KINETICS OF THE CONDENSATION OF ACETALDEHYDE WITH AMMONIA

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Abstract—The reaction of acetaldehyde and ammonia to form α-aminoethanol in water and aqueous t-butanolic solutions at 5° has been studied kinetically by means of spectrophotometry. The reaction is reversible, the rate being expressed as: $v = k_1[CH_3CHO][NH_3]$ for the forward reaction and $v = k_1[CH_3CHOHNH_2]$ for the reverse reaction. The observed forward rate increase only slightly with increasing pH of the solution, while the reverse reaction is subject to acid catalysis over the pH range 9·4–11·1. The forward rate increases with increasing content of t-butanol in the aqueous solvent. A probable mechanism is suggested and discussed.

THE product of the reaction of ammonia with formaldehyde is hexamine, the reaction mechanism being rather complex as reported previously.[1,2] On the other hand, reactions with other aliphatic aldehydes result in the formation of α-aminoalcohols or hexahydrotriazine compounds. The reaction of ammonia with acetaldehyde generally yields crystalline triethylhexahydrotriazine trihydrate (I)[3,4] via α-amino-ethanol (II), but in aqueous solution the triethylhexahydrotriazine may dissociate

I
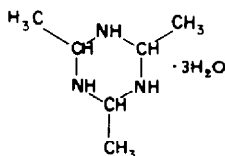
into α-aminoethanol. Since no kinetic studies have been reported on the reaction, the reaction has been studied kinetically in dilute solutions by estimating the concentration of acetaldehyde by means of spectrophotometry to elucidate the probable mechanism of the condensation (1).

$$NH_3 + CH_3CHO \;\rightleftharpoons\; CH_3CH\overset{\displaystyle OH}{\underset{\displaystyle NH_2}{\big<}} \qquad II \qquad\qquad (1)$$
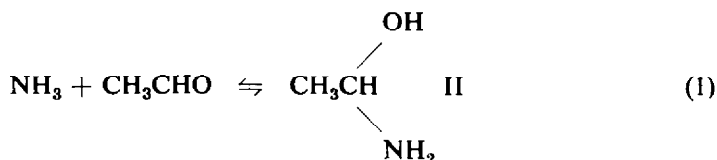
[1a] E. Baur and W. Rüetschi, *Helv. Chim. Acta* **24**, 754 (1941);

[b] J. R. Polley, C. A. Winkler and R. V. V. Nicholls, *Canad. J. Research* **25B**, 525 (1947);

[c] H. H. Richmond, G. S. Myers and G. F. Wright, *J. Amer. Chem. Soc.* **70**, 3659 (1948).

[2] Y. Ogata and A. Kawasaki, *Bull. Chem. Soc., Japan* in press.

[3] O. Aschan, *Ber. Dtsch. Chem. Ges.* **48**, 874 (1915).

[4] E. W. Lund, *Acta. Chem. Scand.* **5**, 678 (1951); **12**, 1768 (1958); *Chem. Abstr.* **46**, 8927 (1952); **54**, 6247 (1960).

RESULTS AND DISCUSSION

The condensation of acetaldehyde with ammonia yields triethylhexahydrotriazine trihydrate (I) which is reported in the literature.[3,4] The IR spectrum shows absorption maxima at wave numbers 3330 and 1510 cm^{-1} corresponding to —NH—, but no maximum corresponding to NH_2. The depression of freezing point in which dimethyl sulphoxide was used as the solvent indicates that the product exists mainly as monomeric α-aminoethanol in this ionizing solvent. Hence it is probable that the product exists also mainly in the form of aminoalcohol in dilute aqueous solution, where the molecular weight cannot be determined because of the easy dissociation of the product to aldehyde and ammonia.

The kinetic data satisfies the mechanism involving Eq. 1. The observed rate data are shown in Table 1.

