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IR spectroscopy as a source of data on bond strengths

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The aim of this work is the estimation of double bond strength, namely C=O bonds in ketones and aldehydes and C=C bonds in various compounds. By the breaking of these bonds one or both fragments formed are carbenes, for which experimental data on the enthalpies of formation (ΔH_f^{298}) are scarce. Thus for the estimation of ΔH_f^{298} of the corresponding carbenes, the empirical equations were proposed based on different approximations. In addition, a quantum chemical calculations of the ΔH_f^{298} values of carbenes were performed, and the data obtained were compared with experimental values and the results of earlier calculations.

Equations for the calculation of C=O bond strengths of different ketones and aldehydes from the corresponding stretching frequencies ν(C=O) were derived. Using the proposed equations, the strengths of C=O bonds of 25 ketones and 12 conjugated aldehydes, as well as C=C bonds of 13 hydrocarbons and 7 conjugated aldehydes were estimated for the first time. Linear correlations of C=C and C=O bond strengths with the bond lengths were established, and the equations permitting the estimation of the double bond strengths and lengths with acceptable accuracy were obtained. Also, the strength of central C=C bond of stilbene was calculated for the first time. The uncertainty of the strengths of double bonds obtained may be regarded as accurate ±10–15 kJ/mol.

1. Introduction

The interrelation of the bond dissociation energy D(C-X) and stretching frequency of respective bond ν(C-X) in the IR spectra was previously established by many authors. The empirical correlations of the stretching frequencies in the IR spectra of polyatomic molecules with the bond energies of corresponding bonds were found, and the appropriate equations were published [1–6]. In our previous papers [7,8] the possibility of the calculation of D(C–H) from the stretching frequencies of different bonds (C–H, O–H, C–O, $C{-}OO^{\bullet}$ [7] and C=O [8]) was shown.

It follows from all the results that the data on the stretching frequencies of different bonds may be regarded as a source of the strengths of the bonds. In this communication the calculations of C–H, C=O and C=C bond strengths, D(C–H), D(C=O), and D(C=C) for different compounds were performed.

2. Data sources

The ν values, if not otherwise stated, were taken from databases [9] (mainly for gas-phase spectra) and [10] (mainly for solutions in CCl_4). The enthalpy of formation (ΔH_f^{298}) values are from Refs. [9,11], or calculated (at the absence of experimental data) by group additivity values (GAV) method [9,11,12].

3. Quantum chemical calculations

The quantum chemical calculations of the formation enthalpies of carbenes were performed using program Priroda [13,14] and the CCSD(T) method. The orbital basis sets L2 [15] have the following contraction schemes: (8s4p2d)/[3s2p1d] for H and (12s8p4d2f)/[4s3p2d1f] for C. To save computational time for the calculation of phenylcarbene and phenyl radical molecules the smaller basis sets were used – L11 [15] (C atom – (10s7p3d)/[4s3p1d], H atom – (6s2p)/[2s1p])). Geometry optimization, vibrational frequency, zero-point vibrational (ZPVE) and thermal (H_{298}) corrections to the energy were calculated by the CCSD(T) method. For comparison, similar calculations were carried out by the DFT method, using the

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following exchange-correlation functionals: PBE, PBE0 and B3LYP. To increase the precision at the DFT calculations the density fitting approximation has not been used.

The enthalpies of formation (ΔH_f^{298}) of carbenes were estimated on the basis of the quantum chemical calculated enthalpy changes (ΔH_r^{298}) in the hydrogen atom abstraction reaction:

$$RCH: + CH_3CH_3 = CH_3CH_2^\bullet + RCH_2^\bullet \tag{1}$$

$$\Delta_r H^\circ{}_{298} = [E(C_2H_5^\bullet) + E(R{-}CH_2^\bullet) - E(C_2H_6) - E(R{-}CH{:})] + [ZPVE(C_2H_5^\bullet) + ZPVE(R{-}CH_2^\bullet) - ZPVE(C_2H_6) - ZPVE(R{-}CH{:})] + [H_{298}(C_2H_5^\bullet) + H_{298}(R{-}CH_2^\bullet) - H_{298}\,(C_2H_6) - H_{298}(R{-}CH{:})] \tag{2}$$

and Hess's law:

$$\Delta H_f^{298}(RCH{:}) = \Delta H_f^{298}(RCH_2^\bullet) + \Delta H_f^{298}\,(CH_3CH_2^\bullet) - \Delta H_f^{298}\,(C_2H_6) - \Delta H_r^{298} \tag{3}$$

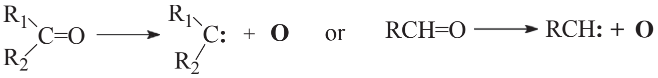
where $\Delta H_f^{298}(C_2H_6)$, $\Delta H_f^{298}(CH_3CH_2^\bullet)$ and $\Delta H_f^{298}(RCH_2^\bullet)$ were taken from Refs. [9,11], if not otherwise stated.

