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Note

HEAT OF FORMATION OF HYDROGEN-BONDED ADDUCTS

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In continuation of our studies [1–6] of the energetics of electron donor–acceptor complexes via empirical correlations and theoretical calculations, we have now extended these to H-bonded systems. In the present communication we have computed the energy parameters of $O-H \cdots O$ and $N-H \cdots S$ types of H-bond systems and proposed an empirical formula for the prediction of the heat of formation (ΔH) of H-bonded adducts.

The energy parameters were calculated employing the method of Sonnessa and Daisey [7] with the following assumptions. We know that the ground state for the H-bonded adducts in the valence bond terminology [8] is represented as

$$\psi_G = a\psi_1 + b\psi_2 + c\psi_3$$

where ψ_1, ψ_2 and ψ_3 are functions of the contributing forms, i.e., London dispersion, electrostatic and covalent, correspondingly, of the H-bonded complex formed between the donor group and the lone electron pair of the acceptor group. For strong interactions where the H-bond energy is of the order of 40 kcal mole^{-1}, $b \sim c > a$. However, for weak interactions where the H-bond energy is in the range 4–10 kcal mole^{-1}, the contribution due to the covalent form can be neglected in comparison with the electrostatic form, i.e., $b \gg c$. Thus, in such cases, according to the Mulliken theory [9], the ground and the excited states of the H-bonded adduct can be written as

$$\psi_G = a\psi_1 + b\psi_2$$

$$\psi_E = a^*\psi_2 - b^*\psi_1$$

where a and b are the weighting factors for the two configurations corresponding to ψ_1 and ψ_2, respectively. By making use of the energy of the H-bond transition $h\nu_H$, where ν_H is the vibrational frequency of the hydrogen-bonded X–H (where X=O or N) stretching band and reasonable values for overlap and the resonance integral, the various energy parameters for the H-bonded adduct can be obtained. The computed value of the energy parameters along with the observed and predicted value of ΔH from the

TABLE 1

Experimental and theoretical energy parameters for the OH · O-type hydrogen bond formed in the dimerization of some carboxylic acids

Acids	$h\nu_H$ [a] (eV)	b/a	$-\Delta H_{calc}$ (kcal mole^{-1})	$-\Delta H_{obs}$ [a] (kcal mole^{-1})	$\delta(\Delta H)$ (kcal mole^{-1})
Formic	0.375	0.305	7.62	7.40	0.22
Acetic	0.378	0.305	7.68	7.30	0.38
Propionic	0.379	0.299	7.40	7.45	0.05
n-Butyric	0.380	0.299	7.42	7.85	0.43
Isobutyric	0.382	0.299	7.46	7.60	0.14
Tetramethylacetic	0.383	0.299	7.48	7.30	0.18

[a] Ref 10.

$\delta(\Delta H) = |\Delta H_{obs} - \Delta H_{calc}|$; $\beta_0 = -0.1$ eV; $S_{01} = 0.1$

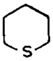
empirical formula

$$\frac{b^2}{a^2 \times \Delta X} = -\frac{\Delta H}{9.48 \times h\nu_H}$$

where $\Delta X = |X_A - X_B|$ (when the electronegative atoms are the same, $\Delta X = 1$, otherwise ΔX is the difference between the electronegativities of the end atoms forming the H-bond) are given in Tables 1 and 2, respectively. It is evident from Tables 1 and 2 that the agreement between the observed and calculated value of ΔH is good. The maximum uncertainty is ±0.43 and

TABLE 2

Experimental and theoretical energy parameters for the NH · · S-type hydrogen bond formed between HNCS and thio compounds

Thio compounds [a]	$h\nu_H$ [b] (eV)	b/a	$-\Delta H_{calc}$ (kcal mole^{-1})	$-\Delta H_{obs}$ [b] (kcal mole^{-1})	$\delta(\Delta H)$ (kcal mole^{-1})
Me_2S	0.383	0.299	3.74	3.48	0.26
MeEtS	0.382	0.299	3.73	3.47	0.26
Et_2S	0.380	0.299	3.71	3.49	0.22
n-Bu_2S	0.380	0.299	3.71	3.59	0.12
t-Bu_2S	0.375	0.305	3.81	4.48	0.67
	0.382	0.299	3.73	3.28	0.45
	0.378	0.305	3.84	3.62	0.22
	0.380	0.299	3.71	3.69	0.02

[a] Me, methyl, Et, ethyl, Bu, butyl

[b] Ref 11.

$\delta(\Delta H) = |\Delta H_{obs} - \Delta H_{calc}|$, $\beta_0 = -0.1$ eV, $S_{01} = 0.1$

±0.67 kcal mole^{-1} while the average uncertainty is ±0.23 and ±0.27 kcal mole^{-1} for O–H···O and N–H···O systems, correspondingly.

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