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A BAKER-NATHAN ORDER IN A HYDROGEN BONDED SYSTEM AT EQUILIBRIUM

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Abstract—Equilibrium constants for hydrogen bonding of n-amyl alcohol to a series of *p*-alkylbenzonitriles have been measured using an IR technique. These constants follow the Baker–Nathan order. The possible significance of this order relative to the hyperconjugation theory and other theories bearing on the Baker-Nathan order is discussed.

THE "Baker-Nathan" or "reverse" order[1] of alkyl substituent effects occurs in a variety of reactions, but the reasons for it remain moot.[2–4] It is widely agreed that hyperconjugation or whatever causes the Baker-Nathan order is more important in excited states (e.g., transition states) than in ground states of molecules.[5] Rate studies illustrate the effect in excited states, and it has been assumed that equilibrium measurements illustrate ground state Baker-Nathan effects. Of the equilibria reported, some give the expected order[6,7] and several give equivocal orders.[8–11] All of the equilibria previously studied involve fairly energetic reactions or separation of charges. This paper reports equilibrium hydrogen bond formation for a set of alkyl substituted benzonitriles. The low energy involved in the formation of this bond and the order of the equilibrium constants help to evaluate some of the theories for the Baker-Nathan order.

RESULTS AND DISCUSSION

Equilibrium constants at 26° for:

$$p\text{-RC}_6\text{H}_4\text{CN} + \text{HOC}_5\text{H}_{11} \rightleftharpoons p\text{-RC}_6\text{H}_4\text{CN}{:}\text{HOC}_5\text{H}_{11} \qquad (1)$$

were determined with n-amyl alcohol for the series R = hydrogen, methyl, ethyl, isopropyl, t-butyl. The IR band intensity of the alcohol-to-nitrile hydrogen bond was measured using four sets of initial concentrations for each substituted nitrile. With a combination of the equilibrium expression and Beer's law, such intensity data can be used to determine the equilibrium constant and the apparent extinction coefficient.

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[1] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1953).

[2] E. Berliner, *Tetrahedron* **5**, 202 (1959).

[3] J. W. Baker, *Hyperconjugation.* Oxford Press, England (1952).

[4] M. J. S. Dewar, *Hyperconjugation.* Ronald Press, New York (1962).

[5] Ref. 3 p. 30 and Ref. 4 p. 13.

[6] N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.* **73**, 553 (1951).

[7] J. W. Baker and M. L. Hemming, *J. Chem. Soc.* 191 (1942); J. W. Baker, *Tetrahedron* **5**, 135 (1959).

[8] J. W. Baker, J. F. J. Dippy, and J. E. Page, *J. Chem. Soc.* 1774 (1937).

[9] H. C. Brown and X. R. Mihm, *J. Amer. Chem. Soc.* **77**, 1723 (1955).

[10] N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.* **77**, 3051 (1955).

[11] E. Berliner, unpublished results on ionization of anilinium ions and 2-nitrophenols mentioned in Ref. 2.

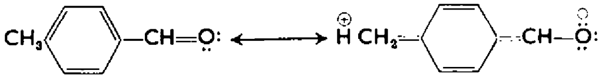
This was first shown for UV spectra[12] and later extended to IR spectra.[13] In these studies as in the earlier studies[12,13] the solvent changes from 40% to 80% carbon tetrachloride, most of the remainder being one of the compounds under study (a nitrile). While these seem like drastic solvent changes, they do not have a significant effect on the spectra and therefore on the equilibrium positions. In fact, excellent, linear intensity-concentration function plots are observed throughout. The validity of these data are also supported by the small effect (±2%) on both the optical density or integrated intensity of the nitrile band in carbon tetrachloride–dimethyl sulfoxide mixtures containing from 25% to 100% dimethyl sulfoxide.[14] Also, only a small effect should be expected in an equilibrium position involving non-charged species when small changes in dielectric constant are made.

The experimental data are given in Table 1. The equilibrium constants and free energies are given in Table 2 along with the equilibrium constants for equilibrium II.[7]

$$p\text{-RC}_6\text{H}_4\text{CHO} + \text{HCN} \rightleftharpoons p\text{-RC}_6\text{H}_4\text{CH(OH)CN} \qquad \text{(II)}$$

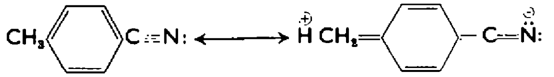
With the possible exception of the ethyl compound, the series definitely follow the Baker-Nathan order.