4. Results and discussion

The main approach to the estimation of the strength of double bonds (C=O and C=C). The strength of any bond may be expressed [11] by the equation

$$D(R\text{-}X) = \Delta H_f^{298}(R) + \Delta H_f^{298}(X) - \Delta H_f^{298}\,(RX) \tag{4}$$

The ΔH_f^{298} are the enthalpies of formation of the species R, X and RX. At the breaking of the C=O bond of a ketone or aldehyde.



one of the species formed is a carbene. The enthalpies of formation of many ketones and aldehydes are tabulated [9] or may be easily calculated by the GAV method [9,12] and the $\Delta H_f^{298}(O) = 249.2$ kJ/mol [9,11]. For the determination of D(C=O) the ΔH_f^{298} values of corresponding carbenes must be known. Unfortunately, the data on the needed values are limited. The same consideration is true for C=C bond; however at the breaking of such a bond two carbenes are formed.

For the calculation of the strengths of the double bonds (C=O and C=C), we must have an adequate approach for estimating the ΔH_f^{298} values of different carbenes. An appropriate way is described below.

C=O bond strengths of ketones. Let us consider the following set of compounds: a ketone R_1-C(O)-R_2, a corresponding hydrocarbon R_1-CH_2-R_2, a radical R_1-$CH^\bullet$-R_2 formed by the breaking of one C–H bond, and a carbene R_1-C:R_2 formed by the breaking of C=O bond of parent ketone. It was shown in Ref. [7] that the quantity $E_S(R^\bullet)$ (radical stabilization energy) may be calculated from the relation

$$E_S(R^\bullet) = D(CH_3{-}H) - D(R{-}H) \tag{5}$$

For hydrocarbons R_1-CH_2-R_2 the corresponding values of $E_S(R^\bullet)$ were found from the equation

Table 1
Enthalpies of formation (kJ/mole) of certain carbenes.

CARBENE (R:)	ΔH_f^{298} (R:)					Δ (ΔH_f^{298}(R:) - ΔH_f^{298} (R:)/eq. (10)/)	
	Method						
	Experiment	Theoretical			Eq. (10)	Experiment	Theory
		See references	This work				
CH_2:	391.0 ± 0.7 [16]		PBE/L2	405.7	379.0	12	26.7
	394.4 ± 0.8 [17]		PBE0/L2	403.5		15.4	24.5
	385.8 ± 15.5 [18]		B3LYP/L2	409.2		6.8	30.2
	391.2 ± 1.6 [19]		CCSD(T)/L2	391.5		12.2	12.5
		390.45 ± 0.65 [20]					11.45
CH_3CH:			PBE/L2	361.7	350.5		11.2
			PBE0/L2	361.7			11.2
			B3LYP/L2	365.9			15.4
			CCSD(T)/L2	354.3			3.8
		354.8 [21]					4.3
$CH_2{=}CH{-}CH$:	390 ± 14 [16]					−13	
	390.4 ± 14.2 [18]					−12.6	
			PBE/L2	416.0	403.0		13.0
			PBE0/L2	416.5			13.5
			B3LYP/L2	419.1			16.1
			CCSD(T)/L2	412.6			9.6
:CHCHO			PBE/L2	258.3	237.8		20.5
			PBE0/L2	262.6			24.8
			B3LYP/L2	265.1			27.3
			CCSD(T)/L2	254.7			16.9
$CH_3{-}CH{=}CH{-}CH$:			PBE/L2	373.3	360.0		13.3
			PBE0/L2	373.7			13.7
			B3LYP/L2	376.2			16.2
			CCSD(T)/L2	369.8			9.8
C_6H_5CH:	430 ± 15 [16]		PBE/L2	459.4	434	−4	25.4
	430 ± 14.6 [18]		PBE0/L2	459.4		−4	25.4
	434.3 ± 9.2 [22]		B3LYP/L2	462.5		0.3	28.5
			CCSD(T)/L11	450.2			16.2
		460.2 ± 8.4 [23]					26.2