TABLE 1. OBSERVED EQUILIBRIUM AND RATE CONSTANTS OF THE REACTION OF ACETALDEHYDE WITH AMMONIA IN AQUEOUS SOLUTIONS CONTAINING ACETIC ACID AT 5°. INITIAL CONCENTRATIONS: AMMONIA, 0·1M; ACETALDEHYDE, 0·1M

Added CH_3CO_2H N	pH	Equilibrium constant M^{-1} apparent K	true[a] K'	$k_1 \times 10^2$ M^{-1} sec^{-1}	$k_{-1} \times 10^4$ sec^{-1}
0·00	11·1	88·0	88·0	1·68 ± 0·03	1·19
·01	10·35	61·6	87·3	1·47 ± 0·01	2·39
·02	10·0	45·2	99·5	1·52 ± 0·02	3·37
·03	9·8	27·8	85·7	1·38 ± 0·01	4·97
·04	9·6	17·4	75·8	1·41 ± 0·02	8·10
·05	9·4	11·9	76·6	1·18 ± 0·01	9·93
			av. 85·5		

^{a} $K' = \dfrac{x_e}{(a - c - x_e)(b - x_e)}$, where c is the concentration of added acetic acid.

The apparent equilibrium constant K for equilibrium 1 varies, while the constant K' is constant (Table 1), where K values are calculated by assuming that added acetic acid deactivates equimolar ammonia. On the other hand, the equilibrium between the reactants and triethylhexahydrotriazine (I) is unlikely because the calculated equilibrium constant varies. Probably the product exists as α-aminoethanol in dilute aqueous solutions. Although the formation of imine has been observed in some amine-carbonyl reactions,[6a,6] the concentration of $NH{=}CHCH_3$ must be low here. since the solution has no indication of absorption maximum at near 230 mμ corresponding to C$=$N bond[5] and also the imine with little conjugation should be less stable than Schiff's base with effective conjugation.

The apparent rate constants for the forward reaction decrease very slightly with increasing acidity, whereas the constants for the reverse reaction increase sharply with

[5a] M. E. Hall, *Analyt. Chem.* **31**, 2007 (1959);

[b] R. P. Linstead and M. Whalley, *J. Chem. Soc.* 3530 (1955);

[c] G. E. Ficken and R. P. Linstead, *Ibid.* 3525 (1955).

[6a] P. Zuman, *Chem. Abstr.* **46**, 6084, 11041 (1952);

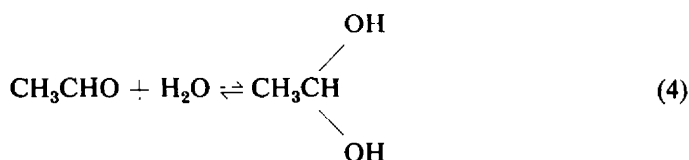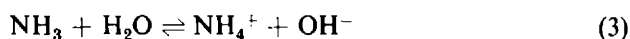[b] P. Zuman, *Chem. Abstr.* **47**, 1650, 7444 (1953);

[c] R. E. Van Atta and D. R. Jamisen, *Analyt. Chem.* **31**, 1217 (1959).

increasing pH of the solution. These results suggest that both reactions are subject to acid catalysis.

Assuming that the reactive species are free ammonia and unhydrated acetaldehyde, the forward rate v_f is expressed as:

$$v_f = k_f[NH_3][CH_3CHO] = k_f \frac{1}{1 + (K_3[H_2O]/[OH^-])} \cdot \frac{1}{1 + K_4[H_2O]}$$
$$\cdot (a - x)(b - x) \tag{2}$$

Here, k_f is the true rate constant for step 1, a and b are the initial stoichiometric concentrations of ammonia and acetaldehyde, respectively, and K's are the equilibrium constants of the subscripted steps.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{3}$$

$$CH_3CHO + H_2O \rightleftharpoons CH_3CH{\overset{\displaystyle OH}{\underset{\displaystyle OH}{\Big\langle}}} \tag{4}$$

