
THERMODYNAMICS OF SOME MODEL REACTIONS USEFUL FOR UNDERSTANDING THEORETICAL BACKGROUND OF CORRELATION ANALYSIS

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Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

Six isodesmic gas-phase reactions have been studied out of which three reactions represent a redistribution of two methyl substituents and the other three represent a redistribution of two chloro substituents between two benzene nuclei. The thermodynamics of these reactions has been evaluated on the basis of the partition functions and observed heats of formation at room temperature. The partition functions have been constructed with the help of observed structural and vibrational data. If the internal rotation was present, the frequency of the corresponding torsional vibrational mode has been determined by a fit to the observed thermodynamic data. The energy characteristics calculated for these reactions (the standard change of Gibbs free energy ΔG_T° , enthalpy ΔH_T° , enthalpy at absolute zero ΔH_0° , and potential energy change ΔE) have been evaluated from the standpoint of their applicability to organic correlation analysis. The studies form a part of a wider project, and, in accordance with the findings already presented within this project elsewhere and concerning reactions of fluorobenzenes, they indicate a certain preferred role of the term ΔH_0° in these contexts.

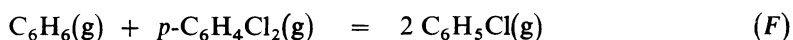
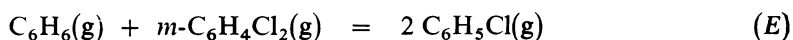
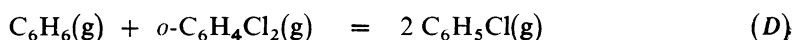
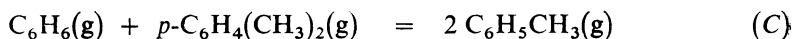
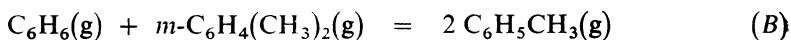
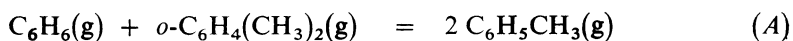
The organic correlation analysis¹⁻³, like e.g. the rules of orbital symmetry by Woodward and Hoffmann, belongs to concepts which in spite of their simplicity are remarkably successful, although a rigorous theoretical reasoning of these concepts starting from basic principles seems to be quite difficult. Although the correlation analysis is focused on the terms of Gibbs free energy (in our contexts we will consider only the standard terms ΔG_T°) there could arise a question¹ whether some terms of simpler nature would be more appropriate for this purpose. In this sense we can gradually reduce ΔG_T° to the standard change of enthalpy at the same temperature (ΔH_T°) or at absolute zero (ΔH_0°) or finally to mere change of potential energy (ΔE).

With the aim to evaluate these problems we constructed⁴ a set of gas-phase reactions involving fluorobenzenes. This present paper extends the study mentioned⁴ by reactions of two further types of substituents, namely methyl and chlorine.

THEORETICAL

The Reactions Considered

Six gas-phase isodesmic reactions (i.e. reactions maintaining the numbers of bonds of individual types) were considered, viz. the reactions involving isomeric xylenes (A)–(C) and those concerning isomeric dichlorobenzenes (D)–(F).



These redistribution reactions correspond to the processes of the type considered in ref.⁴ where the redistributed substituent was fluorine.

Characterization of Reaction Components and Calculations of Energy Terms of Reactions

The calculations were based on the partition functions of the individual reaction components constructed in the usual approximation⁵⁻⁹ of rigid rotor and harmonic oscillator (RRHO); the formulas used are specified in ref.⁹. From thermochemical standpoint, the calculations started from the terms of heats of formation at room temperature according to the compilation⁶. With the help of the calculated functions of heat content, $H_T^\circ - H_0^\circ$, the heats of formation at room temperature were reduced to the absolute zero temperature, and the values of reaction enthalpies ΔH_T° at the non-zero temperatures chosen were derived, too. For the same temperature we also carried out the calculation of the standard changes of Gibbs free energy, ΔG_T° . Above the usual scope of thermodynamic functions, we also extracted (from the ΔH_0° term) the change of the potential energy term, ΔE , along the reactions considered using the term of the quantum correction for zero-point vibrations, $\Delta^{(q)}$:

$$\Delta H_0^\circ = \Delta E + \Delta^{(q)}, \quad (\text{I})$$

where the $\Delta^{(q)}$ term in RRHO approximation is reduced to the well-known summation over the frequencies of vibrational modes⁹.

