THE ACID-CATALYSED ENOLIZATION OF ACETALDEHYDE: THE BASICITY OF ACETALDEHYDE*

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During an attempt to measure the basic strength of acetaldehyde spectro-photometrically, it was observed that in aqueous sulphuric acid solutions the carbonyl absorption of acetaldehyde was quickly swamped by an intense band which appeared at shorter wavelengths. It seems likely that this new absorption is due to crotonal-dehyde, produced in an acid-catalysed aldol condensation. The rate of appearance of an unsaturated condensation product has previously been used as a measure of the rate of the base-catalysed aldol condensation (Bell and McTigue 1960), and this procedure was used in the present work. The pK_a of protonated acetaldehyde has been estimated as $-2 \cdot 7$.

Experimental

All chemicals were purified commercial products. Spectrophotometric meas-urements were made with an Optica CF4 recording spectrophotometer at 25°C.

A strong absorption band, $\lambda_{max.} = 226$ mμ, appeared in an acetaldehyde solution in $3 \cdot 6$M sulphuric acid. Spectra of crotonaldehyde in water and in $3 \cdot 6$M sulphuric acid showed maxima at 224 and 226 mμ respectively. The rate of the condensation reaction was measured as the initial rate of change of optical density at the maximum of the band which appeared in the vicinity of 226 mμ. The exact position of the band maximum was a function of the sulphuric acid concentration. For $[CH_3CHO] < 0 \cdot 01$M, dD/dt decreased noticeably with time, and dD/dt at zero time was estimated graphically (Bell and McTigue 1960).

Reaction order with respect to acetaldehyde; $[H_2SO_4] = 3 \cdot 6$M

$[CH_3CHO]$ (M)	0·01	0·02	0·04	0·10
$10^4 \times (dD/dt)$ (sec^{-1})	1·66	3·5	6·5	16·5
$10^2 \times k_e$ (l mole^{-1} sec^{-1})	1·66	1·75	1·63	1·65

where dD/dt is the rate of change of optical density at zero time, and $k_e = (dD/dt)/[CH_3CHO]$.

Variation of reaction rate with acidity; $0 \cdot 001 \leqslant [CH_3CHO] \leqslant 0 \cdot 01$M

$\log k_e$	$-2 \cdot 86$	$-2 \cdot 12$	$-1 \cdot 58$	$-1 \cdot 04$	$-0 \cdot 86$	$-0 \cdot 31$	$-0 \cdot 28$
H_0	$-0 \cdot 14$	$-0 \cdot 67$	$-1 \cdot 58$	$-1 \cdot 95$	$-2 \cdot 60$	$-4 \cdot 16$	$-4 \cdot 74$

where H_0 is the Hammett acidity function.

Discussion

The first-order nature of the reaction implies that the rate-determining step in the formation of crotonaldehyde is some isomeric change, presumably enolization, in the acetaldehyde molecule, viz.:

$$CH_3CHO \; + \; H^+ \; \rightleftharpoons \; CH_3CHOH^+$$
$$CH_3CHOH^+ \, (+H_2O) \; \xrightarrow{\text{slow}} \; CH_2{:}CHOH + H^+$$
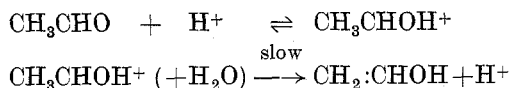
followed by non-rate-determining reactions, for example,

