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# Radical stabilization energy as a measure of the spectral properties and reactivity trends in homologous groups

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ABSTRACT: The existence of linear relationships has been demonstrated between stretching frequencies of R—H, RO—H, $CH_3CON(R)$—H and R—OX (X = H for alcohols and O for peroxy radicals) bonds and radical stabilization energies, $E_s(R^\bullet)$, of related radicals. The correlation equations of $E_s(R^\bullet)$ and R—H bond dissociation energies (BDE), *D*(R—H), with the above stretching frequencies were obtained. From the equations the *D*(R—H) values for different hydrocarbons were calculated and compared with the experimental data. The mean difference between calculated and experimental values for saturated hydrocarbons is 2.3 kJ $mol^{-1}$. The greater differences for some unsaturated hydrocarbons are discussed and explained. The BDEs calculated from the $D(R—H = f(\nu)$ equations may be regarded as the best. The IR spectra of menthol, menadione, 3-methylpent-2-en-4-yn-1-ol and retinol were recorded in solution and the $E_s(R^\bullet)$ values of the corresponding radicals and the *D*(R—H) values of the related C—H bonds in the parent hydrocarbons were estimated for the first time. It is also shown that the radical stabilization energy may be used to estimate the reactivity of organic compounds in free radical reactions. One may conclude that the stabilization energy of the radicals of many organic compounds could be estimated from the vibrational spectra. The $E_s(R^\bullet)$ itself is a useful quantity for predicting kinetic and spectral properties of organic compounds.

KEYWORDS: radical stabilization energy; homologous groups; spectral properties; reactivity trends

## INTRODUCTION

The dependence of the bond dissociation energy (BDE), *D*(R—X), on the properties and structure of the radical $R^\bullet$ formed on bond rupture is well known.[1] The crucial parameter affecting the value of *D*(R—X) is the stabilization energy of $R^\bullet$ $E_s(R^\bullet)$. The quantity is defined[2–4] as

$$E_s(R^\cdot) = D(CH_3\text{-}X) - D(R—X) \qquad (1)$$

One may suppose the value of $E_s(R^\bullet)$ is independent of X[5] and it may be calculated from

$$E_s(R^\cdot) = D(CH_3—H) - D(R—H) \qquad (2)$$

The quantity $E_s(R^\bullet)$, as defined by Eqns (1) and (2), may be regarded as a measure of the unpaired electron conjugation in the radical $R^\bullet$ and has been called by several workers the 'methane-based stabilization energy'.[4] In our previous work the quantity was used to evaluate the dissociation energies of $R—O_2^\bullet$ bonds in peroxy radicals.[5–7] It was also shown that the rate constants of autoxidation propagation reactions both by hydrogen abstraction by peroxy radicals and addition of $RO_2^\bullet$ to C=C bonds are dependent on the $E_s(R^\bullet)$ of the corresponding $R^\bullet$.[7] To calculate the $E_s(R^\bullet)$ values from Eqn. (2) reliable *D*(R—H) values are needed. The methods for the calculation of experimental bond energies in polyatomic molecules are based on using the heats of formation of free radicals formed during the rupture of the bond under consideration. Different complex and laborious experimental techniques are used for determination of the quantities. The techniques and the results obtained have recently been reviewed.[8] In contrast to polyatomic molecules, the bond energies of many diatomic molecules can be found from the spectral data.[9,10] The method has also been applied to polyatomic molecules.[11] The relative ease of the technique stimulated several workers to undertake attempts to uncover empirical correlations of the stretching frequencies in the vibrational spectra of the polyatomic molecules with the bond energies of corresponding bonds. The essential contribution was made by McKean and co-workers. The results of the correlation of the C—H bond strengths and isolated C—H stretching frequencies $\nu^{iso}$ have been

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**Table 1.** $\nu$(O—H) and O—H bond dissociation energies in alcohols

| Alcohol | $D$(O—H) (kJ mol$^{-1}$)[1] | $\nu$(O—H) (cm$^{-1}$)[24] |
|---|---|---|
| MeOH | 436.8 | 3643 |
| EtOH | 436.0 | 3633 |
| *n*-PrOH | 432.6 | 3634 |
| *i*-PrOH | 438.0 | 3620 |
| *t*-BuOH | 439.7 | 3616 |

reviewed by McKean *et al.*[12–14] Correlation equations for other bonds have also been obtained.[15]

