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BAKER-NATHAN ORDER IN n-DONOR-ACCEPTOR SYSTEMS AT EQUILIBRIUM

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Recently Ferstandig (1) has discussed the Baker-Nathan Order (2) in hydrogen-bonded systems at equilibrium. He has pointed out that while in p-alkylbenzonitriles, the $\Delta F°$ for the hydrogen bonded equilibria show the Baker-Nathan Order (2), the reverse order is found for the cyanhydrin formation. As part of an extended programme in the investigation of n-donor-σ-acceptor systems, we have examined the hydrogen bonding of several alkyl derivatives of n-donors with phenol and their charge transfer complexes with iodine. Some of the results with nitrogen, oxygen, sulfur as donor atoms have been given in Table 1 and 2.

Table 1

Hydrogen bonding and charge-transfer interaction of alkyl pyridines (RC_5H_4N)

R	pKa	Hydrogen bonding with phenol		Charge transfer complex with iodine
		$-\Delta F°$ (KCals/mole)	$-\Delta H°$ (KCals/mole)	$-\Delta F°$ (KCals/mole)
H	5.17	2.19	8.23	2.40
4-CH_3	6.02	2.42	8.31	2.84
4-C H_5	6.02	2.16	8.39	2.85
4-i-C_3H_7	6.02	2.42	8.47	3.02
4-t-C_4H_9	5.99	2.46	8.47	3.03

TABLE 2

Hydrogen bonding and charge-transfer interaction of ketones ($R_1(CO)R_2$) and thioureas ($R_1NH(CS)NHR_2$)

				Ketones			Thioureas		
R_1	R_2	α-H		$-\Delta F^\circ$ (H.B.)	$-\Delta H^\circ$ (H.B.)	$-\Delta F^\circ$ (C.T.)	$-\Delta F^\circ$ (H.B.)	$-\Delta H^\circ$ (H.B.)	$-\Delta F^\circ$ (C.T.)
CH_3	CH_3	6	0.00	1.09	3.83	0.12	-	-	5.84
CH_3	C_2H_5	5	-0.10	1.14	3.51	0.11	-	-	-
CH_3	i-C_3H_7	4	-0.19	1.48	3.67	-	1.34	4.04	5.90
CH_3	t-C_4H_9	3	-0.30	1.03	3.19	0.28	1.36	4.20	6.04
i-C_3H_7	i-C_3H_7	2	-0.38	1.21	3.19	0.12	-	-	5.90
t-C_4H_9	t-C_4H_9	0	-0.60	0.99	3.03	-	1.59	4.12	6.45

The thermodynamics of the interaction of alkyl pyridines with phenol and iodine are given in Table 1. In Table 2, data on the ketone-phenol and keton-iodine systems have been summarized along with the number of α-hydrogens available for hyper conjugation as well as the Taft σ^* constants of alkyl groups. A similar tabulation for alkyl thioureas is also presented in Table 2.

If we were to consider the increase in ΔF° $(=-RT\ln K)$ in the order, CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, as the Baker-Nathan Order (1), then all the systems studied (Table 1 and 2) generally show the reverse order in the case of hydrogen bonding equilibria as well as in charge-transfer equilibria with iodine. The only exception to this appears to be the hydrogen bonding equilibria of ketones with phenol (Table 2). The enthalpy data of hydrogen bonding also show the reverse Baker-Nathan Order with the exception of ketones. These results clearly indicate that reverse Baker-Nathan Order is a rule rather than an exception in n-donor-acceptor equilibria, whether equilibrium be related to hydrogen bonding or charge-transfer with halogens. It appears that one should not give undue importance to such empirical orders of reactivity or donor strengths, where several factors are likely to contribute to the observed trends.

The $h\nu_{c.t.}$ of thiourea-I_2 systems however showed the Baker-Nathan Order. Similar observations have been made in n-π^* transitions of carbonyl, nitro and thiocarbonyl compounds(3-7). The Baker-Nathan Order in the electronic spectra of these compounds have been interpreted in terms of hyperconjugation in electronically excited states of molecules(2,3-7).

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