Hence, the apparent rate constant for the forward reaction is expressed as:

$$k_1 = k_f \frac{1}{1 + (K_3[H_2O][H^+]/K_w)} \cdot \frac{1}{1 + K_4[H_2O]} \tag{5}$$

i.e., k_1 should be reversely proportional to the value of $[1 + (K_3[H_2O][H^+]/K_w)]$. Assuming that $K_3[H_2O]$ is $1 \cdot 36 \times 10^{-5}$,[7] $K_4[H_2O]$ is $1 \cdot 785$[8] and K_w is $0 \cdot 185 \times 10^{-14}$,[9] at $5°$, the calculated values of k_f from k_1 by Eq. 5 decreases with decreasing acidity of the solution (Table 2). Since acetic acid is converted almost completely to acetate ion in this pH range, k_f is expressed as:

$$k_f = k_{fw} + k_{fH}[H^+] \tag{6}$$

Here, k_{fw} and k_{fH} are the catalytic constants for water and oxonium ion, respectively. The values of k_{fw} and k_{fH} were calculated to be $4 \cdot 5 \times 10^{-2}$ M^{-1} sec^{-1} and $2 \cdot 6 \times 10^8$ M^{-2} sec^{-1}, respectively. Similarly, the rate constant for the reverse reaction may be expressed as:

$$k_{-1} = k_{rw} + k_{rH}[H^+] \tag{7}$$

The values of k_{rw} and k_{rH} were calculated by the least square method to be $1 \cdot 7 \times 10^{-3}$ sec^{-1} and $2 \cdot 2 \times 10^6$ M^{-1} sec^{-1}, respectively.

It was observed that the conversion or equilibrium concentration of the product increases with a decrease in ionizing power of solvent by the addition of t-butanol to the aqueous solution. This fact may be due to an increase in the rate constants of forward reaction but not to the decrease in the reverse rate. The plot of log k_1 vs. reciprocal of dielectric constant[10], $1/D$, is an approximate straight line. The phenomenon may be ascribed to a decrease in the degree of hydration of acetaldehyde

[7] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* A169, 190 (1938).

[8] The equilibrium constant, K_4, was determined by spectrophotometry according to R. Bieber and G. Trümpler, *Helv. Chim. Acta* 30, 1860 (1947).

[9] S. Glasstone, *Elements of Physical Chemistry* p. 510. D. van Nostrand (1946).

(K_4) and ionization of ammonia (K_3) at initial stages, i.e., to an increase in the relative concentration of reactive species or free acetaldehyde and free ammonia.

The apparent energy and entropy of activation, and the heat of reaction for the forward reaction were calculated to be 6.5 kcal mole^{-1}, -8.7 e.u., and -19.0 kcal mole^{-1}, respectively from the following average values of $k_1 \times 10^2$ M^{-1} sec^{-1}: $5°$, 1.34; $10°$, 1.64; $15°$, 2.00; K M^{-1}: $5°$, 85.5; $10°$, 45.9.

TABLE 2. THE VALUES OF k_f CALCULATED
FROM k_1 AND EQ. 5

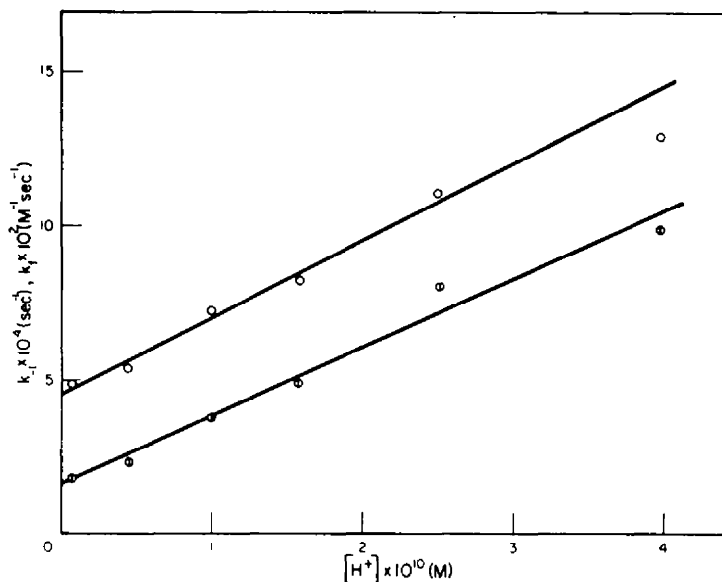| pH	$k_f \times 10^2$, M^{-1} sec^{-1}
9.4	12.96
9.6	11.20
9.8	8.30
10.0	7.35
10.35	5.46
11.1	4.96

