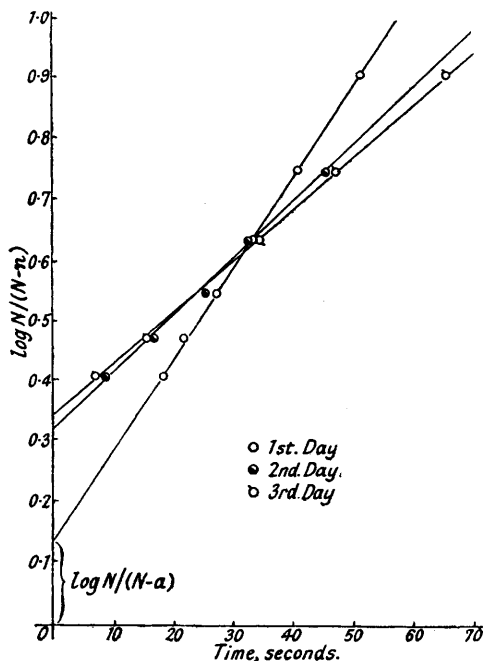
In the final column of the following tables, it is shown that the product $kN/(N-a)$ is practically constant for all the runs. This could be predicted from a kinetic equation of the form

$$-dx/dt = k_1[(N-a)/N][N-a-x] = k_1 f(N-a-x)$$

$$i.e., \quad [(N-a)/N]k_1 t = \log N/(N-n) - \log N/(N-a)$$

This equation is similar to that employed by Henry and Collan (*Z. physikal. Chem.*, 1892, 10, 96) in their study of the acid hydrolysis of esters, where f represented the fraction of acid in the ionic form; *i.e.*, $-dx/dt = fk(a-x)^2$.

The following experimental data show conclusively that the rate of the unimolecular decomposition is determined by the extent to which the slow change in solution has proceeded, the addition of acid removing one of the forms. It is true that, on distillation of aldehyde-ammonia with acid, free aldehyde is obtained, but whether, in dilute solution, the addition of acid yields ammonium chloride or a complex acetaldehyde-ammonium ion is uncertain, and until the true nature of the ionic or molecular species involved is established, the kinetic interpretation must remain speculative. The only conclusions which



Run.	N , c.c.	X .	$\log N/(N-a)$.	$k \times 10^4$.	Temp.	$10^4 kN/(N-a)$.
1	21.50	0.09057	0.470	69	0.9°	203.7
2	21.82	0.09747	0.380	85	1.0	203.9
3	19.33	0.07838	0.340	95	0.9	207.8
4	16.20	0.07240	0.265	110	0.7	202.5
5	15.48	0.03955	0.260	101	0.6	182.0
6	18.00	0.04950	0.250	103	0.6	183.1
7	17.90	0.07276	0.240	122	0.9	212.0
8	17.08	0.07628	0.230	124	0.9	210.6
9	16.20	0.07236	0.200	152	1.1	225.6
10	21.82	0.09747	0.192	145	1.0	225.6
11	19.33	0.07838	0.165	144	0.9	210.6
12	18.28	0.07700	0.150	152	1.0	213.8
13	12.10	0.07240	0.146	160	1.0	223.9
14	21.72	0.05954	0.335	875	17.8	1891
15	14.58	0.03996	0.905	245	17.8	1969
16	22.30	0.09396	0.480	845	17.9	2550
17	15.22	0.06403	0.430	900	17.8	2422
18	22.18	0.08887	0.450	910	17.7	2564

can now be drawn are that the decomposition follows the unimolecular law, the observed rate being a function of $f = (N - a)/N$, which represents the fraction of stable form present at the beginning of any run. Various runs were also taken with the form obtained from ether. The decomposition appeared similar, but the kinetic graphs invariably exhibited curvature and it was impossible to derive any general relation from work with this substance.

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