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Note

On the estimation of gas-phase thermodynamic properties of organic compounds

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Abstract

Some results involving the re-examination and development of Benson group contributions for estimation of gas-phase thermodynamic properties of organic compounds are discussed.

INTRODUCTION

The methods for estimation of the thermodynamic properties of organic compounds are based upon additivity techniques developed by Benson and co-workers [1–3]. These methods have been applied extensively to the prediction of the thermodynamic properties of various gas-phase organic compounds (see, for example, refs. 4–8 and references cited therein). The estimation procedure developed by Benson and co-workers has been incorporated into programs for estimation of the thermodynamic properties of organic compounds (CHETAH, NIST, DIPPR, etc. [9–11]). Unfortunately these programs contain mainly Benson group contribution values which have not been re-examined since 1969. The purposes of this paper are (1) to point out the insufficient accuracy of some group values estimated by Benson in 1969 [2, 3], and (2) to propose a way to estimate missing group contribution values for compounds for which experimental calorimetric data or statistical thermodynamic calculations are non-existent.

RESULTS

The development of Benson group contribution values was part of an effort to create the OLI Databank [12] which contains a great number of various organic compounds of environmental concern. This work required

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TABLE 1

Group contributions to $S^{\ominus}_{\mathrm{int}}(298.15\,\mathrm{K})$ and $C^{\ominus}_{p}(300\,\mathrm{K})$ and values of $S^{\ominus}(298.15\,\mathrm{K})$ and $C^{\ominus}_{p}(300\,\mathrm{K})$ for some ethers and esters ($\mathrm{J\,K^{-1}\,mol^{-1}}$)

Group	$S^{\ominus}_{\mathrm{int}}(298.15\,\mathrm{K})$	$C^{\ominus}_{p}(300\,\mathrm{K})$	
O-(C)$_2$	36.32	14.23	Benson
	29.86	26.30	This work
O-(C)(CO)	35.15	20.31	Benson
	–	17.22	This work

Molecule	$S^{\ominus}(298.15\,\mathrm{K})$			$C^{\ominus}_{p}(300\,\mathrm{K})$		
	Benson [3]	Chao et al.[a] [13]	This work	Benson [3]	Chao et al.[a] [13]	This work
CH_3-O-CH_3	266.8	267.3	267.1	66.0	65.8	65.8
CH_3-O-CH_2-CH_3	313.5	309.3	310.5	86.9	93.7	92.8
CH_3-CH_2-O-CH_2-CH_3	348.8	342.7	342.3	107.8	119.9	119.9
H-CO-O-CH_3	302.7	285.3	287.8	–	64.6	66.5
CH_3-CO-O-CH_3	336.7	324.4	321.8	–	86.4	84.4

[a] Statistical thermodynamic calculation.

the improvement of old group contribution values and also the development of new Benson groups based upon the latest thermodynamic data. An example of new group contributions is given in Table 1. Organic compounds containing the elements C, H, O, S, N, P, Si and the halogens have been considered.

A simple method known in the literature as the "Difference Method" has been very helpful for group calculations as well as for direct estimations of thermodynamic properties. For example, the C_B-(CO) group contributions for $S^{\ominus}_{\mathrm{int}}(298.15\,\mathrm{K})$ and $C^{\ominus}_{p}(T)$ are not included in the published Benson literature [2, 3]. We have tried to estimate these groups values from the data on benzoic acid presented in Stull et al. [14], but had to reject the data because we found a strange temperature-dependent function for the heat capacity group values. $\Delta_f H^{\ominus}(298.15\,\mathrm{K})$, $S^{\ominus}(298.15\,\mathrm{K})$ and $C^{\ominus}_{p}(T)$ values for benzoic acid have been estimated on the assumption that the difference between benzoic acid and benzene is the same as the difference between propenoic acid and ethylene, i.e.

$$C_6H_5\text{–}COOH - C_6H_6 = CH_2\text{=}CH\text{–}COOH - CH_2\text{=}CH_2 \qquad (1)$$

