The Basicities of α-Halogeno-ketones

By GEORGE C. LEVY

(*General Electric Co., Research and Development Center, Schenectady, New York* 12301)

Summary Measurement of ^{1}H n.m.r. chemical shifts gives basicity constants for α-halogen-substituted acetones.

THE effect of α-halogen substitution on ketone basicity has been discussed on a qualitative basis by several authors.[1] According to their studies, the basicity of the carbonyl oxygen in halogenated ketones is significantly decreased with respect to both hydrogen bonding and protonation. However, no actual basicity constants have been reported.

We have now determined quantitatively the basicities of several halogen substituted acetones using ^{1}H n.m.r. chemical shifts. The results of the present work are given in the Table, along with similarly determined constants for ketones of known basicity. The n.m.r.-determined basicity values are compared to spectrophotometrically-determined literature values for the non-halogenated compounds. Even monohalogeno-ketones are extremely non-basic. The reduction in the basicity of acetone due to monohalogen substitution is comparable to the change in basicity observed when a *para*-nitro-group is substituted for a *para*-methoxy-group in the acetophenone series. Multiple halogen substitution produces a further, approximately linear, decrease in ketone basicity (*ca.* 2 H_0 units *per* halogen). It is clear from the data that bromo- and chloro-ketones are not significantly more basic than fluoro-ketones. This fact is somewhat surprising but is consistent with the similar Taft, σ_I, constants for monohalogenated substituents.[2]

A detailed description of the n.m.r. method employed for determination of ketone basicity will be forthcoming.[3] The method relies on the sensitivity of carbonyl group substituent chemical shifts to protonation of the ketone. When the substituent chemical shift is plotted against the acidity of the medium, a "titration curve" is obtained. The mid-point of this curve is taken as the p*K* value, or more exactly, H_0 at $\frac{1}{2}$ protonation. In order to record meaningful data, the internal n.m.r. standard used must be insensitive to acidity change in the media studied. In the strongly acidic systems discussed in this communication, we used either 0·01M-tetramethylammonium chloride or cyclohexane. Ketones were run at 0·1M concentration. Lower concentrations did not significantly change the observed p*K* values. Ketone concentrations greater than 0·5—1·0M resulted in appreciable buffering of the acid media and subsequent loss of accuracy.

TABLE. *Ketone basicity constants*

Compound	$-H_0$ at ($\frac{1}{2}$) protonation[a]	Literature values[b]
Monofluoroacetone	10·7	
Monochloroacetone	10·6	
Monobromoacetone	10·6[c]	
1,3-Difluoroacetone	12·7[d]	
1,1,1-Trifluoroacetone ..	14·7	
1,1,1-Trichloroacetone ..	14·6	
1,1,2,2-Tetrafluoroacetone ..	*ca.* 17[e]	
Acetone	7·5	7·5
p-Methoxyacetophenone ..	4·9	4·8
p-Nitroacetophenone ..	8·5	8·5

[a] At 26° (±2°). Estimated maximum error ±0·3 unit. Probable error <0·2.

[b] Spectrophotometric (ref. E. M. Arnett, *Prog. Phys. Org Chem.*, 1963, **1**). Corrected to present H_0 scale (M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.)

[c] Decomposes readily.

[d] Estimated error <±0·5 unit.

[e] Cannot be fully protonated.

Advantages of the n.m.r. technique for the present study include the ability to work at variable temperatures, rapidity of measurement, and the insensitivity of the method to appreciable ketone decomposition. The acid media used in equilibrium measurements included the H_2SO_4–H_2O, H_2SO_4–CF_3CO_2H, H_2SO_4–FSO_3H, and FSO_3H–SbF_5 systems.[4]

(*Received, August* 14*th*, 1969; *Com.* 1250.)

---

[1] (a) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, 1965, **42**, 2752; (b) D. Cook, *J. Amer. Chem. Soc.*, 1958, **80**, 49; (c) P. Greenzaid, Z. Luz, and D. Samuel, *Trans. Faraday Soc.*, 1968, **64**, 2780, 2787.

[2] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2441, and earlier references.

[3] Oral presentation, 158th National Meeting, American Chemical Society, New York, September, 1969.

[4] The FSO_3H–SbF_5 system has been evaluated by R. J. Gillespie (personal communication).