With regard to C—H bonds, McKean *et al.*[12–14] used data for the same correlation for C—H bonds adjacent to single, double and triple CC bonds, to C≡N and to carbonyl groups of different types. One may consider that this is one of the main reasons for the substantial discrepancy between the experimental bond strength values and those found from the published correlation equations.[12–14]. Recently, a quantum-chemical calculation was undertaken to establish the correlation under consideration, but the calculated $D$(C—H) values differed considerably from the experimental values.[16] At the same time, the interrelation of bond energy and the stretching frequency of the bond is beyond question.

In this work another approach was used. The stretching frequencies of different bonds were correlated with the stabilization energies of hydrocarbon $\pi$-radicals formed by rupture of the same or adjacent bonds. The correlations were established and proved to be useful for calculating from the spectral data the stabilization energies of radicals and then the C—H bond energies and the reaction rate constants for some complex molecules including vitamins and other biologically active compounds.

## EXPERIMENTAL

2-Methyl-1,4-naphthoquinone (vitamin K$_3$, menadione) was obtained from its sodium bisulfite by alkaline hydrolysis, extraction with hexane and recrystallization from the solvent. It was dried *in vacuo* and stored at about −15 °C under reduced pressure (~5 × 10$^{-3}$ mmHg). 3-Methylpent-2-en-4-yn-1-ol of technical grade was vacuum distilled. The purity of the final product was 99.8% as shown be GLC. 2-Isopropyl-5-methylcyclohexanol (menthol) of Chemical Reference Substance grade was used as received. (All-*E*)-retinol was kindly supplied by Dr A. A. Khodonov (Moscow State Academy of Fine Chemical Technology) and was used without additional treatment. The solvents (hexane, CCl$_4$) were purified by standard techniques. CCl$_4$ was dried over CaCl$_2$ and Al$_2$O$_3$. The IR spectra in CCl$_4$ were recorded on a Specord M80 spectrophotometer (Carl Zeiss, Jena, Germany).

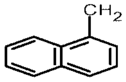
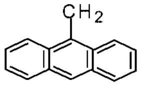
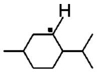
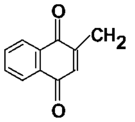
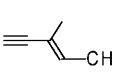
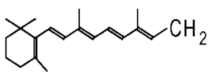
## RESULTS AND DISCUSSION

As mentioned in the Introduction, a correlation has been found between the C—H bond dissociation energies and the stretching frequencies of corresponding bonds. Now we show that relationships between radical stabilization energies and stretching frequencies are more convenient and practicable.

Independently of the quantity used for correlation [bond strength or radical stabilization energy defined by Eqn. (2)], reliable $D$(R—H) values are needed. The dissociation energies of primary, secondary and tertiary C—H bonds of hydrocarbons are tabulated in several reviews.[1,17–22] The data have considered critically, and the recommended bond energy values for several hydrocarbons have been tabulated.[8] The data used in this work were taken from Refs 19 and 20 for CH$_3$—H, C$_2$H$_5$—H, *i*-C$_3$H$_7$—H, *s*-C$_4$H$_9$—H and *t*-C$_4$H$_9$—H (the most precise values, essentially the same as the recommended ones[8]), Ref. 8 for CH$_2$CHCH$_2$—H and C$_6$H$_5$CH$_2$—H and Refs 1, 17, 18 and 23 for other hydrocarbons.