$$CH_3CHOH^+ + CH_2{:}CHOH \longrightarrow aldol + H^+,$$
$$Aldol \longrightarrow Crotonaldehyde + H_2O.$$
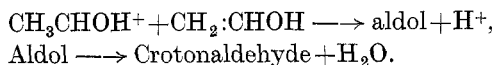
If we let K_a be the acidity constant of CH_3CHOH^+, k' the rate constant for the rate-determining step, and h_0 the acidity according to the usual Hammett function ($H_0 = -\log h_0$), then it can be shown that $k_e = k'h_0/(K_a + h_0)$. This relation leads to a nonlinear dependence of reaction rate on acidity, and by choosing $pK_a = -2\cdot7$ and $\log k' = -0\cdot28$ we obtain the solid line shown in Figure 1. The two limiting cases
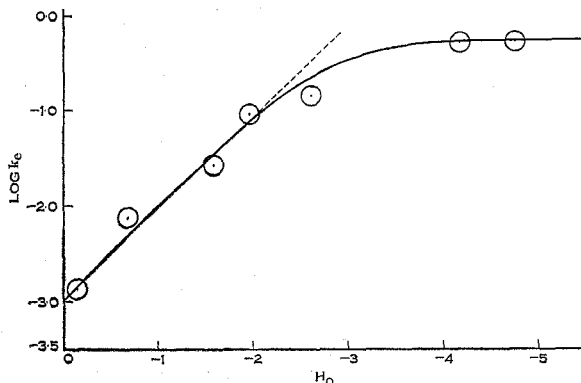

Fig. 1.—Acidity dependence of reaction rate.

of high acidity ($k_e = k'$), and low acidity ($\log k_e = -H_0 + \log[k'/K_a]$), are quite well defined, and the experimental points fall on the line within the limits of experimental error.

We would expect acetaldehyde to be a weaker base than acetone because of the electron-releasing effect of the methyl group, and a pK_a of $-2\cdot7$ for protonated acetaldehyde supports by inference the value of $-1\cdot6$ obtained for protonated acetone (Nagakura, Minegishi, and Stanfield 1957), although this work has been recently criticized (Campbell and Edwards 1960). The pK_a of protonated formaldehyde has recently been determined spectrophotometrically as $-3\cdot6$ (McTigue and Sime, unpublished data) which seems consistent with the above values.

The rate of enolization of acetaldehyde closely follows h_0 at low acidities, thus providing an example of an enolization reaction with a probable $A2$ mechanism, and an h_0 rate dependence, in disagreement with the original Zucker–Hammett hypothesis. This behaviour supports the interpretation of Archer and Bell (1959)

of the [H⁺]–dependence of acetone enolization, and raises doubts about the usual interpretation of the acidity dependence of acetophenone enolization (Zucker and Hammett 1939). An absolute value of k' cannot be obtained directly from the data presented here, since too little is known of the chemistry of the steps following the enolization. However we can make use of the curve D versus t plots observed at low acetaldehyde concentrations and high acidities to calculate a first-order rate constant in the usual fashion. Under these conditions we have the true first-order rate constant for the reaction, $k_1 = 0 \cdot 006$ sec⁻¹ and using 10,000 as the extinction coefficient for crotonaldehyde at 226 mμ, we calculate that $\sim 5\%$ of the acetaldehyde which enolizes is converted to crotonaldehyde. The above value of k_1 leads to $k_1/[H^+] = 1 \times 10^{-5}$ l mole⁻¹ sec⁻¹ at low acidities, compared with values of $2 \cdot 8 \times 10^{-5}$ and $1 \cdot 3 \times 10^{-5}$ respectively for the enolization of acetone (Archer and Bell 1959) and acetophenone (Zucker and Hammett 1939) at 25°C.

References

ARCHER, G., and BELL, R. P. (1959)—*J. Chem. Soc.* **1959**: 3228.
BELL, R. P., and McTIGUE, P. T. (1960)—*J. Chem. Soc.* **1960**: 2983.
CAMPBELL, H. S., and EDWARDS, J. T. (1960)—*Canad. J. Chem.* **38**: 2109.
NAGAKURA, S., MINEGISHI, A., and STANFIELD, K. (1957)—*J. Amer. Chem. Soc.* **79**: 1033.
ZUCKER, L., and HAMMETT, L. P. (1939)—*J. Amer. Chem. Soc.* **61**: 2779.