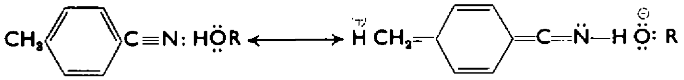
The opposing directions of K's for the two sets of equilibria are at first glance surprising. Baker rationalized the order of his substituents using the resonance theory with hyperconjugative contributions. He said that the stabilizing structures for the aldehyde (III) are absent in the cyanohydrin product.


(III)

Therefore, the groups which hyperconjugate best stabilize the starting material best and tend to react less (have lower equilibrium constants).

The hydrogen bonded nitrile order is more difficult to rationalize because of the similar resonance contributions in the reactant and the product. However, assuming hyperconjugation, resonance stabilization probably does more for V than IV because of its more extended electronic system.


(IV)


(V)

Therefore, the product is more stabilized by hyperconjugation than the reactants in reaction I. The equilibrium constants should be largest for hyperconjugating substituents, so both I and II follow a rationalized Baker-Nathan order.

The occurrence of the "reverse" alkyl substituent effects for equilibria I and II and many rate studies may have a common explanation. If this is true then something is to be learned for all cases from the present hydrogen bonding case. It represents the lowest energy reaction yet reported to show the Baker-Nathan effect. Hydrogen bond formation generates only 3–7 kcal/mole, and the energy of activation for its formation is probably small.

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[12] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* **71**, 2703 (1949).

[13] L. L. Ferstandig, *J. Amer. Chem. Soc.* **84**, 3553 (1962).

[14] C. D. Ritchie, B. A. Bierl, and R. J. Honour, *J. Amer. Chem. Soc.* **84**, 4687 (1962).

Structures such as V show how hyperconjugation can be used to explain the Baker-Nathan effect for this system. However, there remains a question of the plausibility of these structures contributing in a significant way to the low energy hydrogen bonded hybrid. While the order fits the hyperconjugation theory, the energies may not.

TABLE 1. EQUILIBRIUM DATA FOR p-RC_6H_4CN AT 26°

Quantities, ml[a] n-Amyl alcohol	p-RC_6H_4CN	CCl_4	Absorbance[b]	Base, mole fraction^{-1}	Slope $\times 10^3$	Intercept $\times 10^3$	ε l. m^{-1} cm^{-1}
	R = H						
0·0242	0·994	3·98	0·256	5·24	1·65	8·26	122
0·0242	1·99	2·98	0·338	2·59			
0·0242	2·99	1·99	0·395	1·71			
0·0115	0·994	0·994	0·441	2·06			
	R = CH_3						
0·0247	0·798	6·63	0·284	8·25	0·818	8·81	114
0·0247	1·60	5·33	0·361	3·91			
0·0247	2·40	4·03	0·416	2·47			
0·0118	0·798	1·87	0·458	3·05			
	R = C_2H_5						
0·0247	0·738	4·24	0·211	11·1	0·955	10·2	98
0·0247	1·99	2·98	0·323	3·10			
0·00607	0·472	0·522	0·406	2·55			
0·00944	0·472	0·525	0·268	5·50			
	R = i-C_3H_7						
0·0247	0·994	3·98	0·243	7·26	1·07	10·8	93
0·0247	0·738	4·24	0·202	9·99			
0·0247	1·99	2·98	0·315	3·34			
0·0118	0·994	0·994	0·373	2·56			
	R = t-C_4H_9						
0·0247	0·994	3·98	0·248	7·95	1·10	8·96	112
0·0247	1·99	2·98	0·340	3·60			
0·0247	2·99	1·99	0·378	2·16			
0·0118	0·994	0·994	0·451	2·74			

[a] Densities (g/ml) used to calculate mole fractions: n-amyl alcohol, 0·8144; CCl_4, 1·595; R = H, 1·021; R = CH_3, numbers in table refer to wt in g; R = C_2H_5, 0·970; R = i-C_3H_7, 0·962; R = t-C_4H_9, 0·9515.