The reason for using the $E_s$(R$\cdot$) values for correlation with the stretching frequencies of different bonds lies in the fact that for different compounds the dissociation energies of the same bonds do not change appreciably or are not known at all. The data presented in Table 1 clearly show the absence of any relation between $D$(RO—H) and $\nu$ (O—H). In contrast, there are clear relationships of $E_s$(R$\cdot$) and $\nu$ (RO—H) for different ROHs and also stretching frequencies of other bonds. Previously we considered $E_s$(R$\cdot$) as a driving force for the autoxidation process of organic compounds.[7] The quantity may also be considered as a driving force for changes in the stretching frequencies in the homologous series. The C—H stretching frequencies used in this work are, if not indicated, otherwise the isolated stretching frequencies ($\nu^{iso}$),[12] i.e. the C—H stretching frequencies in molecules in which all hydrogen atoms but one are replaced by deuterium. According to numerous spectral data, C—H bonds of the same type are non-equivalent depending on their orientation relative to the carbon skeleton of the molecule.[12–14,25] It is seen from the correlations obtained by McKean *et al.*[12–14] that the lower stretching frequencies correspond to the lower bond strengths of the same bond. The C—H bond energies are determined mainly by the use of different chemical reactions, and it is obvious that the weaker bonds are more reactive than the stronger bonds. Therefore, in this work the lower values of $\nu^{iso}$ were used for the correlation. The following procedure was applied for obtaining the correlation equations and for calculating the $E_s$(R$\cdot$) and BDE values. The $E_s$(R$\cdot$) and BDE data used for the correlation are the most reliable ones (mainly from Ref. 8) and are shown in Table 2 in bold type. The correlation equations obtained are listed in Table 3.

**Table 2.** R—H bond and radical stabilization energies and stretching frequencies values for different compounds[a]

| R | $D$(R—H) (kJ mol$^{-1}$) | $E_S$(R•) (kJ mol$^{-1}$) | Stretching frequencies (cm$^{-1}$) $\nu$(R—H) | $\nu$(RO—H)[34] | $\nu$(R—OH)[24,30,37] | $\nu$(N—H) in MeCONHR[24,34] |
|---|---|---|---|---|---|---|
| $CH_3$ | **439.0**[8,19] | **0** | 2992[25] | 3643.7 | | 3478 |
| $C_2H_5$ | **422.8**[8,20] | **16.2** | 2950[25] | 3635.4 | 1048 | 3462 |
| *n*-$C_3H_7$ | 422.5[18] | 16.5 | 2937[25] | 3638.6 | 1054 | 3461 |
| *i*-$C_4H_9$ | 422.7[17] | 16.3 | 2943.4[26] | 3640.4 | | 3471 |
| $CH_3C(CH_3)_2CH_2$ | 418.4[1] | 20.6 | 2934.3[12] | 3642[30] | 1052 | |
| *n*-$C_4H_9$ | 422.2[b] | 16.8 | 2936.5[25] | 3638.6 | 1047 | 3460 |
| *i*-$C_3H_7$ | **412.7**[8,20] | **26.3** | 2918[27] | 3626.4 | 1110 | |
| *s*-$C_4H_9$ | **411.1**[8,20] | **27.9** | 2907[25] | 3628.0 | 1105 | 3450 |
| $(CH_3)_2CHCHCH_3$ | 409.5[b] | 29.5 | | 3631.6 | 1091 | |
| *t*-$C_4H_9$ | **403.5**[8,20] | **35.5** | 2880[27] | 3616.3 | | 3453 |
| *c*-$C_6H_{11}$ | 400.0[1] | 23.0 | 2891[25] | 3623.9[35] | | |
| $C_6H_5CH_2$ | **370.3**[8] | **68.7** | 2934[28] | 3616[24] | 1015 | |
| $CH_2CHCH_2$ | **369.0**[8] | **70.0** | 2931[14] | 3612[24] | 1028 | |
| $CH_3CH{=}CHCH_2$ | 358.2[1] | 85.4 | 2928[29] | | | |
| $C_6H_5CHCH_3$ | 357.7[1] | 81.3 | | | 1073 | |
|  | 356.0[1] | 83.0 | 2927[c30] | | | |
| $CH_2{=}CH(CH_3)CH_2$ | 373.0[17] | 66.0 | 2924[31] | | | |
| $CH_2CHCHCHCH_2$ | 349.7[d] | 95.6 | 2897.6[c30] | | | |
| $CH_3CHCH{=}CH_2$ | 375.0[17] | 64.0 | | | 1058 | |
|  | 351.9[23] | 97 | 2919[c30] | 3616[36] | | |
| $(C_6H_5)_2CH$ | **351.4**[1,23] | **87.6** | 2894[c30] | | 1014 | |
| $(C_6H_5)_3C$ | 338.9[23] | 125.2 | 2897[d32] | 3612[24] | | |
|  | | | | 3628 (This work) | | |
|  | | | 2945[c] (This work) | | | |
|  | | | | 3616 (This work) | 1008 (This work) | |
|  | | | | 3616 (This work) | 994 (This work) | |

[a] The BDE and $E_s$(R•) values used to obtain the correlation equations (Table 3) are printed in bold type.