From eqn. (1)

$$C_6H_5\text{–}COOH = C_6H_6 + CH_2\text{=}CH\text{–}COOH - CH_2\text{=}CH_2 \qquad (2)$$

The $\Delta_f H^{\ominus}(298.15\,\mathrm{K})$, $S^{\ominus}(298.15\,\mathrm{K})$ and $C^{\ominus}_{p}(T)$ values for benzoic acid

TABLE 2

Comparison of the thermodynamic properties of benzaldehyde estimated by the difference method with experimental or statistical calculation data

$\Delta_f H^{\ominus}$(298.15 K) (kJ mol^{-1})	$S^{\ominus}$(298.15 K) (J K^{-1} mol^{-1})	$C_p^{\ominus}$(300 K) (J K^{-1} mol^{-1})	$C_p^{\ominus}$(1000 K) (J K^{-1} mol^{-1})	
−19.2	344.1	110.4	253.5	This work, eqn. (3)
−53.9	333.7	110.1	255.6	This work, eqn. (4)
−36.7	336.7	112.3	255.0	Exp. [16, 17]

were estimated from eqn. (2), utilizing the data for benzene, propenoic acid and ethylene in the TRC tables [15]. Then the C_B-(CO) group contribution values were estimated. The uncertainty of this estimation was evaluated from the difference approach to benzaldehyde, for which $\Delta_f H^{\ominus}$(298.15 K) and $S^{\ominus}$(298.15 K) were obtained from the experimental measurements [16, 17], and the $S^{\ominus}$(298.15 K) and $C_p^{\ominus}(T)$ values were calculated by a statistical mechanical technique [17].

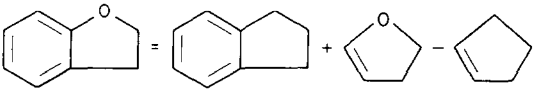
Two equations were considered in order to estimate the thermodynamic properties of benzaldehyde

$$C_6H_5\text{–}CHO = C_6H_6 - CH_3\text{–}CH_2\text{–}CHO - CH_3\text{–}CH_3 \qquad (3)$$

$$C_6H_5\text{–}CHO = C_6H_6 - CH_2\text{=}CH\text{–}CHO - CH_2\text{=}CH_2 \qquad (4)$$

The thermodynamic properties for benzene, propionaldehyde, acrolein and ethylene were taken from the TRC tables [15]. As one can see from Table 2, the experimental value of $\Delta_f H^{\ominus}$(298.15 K) falls between the values estimated using eqns. (3) and (4) and the $S^{\ominus}$(298.15 K) and $C_p^{\ominus}(T)$ values estimated from eqn. (3). Equation (4) seems to take into account nearest neighbor interactions more precisely; therefore, the similar eqn. (2) used for benzoic acid should also be precise enough.

No thermodynamic properties are known for many complicated organic compounds, including polycyclic compounds with heteroatoms. However, they can be estimated with a reasonable accuracy using the difference method. Steele and Chirico [18] measured the enthalpy of formation and the entropy of gaseous 4,5-dihydro-2,3-benzofuran. In order to estimate the heat capacity values for that molecule, the formal equation



(5)

may be considered. Based upon the literature data for thermodynamic properties of indane, 2,3-dihydrofuran and cyclopentene [19–21], the functions $\Delta_f H^{\ominus}$(298.15 K), $S^{\ominus}$(298.15 K), and $C_p^{\ominus}$(298.15 K) were obtained according to eqn. (5) (experimental data in parentheses): −48.2 (−46.5) kJ mol^{-1}, 347.9 (345.8) and 124.5 J K^{-1} mol^{-1}. The estimated values of the enthlapy of formation and the entropy are in good agreement with experimental data and we expect that the estimation of $C_p^\ominus$ is also accurate.

CONCLUSION

The difference method, based on the additivity principles and the Benson group additivity technique, has been successfully applied for estimation of the thermodynamic properties of many complicated organic compounds which have been included in the OLI Environmental Databank [12].

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