

THE BASICITY OF ACETALDEHYDE

George C. Levy and Joseph D. Cargioli

General Electric Research & Development Center, Schenectady, New York 12301

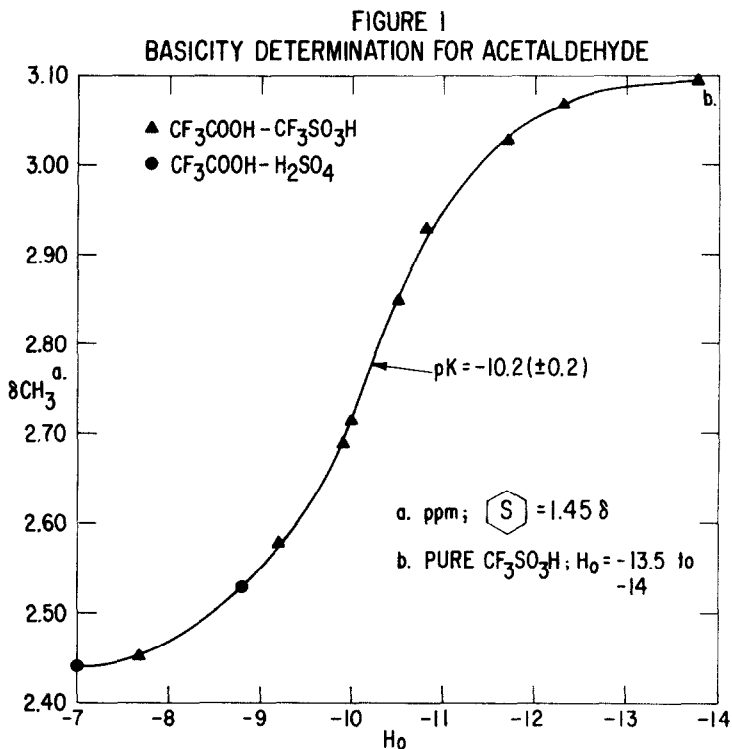
(Received in USA 12 December 1969; received in UK for publication 9 February 1970)

The protonation of ketones can be monitored by nmr.¹ Graphs plotting carbonyl substituent chemical shifts against (Hammett) medium acidity yield accurate pK values (actually H₀ values at half-protonation). Basicity constants determined in this way reproduce spectrophotometrically determined values found in the literature.^{1,2} Ketone and aldehyde basicity constants reported as H₀ values at half-protonation are not thermodynamically defined with respect to protonation in dilute aqueous acid. Nevertheless, for comparisons of similar compounds half-protonation values indicate real differences in basicity.

We have now used the nmr method to determine the basicity of acetaldehyde. Spectrophotometric determinations for acetaldehyde have not been reported, largely as a result of the instability of the system, and because hydration of the carbonyl group rapidly occurs in aqueous media. Using the non-aqueous acid systems CF₃COOH—H₂SO₄ and CF₃COOH—CF₃SO₃H it is possible to obtain accurate data for acetaldehyde over the entire range of protonation.

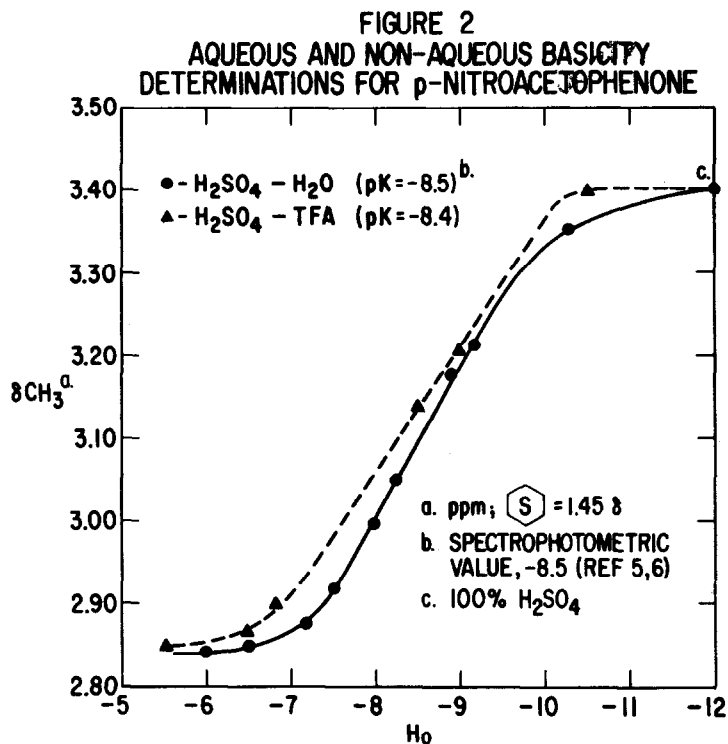
Acetaldehyde was added to the acid media at 0°, mixed thoroughly, and then warmed to 26° in the probe of the nmr spectrometer.³ The spectra were recorded within 3-5 min.