[b] Our estimation: it was accepted that the difference between $D$(R—H)s of primary C—H bonds of $C_3H_8$ and $C_4H_{10}$ is equal to that of $C_2H_6$ and $C_4H_{10}$ and the difference between secondary $D$(R—H)s of $C_3H_8$ and $C_4H_{10}$ is equal to that of $C_4H_{10}$ and $C_5H_{12}$.

[c] Spectra of non-deuterated compounds were recorded in solutions. To the evaluated 'average'[33] CH stretching frequencies an addition of 15 cm$^{-1}$ was made to adjust to the gas-phase values.[12]

[d] Calculated by using $\Delta H_f$ (R•) = 207.5 kJ mol$^{-1}$.[38]

From Tables 2 and 3 and Figs 1–4, the following conclusions can be drawn:

1 Unknown C—H bond energies may be estimated not only from the $D$(C—H) [or $E_s$(R•)] –$\nu$(C—H) dependences but also from the corresponding relations for stretching frequencies of other bonds.

2 The dependences of $E_s$(R•) and $D$(R—H) on C—H frequencies for saturated and unsaturated compounds are different.

3 Also different are the relations of the quantities to the $\nu$(O—H), namely $E_s$(R•) and $D$(R—H) depend on $\nu$(O—H) for the saturated compounds only. For the unsaturated compounds, independent of their type,

**Table 3.** The correlation equations

| Equation | Bond | $A/A'$ | $B/B'$ | $r$ | SD[f] |
|---|---|---|---|---|---|
| $E_s(R^\bullet) = A - B\nu$ | | | | | |
| (3) | C—H[a] | 987.3 | 0.330 | 0.998 | 0.98 |
| (4) | C—H[b] | 1459 | 0.474 | 0.999 | 0.09 |
| (5) | O—H[b] | 3606 | 0.987 | 0.967 | 2.50 |
| (6) | C—O[c] | 1850 | 1.744 | 0.952 | 6.21 |
| (7) | C—O[d] | 784 | 0.684 | 0.970 | 6.86 |
| (8) | C—OO•[e] | 167 | 0.184 | 0.992 | 2.40 |
| (9) | $CH_3CON(R)$—H | 3974 | 1.143 | 0.972 | 2.61 |
| $D(R—H) = A'\nu + B'$ | | | | | |
| 10 | C—H[a] | 0.330 | −548.3 | 0.998 | 0.98 |
| 11 | C—H[b] | 0.474 | −1020 | 0.999 | 0.09 |
| 12 | O—H[a] | 0.987 | −3167 | 0.967 | 2.50 |
| 13 | C—O[c] | 1.744 | −1411 | 0.952 | 6.21 |
| 14 | C—O[d] | 0.684 | −345 | 0.970 | 6.86 |
| 15 | C—OO•[e] | 0.184 | 272 | 0.992 | 2.40 |
| 16 | $CH_3CON(R)$—H | 1.143 | −3535 | 0.972 | 2.61 |

[a] Saturated R in RH or ROH.
[b] Unsaturated R in RH.
[c] Primary alcohols.
[d] Secondary alcohols.
[e] Values of $\nu$(R—OO•) from Ref. 39
[f] Standard deviation.

$\nu$(O—H) is nearly constant and equal to about $3614 \pm 2\ \mathrm{cm}^{-1}$ (Table 2).