The choice of molecular parameters for benzene and toluene is identical with that described in ref.⁴. The structural parameters of the remaining reaction components in the processes (A)–(F) were taken from tables¹⁰. The vibrational frequencies for *o*-, *m*-, and *p*-xylenes were taken from refs^{11–13} and from the compilation¹⁴; hence two sets of vibrational frequencies were considered side by side for each of the xylenes. The vibrational data of *o*-, *m*-, and *p*-dichlorobenzene were taken from refs^{11–13}. The vibrational data sets used^{11–14} were considered more uniform than the remaining sets given in literature^{15,16}.

In xylenes there exist¹⁵ two motions of the type of internal rotation which are quite near to free internal rotation^{15,17–19}. In a thermodynamic evaluation these motions can be treated as either free internal rotation, or hindered internal rotation, or torsional vibration. For the sake of consistence with the quality of description of the other species (as well as consistence with the procedure used in ref.⁴) and in order to maintain the framework of the RRHO approximation of partition functions, we treated these two motions as harmonic torsional vibrations. In order to obtain the frequencies of these torsional vibrations, we chose (like in analogous situations in ref.⁴) to complement them by calculation in terms of the observed values of the remaining 46 frequencies so as to reproduce the observed values of entropy term¹⁵. Also these fitted frequencies were rounded off to units of cm^{-1} to maintain the formate used for presentation of observed frequencies. Table I presents a survey of these torsional frequency values evaluated by fitting (the above-mentioned rounding-off of their values has the consequence that in some cases the

TABLE I
Comparison of observed and calculated entropy data for the fitted torsional-frequency approach

Species ^a	$S_{298.15}^{\circ}$ $\text{J K}^{-1} \text{mol}^{-1}$ ^b	Vibrational data ^c	ω_{tors}^d cm^{-1}	$S_{298.15}^{\circ}$ $\text{J K}^{-1} \text{mol}^{-1}$ ^e
<i>o</i> -CH ₃ C ₆ H ₄ CH ₃ (g)	353.5 ± 1.3	ref. ¹⁴	123	353.6
		ref. ¹¹	96	353.6
<i>m</i> -CH ₃ C ₆ H ₄ CH ₃ (g)	358.2 ± 1.3	ref. ¹⁴	86	358.2
		ref. ¹²	47	358.2
<i>p</i> -CH ₃ C ₆ H ₄ CH ₃ (g)	352.6 ± 1.3	ref. ¹⁴	112	352.7
		ref. ¹³	40	352.6

^a Standard state — an ideal gas at 1 atm = 101 325 Pa pressure. ^b Observed values surveyed in ref.¹⁵. ^c Source of 46 vibrational frequencies. ^d Fitted torsional frequency. ^e Calculated value.

difference between the observed and calculated values of entropy term is non-zero). Generally speaking, this procedure is inferior to the approach of hindered internal rotation, nevertheless it can be shown to be sufficient for our purposes. If the value of frequency of torsion mode is adjusted so as to precisely reproduce the value of entropy term at a certain temperature, then, of course, also the values calculated in this way for a certain neighbourhood of this temperature point can be considered precise. Furthermore, as the significance of the motion considered decreases with decreasing temperature till it finally fades away, the RRHO procedure thus adjusted can be used quite well for all temperatures below that used for the fit. Questionable, of course, is the applicability of this approach at the temperatures considerably higher, but this region is not crucial in our context, the reduction from room temperature to the absolute zero being primary. For completeness let us note that in refs^{15,19} *p*-xylene is ascribed the symmetry point group D_{2h} (due perhaps to inaccurate analogy with *para*-disubstituted benzenes with monoatomic substituents; similarly toluene is ascribed¹⁵ the C_{2v} point group instead of the more realistic⁴ symmetry of C_s). In our context, in accordance with the view presented in ref.¹⁴, we adopt the point group C_{2h} for the symmetry of rigid *p*-xylene structure.

