Restricted Rotation in Substituted Acetophenones and Benzaldehydes: an Interesting Solvent Effect

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PROTON SPECTROSCOPY has been employed as a tool for the estimation of potential barriers to rotation about σ-bonds to carbonyl groups in several systems in which this bond possesses some π-character.[1] Amides and closely related derivatives have received most attention, but estimates for some benzaldehydes have been presented.[2] We report results for the *p*-*NN*-dimethylamino- (A) and *p*-methoxy- (B) derivatives of benzaldehyde (I) and acetophenone (II), obtained by examination of the temperature dependence of their ^{1}H n.m.r. spectra in toluene solution. Comparison with the results for (IA) in vinyl chloride solution reveals an interesting solvent effect.

These compounds exist in either of two equivalent planar forms, (i), which are stabilized by resonance interactions such as (ii). Because of resonance contributions, the barrier to rotation about the C(1)–CO bond is appreciable and will depend on substituents X and R. Toluene was chosen as

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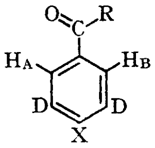
TABLE

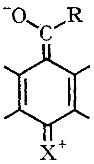
Spectral data for ortho-*protons in* (I) *and* (II)

Compound	Solvent	Chemical shift ν_{AB} (c./sec.)[a]	T_c (°C)	$\Delta F^{\ddagger}$ (kcal./mole)[b] at T_c	at 300°K
$[^2H_2]$-(IA)	$[^2H_8]$toluene	71	−56	10·5	12·9
	vinyl chloride	14	−73	10·2	9·2
$[^2H_2]$-(IB)	$[^2H_8]$toluene	88	−75	9·4	12·4
$[^2H_2]$-(IIA)	$[^2H_8]$toluene	80	−92	8·5	9·1
$[^2H_2]$-(IIB)	$[^2H_8]$toluene	—	−116	$\leqslant$7·3	—
	vinyl chloride	—	−142	~6·5	—

[a] at 60 Mc./sec.; [b] ± 0·5 kcal./mole.



(i)



(ii)

solvent since relatively large chemical shift differences can be expected for the two *ortho*-environments in (i) because of solute–solvent association.[3] The 3,5-dideutero-derivatives were examined, with spin-decoupling at 9·2 Mc./sec., to obtain simple AB spectra for the aryl protons. Analysis of the spectra[4] below the coalescence temperature, T_C, allowed estimates of the rate of rotation, *k*, over a temperature range. Using the Eyring rate equation, $\Delta F^{\ddagger}$ was calculated for each case. In addition, $\Delta F^{\ddagger}$ was determined at T_C from the single *k* value. The results are collected in the Table and, for comparisons, $\Delta F^{\ddagger}$ is given at 300°K.

Anet and Ahmad[2] have reported $\Delta F^{\ddagger}$ values for (IA) and (IB) in methylene chloride and vinyl chloride, respectively, as 10·8 and 9·2 kcal./mole, in good agreement with the present data if compared *at the coalescence temperature*, T_C. Our data, however, indicate a significant temperature dependence of $\Delta F^{\ddagger}$ for $[^2H_2]$-(IA), which is solvent dependent. $[^2H_2]$-(IB) and $[^2H_2]$-(IIA) exhibit similar behaviour in toluene solution. Unfortunately the low barrier for $[^2H_2]$-(IIB) precludes measurement of the temperature dependence of $\Delta F^{\ddagger}$ by the method employed. We suggest that an entropy contribution due to solute–solvent association in toluene solution is responsible for the observations. Further studies of solvent effects on this barrier are in hand using a different experimental technique, to extend our rate measurements over a larger temperature range (*i.e.*, above T_C).

(*Received, January* 30*th*, 1967; *Com.* 089.)

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[1] For general reviews, *cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon, London, 1965, p. 553; L. W. Reeves in "Advances in Physical Organic Chemistry", Vol. 3, ed. V. Gold, Academic Press, New York, 1965, p. 252; K. H. Abramson, P. T. Inglefield, E. Krakower, and L. W. Reeves, *Canad. J. Chem.*, 1966, **44**, 1685.

[2] F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, **1964**, **86**, 119.

[3] R. E. Klinck and J. B. Stothers, *Canad. J. Chem.* **1962**, **40**, 1071, 2329; **1966**, **44**, 37; R. E. Klinck, Gurudata, and J. B. Stothers, *Canad. J. Chem.*, 1967, **45**, 213.

[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, p. 224.