FIG. 1. Plots of the rate constant vs. [H$^+$] for the reaction of acetaldehyde with ammonia
and the reverse one at 5°
O : forward   ⊕ : reverse

The deviation of the Arrhenius plot from the straight line at higher temperature is probably due to the aldol condensation of acetaldehyde. At 5° the aldol condensation of acetaldehyde is negligible at pH below 11, but at pH above 11 it becomes appreciable, which was confirmed in a buffer solution of acetaldehyde in the absence of ammonia.

[10] Dielectric constants of aqueous t-butanol mixtures were calculated by means of Akerlöf's equation. G. Akerlöf, *J. Amer. Chem. Soc.* **54**, 4125 (1932).

These results suggest a probable mechanism involving a simultaneous attack of ammonia and acid (HA) on acetaldehyde analogous to that in the reaction of aromatic aldehyde and semicarbazide in acidic media[11]
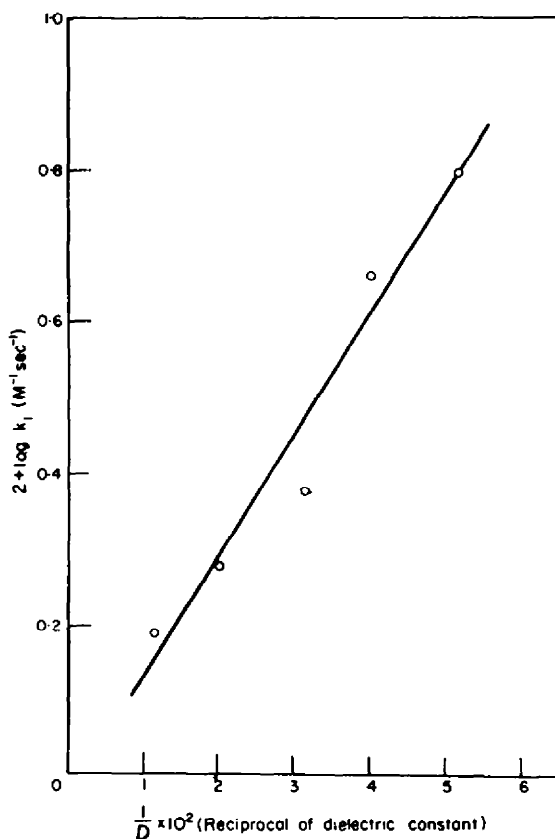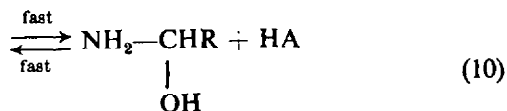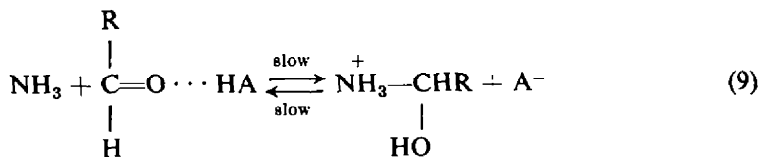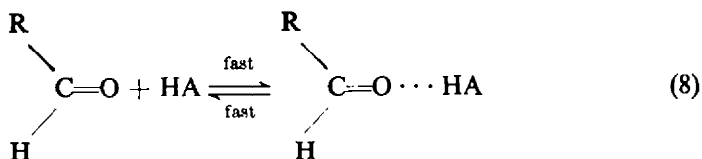
$$
\begin{array}{c}
\underset{H}{\overset{R}{\diagdown}} C{=}O + HA \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \quad \underset{H}{\overset{R}{\diagdown}} C{-}O \cdots HA
\end{array} \tag{8}
$$

$$
NH_3 + \underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}{=}O \cdots HA \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} \overset{+}{N}H_3{-}\underset{HO}{\overset{|}{C}}HR + A^- \tag{9}
$$

$$
\underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} NH_2{-}\underset{OH}{\overset{|}{C}}HR + HA \tag{10}
$$