RESULTS AND DISCUSSION

Table II presents the quantities ΔE , ΔH_0° , and the temperature evolution of the terms ΔH_T° and ΔG_T° for the reactions (A)–(C), Table III presenting the corresponding data for (D)–(F). The comparison of the results obtained for the reactions (A)–(C) by application of two different sets of vibrational frequencies (namely according to ref.¹⁴ and to refs^{11–13}) indicates the sensitivity of the whole scheme to the choice of values of vibrational frequencies: inaccuracy in the region of both low and high frequency values can be serious. The inaccuracy at low frequencies can have perceptible consequences for the terms ΔH_T° and ΔG_T° without being markedly significant for $\Delta^{(a)}$ or ΔE terms. On the other hand, the inaccuracy at high frequencies need not affect the quantities ΔH_T° and ΔG_T° but can be quite significant for the $\Delta^{(a)}$ and ΔE terms. (Of course, our way of considering the ΔE values is affected by the way of generating them; when looking from the standpoint of known potential energy hypersurface, then, naturally, the ΔE term is invariant to the values of vibrational frequencies.) From what was given it follows that for the purpose of our scheme relatively high requirements must be met with regard to the quality of the input set of vibrational frequencies. At the same time, however, we cannot generally declare that the vibrational spectra of molecules of the dimensions considered in reactions (A)–(F) already are safely analyzed; sometimes frequencies of some modes can be missing and assignments of others can be questionable (e.g. a confusion with combination frequencies). Another difficulty consists in the fact that we would require the frequencies of the species in gas phase whereas it is typical that only the values ob-

tained by measurements in condensed phases are available. Finally, these measurements nevertheless lead to the values of fundamental frequencies, i.e. not to the

TABLE II

Standard^a changes of Gibbs free energy ΔG_T° , enthalpy ΔH_T° , and enthalpy at the absolute zero temperature ΔH_0° , and potential-energy changes ΔE along three reactions with xylenes

Reaction ^b	ΔE kJ mol ⁻¹	ΔH_0° kJ mol ⁻¹	T K	ΔH_T° kJ mol ⁻¹	ΔG_T° kJ mol ⁻¹
$C_6H_6(g) + o\text{-}CH_3C_6H_4CH_3(g) =$ $= 2 C_6H_5CH_3(g)$	-3.08	-1.14	100	-1.47	-3.73
	-0.22	-1.47		-1.87	-3.92
			200	-1.77	-5.86
				-2.00	-5.89
			298	-1.92	-7.82
				-1.92	-7.81
			300	-1.93	-7.87
				-1.92	-7.85
			400	-2.05	-9.82
				-1.74	-9.85
$C_6H_6(g) + m\text{-}CH_3C_6H_4CH_3(g) =$ $= 2 C_6H_5CH_3(g)$	-2.23	0.79	100	0.30	-1.51
	-0.82	-0.50		-1.18	-2.23
			200	-0.004	-3.18
				-0.89	-3.33
			298	-0.17	-4.70
				-0.17	-4.67
			300	-0.17	-4.73
				-0.15	-4.70
			400	-0.30	-6.23
				0.69	-6.35
			600	-0.51	-9.15
				1.97	-10.17
			800	-0.67	-12.00
				2.57	-14.33
			1 000	-0.81	-14.82
			2.71	-18.57	

TABLE II
(Continued)

Reaction ^b	ΔE kJ mol ⁻¹	ΔH_0° kJ mol ⁻¹	T K	ΔH_T° kJ mol ⁻¹	ΔG_T° kJ mol ⁻¹
$C_6H_6(g) + p\text{-}CH_3C_6H_4CH_3(g) =$ $= 2 C_6H_5CH_3(g)$	-1.36	-0.28	100	-0.59	-2.84
	14.11	-2.44		-3.07	-4.08
			200	-0.78	-4.99
				-2.27	-5.31
			298	-0.88	-7.03
				-0.88	-7.08
			300	-0.88	-7.08
				-0.85	-7.12
			400	-0.95	-9.13
				0.77	-9.45
		600	-1.03	-13.19	
			3.68	-15.22	
		800	-1.06	-17.24	
			5.83	-21.86	
		1 000	-1.08	-21.28	
			7.35	-28.97	

^a Standard state — an ideal gas at 1 atm = 101 325 Pa pressure. ^b The values in the upper and lower lines are based on vibrational data from ref.¹⁴ and refs¹¹⁻¹³, respectively.

harmonical frequencies which, strictly speaking, the RRHO partition functions necessitate as the input. On the other hand, the contributions of vibrational motions to the ΔH_T° and ΔG_T° values are not really significant until at higher temperatures, whereas at low temperatures, therefore, the factors given are not critical, which is also manifested in the fact that at low temperatures we can observe a reasonable agreement between e.g. the entropy terms which would result from the approach used in the present report with the values available in literature^{6,15}, being based on other input data. In this context let us note that for isomeric xylenes a better accordance with the entropy data¹⁵ can be seen in the results based on the vibrational sets¹¹⁻¹³ as compared with those based on the data¹⁴.

