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A POSSIBLE SOURCE OF THE BAKER-NATHAN ORDER OBSERVED IN THE ADDITION OF HYDROGEN CYANIDE TO PARA-ALKYL BENZALDEHYDES

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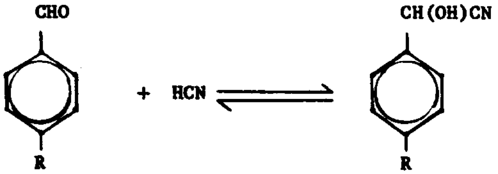
THE trend in the equilibrium constants for the addition of HCN to *para*-alkyl-benzaldehydes:



R = Me; Et; s-Pr and t-Bu has often been quoted as providing reasonably conclusive evidence for hyperconjugation.[1,2] Since the importance of hyperconjugation in the *ground states* of molecules has recently been the subject of considerable iconoclastic scrutiny[3] it is of particular interest to examine sources other than those which are electronic in origin to account for the experimentally observed order in the above series of reactions. Two sources which merit consideration are: (a) solvation differences between the cyanhydrin and the aldehyde; (b) the 'ponderal effect' of the *para*-alkyl groups (*cf.* Ingold[4]). The possibility that solvation differences might be important in determining the Baker-Nathan order has been considered by several workers particularly in relation to

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[1] J.W. Baker, *Tetrahedron* 5, 135 (1959).

[2] J.W. Baker, *Hyperconjugation*. Oxford University Press (1952).

[3] M.J.S. Dewar and H.N. Schmeising, *Tetrahedron* 5, 166 (1959).

[4] C.K. Ingold, *Quart. Rev.* 11, 1 (1957).

a rate study of the methanolysis of para-alkyl-benzyl chlorides.[5] However, in the present instance this effect appears as a difference between two similar neutral structures, i.e. the cyanhydrin and aldehyde, and in consequence we deem it of secondary importance, contrasting with the above mentioned study[5] where one of the states (the activated complex) is charged. If solvation differences are ignored the equilibrium may be discussed in the gas phase and the 'ponderal effect' of the para-alkyl groups evaluated by means of equation (1) derived from statistical mechanics:[6]

$$- \log K = \frac{\Delta E_0^0}{2.3026\ RT} - 3/2 \log \frac{M_P}{M_R^1 M_R^2} - \log \frac{I_P}{I_R^1 I_R^2} \qquad (1)$$

with the assumptions that vibrational factors are unimportant and symmetry factors are not involved. The symbols in equation (1) have their usual significance and the subscripts P refer to the product (cyanhydrin) and R the reactants (1 refers to the HCN molecule and 2, the aldehyde). Because of the molecular complexity of the aldehyde and cyanhydrin it is not feasible to evaluate the final (rotational) term in equation (1), however, the third (translational) term is readily computed and may be compared with the observed values of log K.[2] The relevant data is given in Table 1 and illustrated graphically in Fig. 1.

It is apparent from the slope of the log K vs. 3/2 log $M_P/M_R^1 M_R^2$ plot that the variation of the latter quantity will account for ca. 40 per cent in the former as the structure of the R group is varied. Although the proposed rationalization of the Baker-Nathan order offered here has obvious limitations, it serves to emphasize that the interpretation of relatively

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[5] R.A. Clement, J.N. Naghizadeh and M.R. Rice, J. Amer. Chem. Soc. 82, 2449 (1960).

[6] J.R. Partington, An Advanced Treatise on Physical Chemistry Vol. 1, Section IV, p. 375. Longmans, Green, London (1949).

TABLE 1

R	-log K	$-3/2 \log M_P/M_R^1 M_R^2$
Me	2.047	2.015
Et	2.088	2.028
s-Pr	2.095	2.038
t-Bu	2.126	2.047

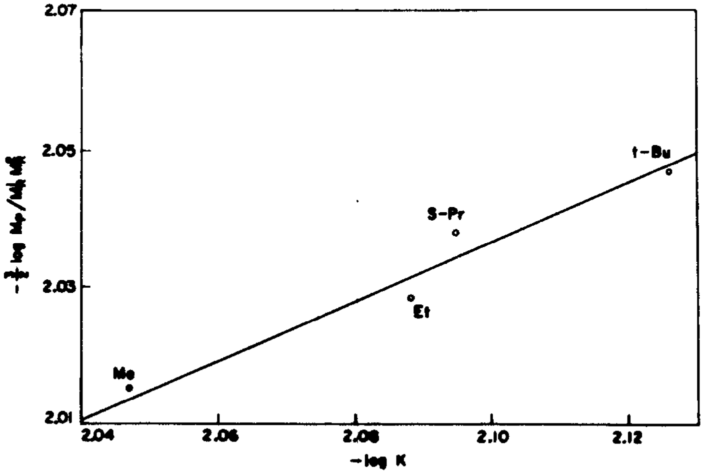

FIG. 1

small reactivity differences on an electronic basis alone is fraught with considerable uncertainty, and it may well be that the 'ponderal effect' would suffice to account for the complete trend in log K if it were also possible to evaluate the rotational term in equation (1).