The rapid determinations in non-aqueous media largely removed problems associated with condensation and hydration of the acetaldehyde. Nevertheless, some condensation products were observed in the stronger acid systems.⁴ The experimental data are plotted in Figure 1. The curve shown does not correspond exactly to species and time averaged chemical shifts. Hydrogen bonding and other medium effects preclude precise calculation of base/protonated base ratios except close to the half-protonation value.



The observed pK value, -10.2, indicates that acetaldehyde is less basic than expected. Predictions of the basicity constant for acetaldehyde based on the constant observed for acetone and the analogous structural difference between benzaldehyde and acetophenone have led to an estimate of pK -8.5.^{5,6}

It could be argued that non-aqueous basicity constants are not comparable to basicity constants determined in $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$. However, nmr data suggest that at high acidity there is little difference between protonation behavior in aqueous and non-aqueous media. Thus the experimental curves for p-nitroacetophenone in $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ and $\text{CF}_3\text{COOH}-\text{H}_2\text{SO}_4$ are nearly equivalent (Figure 2).



The newly determined basicity value for acetaldehyde supports the non-protonation mechanism proposed by Pocker and Dickerson⁷ for hydration of acetaldehyde (and other aliphatic aldehydes) in dilute aqueous acids. The low basicity of acetaldehyde supports Pocker and Dickerson's conclusion that mechanisms such as that proposed by Gruen and McTigue⁸ may not be tenable.

ACKNOWLEDGEMENT

$\text{CF}_3\text{SO}_3\text{H}$ was given to us by The Minnesota Mining & Manufacturing Company. The acidity of the $\text{CF}_3\text{COOH}-\text{CF}_3\text{SO}_3\text{H}$ system was evaluated using $\text{FCH}_2\text{COCH}_3$ ¹ and cyclobutanone⁹ as indicator bases.

REFERENCES AND NOTES

- (1) G. C. Levy, Chemical Communications, 1257 (1969).
- (2) Spectrophotometric constants reproduced $\pm 0.1 - \pm 0.2$.
- (3) A Varian A-60 spectrometer equipped with variable temperature control was used. Probe temperature with N_2 flowing and the control system switched off was $26^\circ \pm 2^\circ$.
- (4) The half-life of the acetaldehyde—protonated acetaldehyde mixture in CF_3COOH — CF_3SO_3H (H_0 , -10.7) was ~ 15 min. In CF_3COOH — H_2SO_4 (H_0 , -5.5) $T_{1/2}$ was ~ 15 hrs.
- (5) E. M. Arnett, Prog. Phys. Org. Chem., 1 (Interscience, New York) 1963; M. L. Ahrens and H. Strehlow, Disc. Faraday Soc., 39, 113 (1965).
- (6) pK Values corrected to the H_0 scale as evaluated by M. J. Jorgenson and D. R. Hartter, J. Am. Chem. Soc., 85, 878 (1963).
- (7) Y. Pocker and D. G. Dickerson, J. Phys. Chem., 73, 4005 (1969).
- (8) L. C. Gruen and P. T. McTighe, J. Chem. Soc., 5224 (1963).
- (9) G. C. Levy, unpublished data.