These sharp distinctions between the saturated and unsaturated compounds in the case of $E_s(R^\bullet)$ undoubtedly reflect the difference in the type of unpaired electron interaction with the rest of the molecule: hyperconjugation for the radicals of saturated hydrocarbons and delocalization of the unpaired electron over the whole $\pi$-system for the conjugated compounds. Since there is a linear relationship between $D$(R—H) and $E_s(R^\bullet)$ [Eqn. (2)], the observed distinctions also hold for $D$(R—H)–$\nu$ relations. It is worth noting that the existence of different correlations for different classes of compounds was perhaps first anticipated by Bernstein, as mentioned by McKean.[14]

Equations (10)–(14) (Table 3) were used to calculate $D$(R—H) values from the corresponding stretching frequencies (Table 2). The results are presented in Table 4 along with experimental $D$(R—H) values. The coincidence of the calculated and experimental values is excellent for saturated hydrocarbons [the mean differences between the calculated and experimental $D$(R—H)s are 1.8, 4.0 and $5.5\ \mathrm{kJ\ mol}^{-1}$ by using Eqns (10)

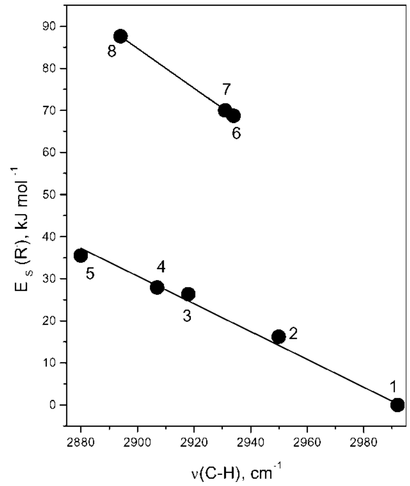


**Figure 1.** Relationship between stretching frequency of C—H bonds in hydrocarbons and of stabilization energy of corresponding radicals (Table 2). (1) $CH_3$; (2) $C_2H_5$; (3) *i*-$C_3H_7$; (4) *s*-$C_4H_9$; (5) *t*-$C_4H_9$; (6) $C_6H_5CH_2$; (7) $CH_2CHCH_2$; (8) $(C_6H_5)_2CH$

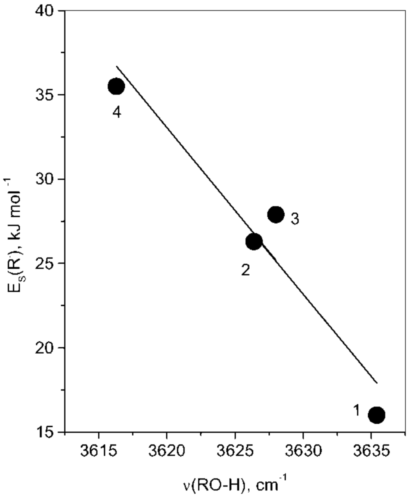


**Figure 2.** Correlation of $\nu$(O—H) frequencies of different alcohols (ROH) with stabilization energy of radicals R•. (1) $C_2H_5$; (2) *i*-$C_3H_7$; (3) *s*-$C_4H_9$; (4) *t*-$C_4H_9$

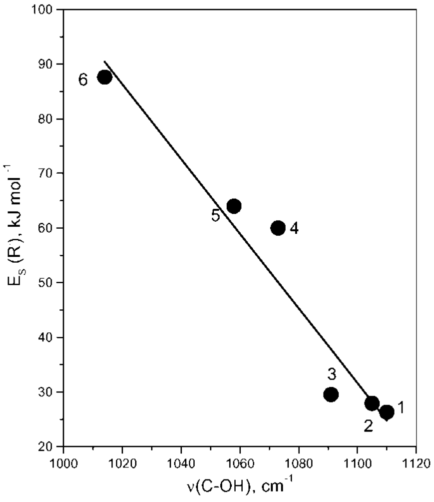


**Figure 3.** Relationship between ν(C—O) frequencies of secondary alcohols (R—OH) and $E_S$(R•) values of corresponding carbon radicals (Table 2). (1) 2-Propanol; (2) methylethyl carbinol; (3) methylisopropyl carbinol; (4) methylphenyl carbinol; (5) methylvinyl carbinol; (6) diphenyl carbinol