[b] Absorbance with 0·964 mm cell at peak maxima (in usual order: 3544, 3540, 3546, 3552, 3539 cm^{-1}).

TABLE 2. EQUILIBRIUM CONSTANTS AND FREE ENERGY FOR I AND II

R	Hydrogen bonding (I) at 26° K (Mole fraction^{-1})[a]	 $-\Delta F°$ (Cal)	Cyanohydrin (II)[7] at 20° K (l/m) $\times 10^{-1}$	 $-\Delta F°$ (Cal)
H	5·00 ± 0·08	960	2·24	3170
CH_3	10·8 ± 0·2	1420	1·11	2760
C_2H_5	10·8 ± 0·5	1420	1·22	2820
i-C_3H_7	10·1 ± 0·3	1380	1·24	2830
t-C_4H_9	8·1 ± 0·2	1250	1·33	2870

[a] Based on the standard error for the least squares line. The errors also parallel the square of the correlation coefficients, respectively: 0·994, 0·987, 0·910, 0·975, and 0·986.

The present data provide some evidence against steric inhibition of solvation[15,16] as being responsible for alkyl substituent effects. Because the hydrogen bonds formed are weak, low energy, noncharged transition states may be inferred. These probably require only little additional solvation stabilization, and so steric factors near the substituent cannot be important. Therefore, an inductive order rather than the observed Baker-Nathan order would be predicted by the substituent solvation theory. Good rate data on hydrogen bond formation could provide decisive information on this point.

This work does not test the explanation offered by Brown[17] based on dispersion and induction forces but may be compatible with it. The cyano group is quite polarizable. As such it probably interacts appreciably with the *p*-alkyl substituent, having its largest interaction with the most polarizable group, t-butyl.[17] This interaction may be represented by IV and, in the bonded state, by V. It remains moot which is the more stable.

In the same work[17] Brown has shown that dipole moments for the alkylbenzonitriles in dioxane and chloroform when corrected for the induced moment are in the Baker-Nathan order. He attributes this to the role of solvent on electron releasing abilities of alkyl groups. In the solvent mixtures used in this work, the corrected dipole moments may also follow the Baker-Nathan order, thus correlating with the experimental order found for bonded species. Brown believes that the explanation still lies in dispersion and induction forces and not in hyperconjugative electron-release even where the Baker-Nathan order obtains.

The forces Shiner[18] suggests to explain the Baker-Nathan effect, elimination-type driving forces on the alkyl group, would be difficult to distinguish from the dispersion-induction force explanation with equilibrium data. Rate data on the hydrogen bonding reaction (I) could help distinguish these two.

EXPERIMENTAL

Materials. All the materials were reagent grade, freshly distilled with care taken to separate water in the forerun as the azeotrope. The nitriles had physical constants equivalent to those in the lit.[17,19]

Infrared spectra. The spectra were measured on a Perkin-Elmer Model 21 using a LiF prism under high resolution conditions with a 0·964 mm NaCl sample cell and similar reference cell. Intensities were reproducible to about ±2%; wave numbers were reproducible to about ±3 cm^{-1}, recording the water vapor band at 3566 cm^{-1} on each critical spectrum.[20] All measurements were made at 26° ± 1·0°, the majority being ±0·5°.[21]

The solutions were prepared using calibrated pipets and volumetric flasks. The n-amyl alcohol, because of the low concentration used, was introduced as a more concentrated solution in CCl_4. The nitrile concentration varied from 20–60 volume per cent, the remainder being CCl_4. The solutions in the reference cell were identical to the sample except that alcohol was omitted.

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[15] W. M. Schubert and W. A. Sweeney, *J. Org. Chem.* **21**, 119 (1956).

[16] C. C. Price and D. C. Lincoln, *J. Amer. Chem. Soc.* **73**, 5836 (1951).

[17] T. L. Brown, *J. Amer. Chem. Soc.* **81**, 3229, 3232 (1959).

[18] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **76**, 1603 (1954).

[19] I am indebted to Prof. T. L. Brown for samples of ethyl- and isopropylbenzonitrile.

[20] A. R. Downie, M. C. Magoon, T. Purcell, and B. Crawford, Jr., *J. Opt. Soc. Amer.* **43**, 941 (1953).

[21] The help of R. A. Ferstandig in making the IR measurements is gratefully acknowledged.