FIG. 2. Plot of log k_1 vs. $1/D$ for the reaction of ammonia with acetaldehyde in various mixtures of t-butanol-water containing 0·02M acetic acid at 5°

[11] E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.* **84**, 4319 (1962).

It has been suggested that the rate-determining step for the butylamine-sulphonic acid-catalysed reaction of benzaldehydes with anilines in benzene is the attack of aniline on protonated aldehyde.[12]

EXPERIMENTAL

Materials. Ammonia used was of G. R. grade. Commercial acetaldehyde of C. P. grade was redistilled 5 times (b.p. 22–23°). It gave UV absorption spectrum with a single maximum at 278 mμ. Commercial acetic acid and t-butanol were redistilled, and had no absorption at wave-length over 265 mμ.

The reaction products criterion. A crystalline product, m.p. 92–93°[3] (in a sealed tube), was obtained in 74% yield by the condensation of conc. NH_4OH aq. (0·6 mole) with aqueous acetaldehyde (0·29 mole) at room temp. The product was composed of equimolar ammonia and acetaldehyde, having the characteristic IR spectra[13] of OH and NH: $\nu_{max.}^{Nujol}$ cm^{-1} 3440 (—OH), 3330 (—NH—)[14], 1510 (—NH—)[14], but no absorption maximum corresponding to C=N (1690–1640) or NH_2 (1650–1590) band was observed. The product had little absorption at wave-length over 250 mμ. The product was hexahydrotriazine trihydrate, but the determination of the molecular weight by means of depression of freezing point of a dimethyl sulphoxide solution gave the values of 62·1 and 62·7 which agree with that of α-aminoethanol (61·1). Hence it should exist as α-aminoethanol at least in this solvent.

Typical procedure for kinetic study. The rates were measured by following the decrease of the carbonyl peak at 278 mμ with a Shimadzu SV 50A spectrophotometer. 0·2 M Ammonia (50 ml) containing an appropriate amount of acetic acid and 0·2 M acetaldehyde (50 ml) were mixed in a flask and thermostated at 5°. Aliquots (about 4 ml) were pipetted out and introduced into cells at regular intervals of time, and the extinctions at 278 mμ were determined spectrophotometrically.

The forward and reverse rate constants were calculated by means of the following equations derived from Eq. 1.

$$k_1 = \frac{1}{t} \frac{2 \cdot 303 \, x_e}{ab - x_e^2} \log \frac{(ab - xx_e)x_e}{(x_e - x)ab} \tag{11}$$

$$k_{-1} = \frac{1}{K} k_1 = \frac{(a - x_e)(b - x_e)}{x_e} k_1 \tag{12}$$

Here, k_1 and k_{-1} are the apparent rate constants for the forward and reverse reactions, respectively, a the initial concentration of ammonia and b that of acetaldehyde, x the concentration of consumed acetaldehyde at time t and x_e that at the equilibrium, and K is the equilibrium constant of step 1. Since the reaction was fast, the values of k_1 were calculated from the slopes of plots of log $[x - (ab/x_e)/(x - x_e)]$ vs. t.

[11] E. R. Pratt and M. J. Kamlet, *J. Org. Chem.* 26, 4030 (1961).

[13] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (2nd Ed.) pp. 95, 248. Wiley, New York (1958).

[14] R. A. Russel and H. W. Thompson, *J. Chem. Soc.* 483 (1955); D. A. Barr and R. N. Haszeldine, *Ibid.* 4169 (1955).