Generally, the results of Tables II and III confirm the conclusions already made for the isodesmic reactions in ref.⁴. It is confirmed that the quantum correction for the zero-point vibrations $\Delta^{(q)}$ is little significant for isodesmic reactions in contrast to that for non-isodesmic reactions. In other words this means a relative nearness of the terms ΔH_0° and ΔE . The failure of this rule in the reaction (C) with application

of the vibrational data¹³ obviously indicates some inconsistency in these vibrational data. (The difference between both energy terms in this case corresponds to the frequency of $2\,766\text{ cm}^{-1}$. This data could be interpreted also as an inaccuracy of 17.7 cm^{-1} loading each of the 156 frequencies of vibrational modes involved in reaction (C). However, that value of 17.7 cm^{-1} makes less than 0.6% of the highest frequency values involved.) Similar differences (in accordance with conclusions⁴) between isodesmic and non-isodesmic reactions consist in the fact that for the isodesmic reactions the terms of ΔH_T° and ΔG_T° (after correcting the latter for symmetry

TABLE III

Standard^a changes of Gibbs free energy ΔG_T° , enthalpy ΔH_T° , and enthalpy at the absolute zero temperature ΔH_0° , and potential-energy changes ΔE along three reactions with chlorinated benzenes

Reaction	ΔE kJ mol ⁻¹	ΔH_0° kJ mol ⁻¹	T K	ΔH_T° kJ mol ⁻¹	ΔG_T° kJ mol ⁻¹
$\text{C}_6\text{H}_6(\text{g}) + o\text{-C}_6\text{H}_4\text{Cl}_2(\text{g}) =$ $= 2\text{C}_6\text{H}_5\text{Cl}(\text{g})$	-7.94	-9.15	100	-9.24	-10.92
			200	-9.26	-12.59
			298	-9.20	-14.23
			300	-9.20	-14.27
			400	-9.14	-15.96
			600	-9.02	-19.40
			800	-8.91	-22.88
1 000	-8.81	-26.38			
$\text{C}_6\text{H}_6(\text{g}) + m\text{-C}_6\text{H}_4\text{Cl}_2(\text{g}) =$ $= 2\text{C}_6\text{H}_5\text{Cl}(\text{g})$	-4.74	-5.57	100	-5.65	-7.21
			200	-5.70	-8.74
			298	-5.69	-10.23
			300	-5.69	-10.27
			400	-5.67	-11.79
			600	-5.62	-14.87
			800	-5.57	-17.96
1 000	-5.51	-21.06			
$\text{C}_6\text{H}_6(\text{g}) + p\text{-C}_6\text{H}_4\text{Cl}_2(\text{g}) =$ $= 2\text{C}_6\text{H}_5\text{Cl}(\text{g})$	-1.45	-2.13	100	-2.24	-4.44
			200	-2.27	-6.62
			298	-2.26	-8.76
			300	-2.26	-8.80
			400	-2.24	-10.99
			600	-2.20	-15.37
			800	-2.17	-19.76
1 000	-2.12	-24.16			

^a Standard state — an ideal gas at 1 atm = 101 325 Pa pressure.

effects¹⁻³) are mutually quite near at low temperatures (namely, e.g.⁴, until 500 K). From the standpoint of correlation analysis, on the whole this means that for isodesmic reactions the terms ΔE , ΔH_0° , ΔH_T° , and for-symmetry-corrected ΔG_T° are mutually interchangeable for its purposes. Then, of course, it would be better to prefer, out of this tetrad, the temperature-independent quantities, and, out of the pair ΔE and ΔH_0° , the latter term, since it is directly available by temperature extrapolation of observed data.

The nearness of the term ΔH_T° and for-symmetry-corrected term ΔG_T° in isodesmic reactions at low temperatures can be seen from the expression⁵⁻⁹ of the relation between ΔG_T° and ΔH_0° in terms of the partition functions Q_i for the components of a general reaction $A(g) + B(g) = C(g) + D(g)$:

$$\Delta G_T^\circ = \Delta H_0^\circ - RT \ln (Q_C Q_D / Q_A Q_B). \quad (2)$$

If we now focus our attention to the contribution ($t-r$) of translation and rotation (since the contributions of vibrations are little significant at low temperatures), we can show that it is (under the presumption that all four reaction components are nonlinear molecules):

$$\left(\ln \frac{Q_C Q_D}{Q_A Q_B} \right)_{t-r} = \frac{3}{2} \ln \frac{m_C m_D}{m_A m_B} + \frac{1}{2} \ln \frac{J_C J_D}{J_A J_B} - \ln \frac{\sigma_C \sigma_D}{\sigma_A \sigma_B}, \quad (3)$$

where m_i denotes the mass of the i -th reactant, J_i is its product of main moments of inertia, and σ_i denotes its symmetry number. In isodesmic reactions of our type (A)–(F) it is justified to presume significant cancellation between the numerator and denominator of the first two fractions at the right-hand side of Eq. (3). Therefrom it really follows that, at the temperatures at which the vibrational contribution is not yet substantial, we can expect a considerable nearness of the ΔG_T° term corrected for symmetry and the ΔH_T° and ΔH_0° terms in these isodesmic reactions.

From Eq. (2) it automatically follows (if $Q_i \neq 0$):

$$\lim_{T \rightarrow 0} \Delta G_T^\circ = \lim_{T \rightarrow 0} \Delta H_T^\circ = \Delta H_0^\circ. \quad (4)$$

However, for completeness from methodological standpoint it can be interesting to note that at very low temperatures (which are not covered in Tables II and III) one artefact of the conventional formulas for the translational and rotational partition functions can make itself felt. This problem has been investigated in the most detail^{20,21} with the conventional formula for the partition function of free internal rotation, however, the conclusions are analogously valid also for the translation and overall rotation. The essence of this problem lies in the fact that, compared to

physical requirements, the formulas conventionally adopted for the partition functions mentioned do not meet the requirement of non-zero limit for $T \rightarrow 0$. This results in anomalous behaviour of these partition functions (as well as of the thermodynamic functions derived therefrom) at very low temperatures. However, the low temperatures in question are still substantially lower than the lowest temperature considered in Tables II and III. Similarly it is from methodological standpoint also noteworthy that the quantum correction $\Delta^{(q)}$ involves²²⁻²⁴, in a rigorous approach, still other contributions beside the term given by the harmonic vibrational frequencies, nevertheless, in our context it is well justified to omit these higher corrections.

Another interesting methodological aspect is a possible question whether or not the choice of the standard state may interfere with the procedures of correlation analysis. This problem could really become topical in connection with the recent criticism²⁵⁻²⁷ of the concept of the so-called entropy-controlled reactions where it was shown that the relatively widespread ignoring of the conventional nature of choice of standard state can lead even to physically quite erroneous conclusions. However, correlation analysis remains intact if the same choice of standard state is used for all reactions of the series considered. Then any change in the choice of standard state will only cause a constant shift in all the members of the reaction series (for reactions with overall zero change in number of components along the reaction this shift is zero any way), this shift being, of course, insignificant for the correlation itself.

In the context of correlation analysis, the consecutive transition from ΔG_T° to ΔH_0° or, as the case may be, to ΔE is relevant. On the other hand, for the present numerical quantum chemistry^{9,28} the primary quantity is ΔE , whereas the transition to ΔG_T° is only a secondary process with larger computational demands. If we intended to base the correlation analysis on the outputs of computational chemistry for a selected reaction series (which, of course, is rather dubious with regard to the present precision²⁸ of quantum chemistry data obtained for the reactions of the type (A)-(F)), we would obviously adopt the ΔE terms as the most easily available. Nevertheless it must not be forgotten that if we abandon the present limits given by the Born-Oppenheimer approximation²⁹, then rather the total wave function and total ground-state energy will appear in the foreground as the true object^{30,31} of theoretical chemistry, hence again the ΔH_0° term.

Other aspects of the reactions (A)-(F) in relation to correlation analysis (inclusive of construction of a simple reaction series – also involving the reactions from ref.⁴ – for application of the Hammett equation) will be dealt with elsewhere³².

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