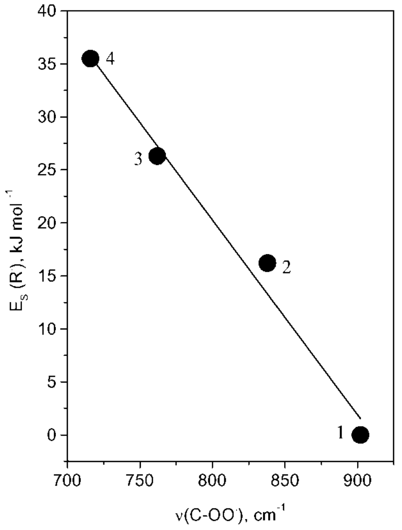


**Figure 4.** Correlation of ν(C—O) frequencies of peroxy radicals[39] with $E_S$(R•) values of corresponding carbon radicals R•. (1) $CH_3O_2$•; (2) $C_2H_5O_2$•; (3) *i*-$C_3H_7O_2$•; (4) *t*-$C_4H_9O_2$•

($\nu_{C—H}$), (11) ($\nu_{O—H}$) and (12) ($\nu_{C—OH}$) (Table 3), respectively]. For conjugated compounds the differences are larger: 6.4 kJ mol$^{-1}$ by using $\nu_{C—H}$ and 11.4 kJ mol$^{-1}$ by using $\nu_{C—OH}$. Thus, Eqn. (10) permits the calculation of *D*(R—H)s in saturated compounds with high precision. It is worth noting that the difference between the calculated and experimental quantities does not exceed (with the exception of cyclohexane, see the discussion below) 2.2 kJ mol$^{-1}$ (0.5 kcal mol$^{-1}$), which is better than the accuracy of the experiment (8.5–12.2 kJ mol$^{-1}$).[8]

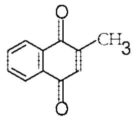
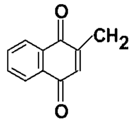
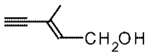
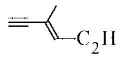
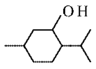
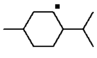
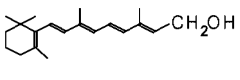
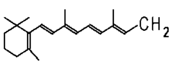
The greater difference between the calculated and

**Table 4.** Experimental and calculated bond dissociation energies

| Radical | *D*(R—H)$^{exp}$ (kJ mol$^{-1}$) (Table 2) | *D*(R—H)$^{calc}$ (kJ mol$^{-1}$) Calculated by Eqns (10)–(14) ν(R—H) | ν(RO—H) | ν(R—OH) | Δ*D* = *D*$^{calc}$−*D*$^{exp}$ (kJ mol$^{-1}$) *D*(R—H) calculated from ν(C—H) | ν(O—H) | ν(C—OH) |
|---|---|---|---|---|---|---|---|
| $CH_3$ | 439.0 | 439.0[a] | | | | | |
| $C_2H_5$ | 423.0 | 425.2 | 421.2 | 416.2 | 2.2 | −1.8 | −6.8 |
| *n*-$C_3H_7$ | 420.0 | 420.9 | 424.5 | 426.6 | 0.9 | 4.5 | 6.6 |
| *n*-$C_4H_9$ | 422.2 | 420.7 | 424.5 | 414.4 | −1.5 | 2.3 | −7.8 |
| *neo*-$C_5H_{11}$ | 418.4 | 420.0 | 427.9 | 423.1 | 1.6 | 9.5 | 4.7 |
| *i*-$C_4H_9$ | 422.7 | 422.9 | 426.3 | — | 0.2 | 3.6 | |
| *i*-$C_3H_7$ | 412.5 | 414.6 | 412.4 | 412.3 | 2.1 | −0.1 | −0.2 |
| *s*-$C_4H_9$ | 411.1 | 411.0 | 414.0 | 408.8 | −0.1 | 3.1 | −2.1 |
| $(CH_3)_2CHCHCH_3$ | 409.5 | | | 399.1 | | | −10.4 |
| *c*-$C_6H_{11}$ | 400.0 | 405.7 | 410.0 | | 5.7 | 10.0 | |
| *t*-$C_4H_9$ | 403.8 | 402.1 | 402.5 | | −1.7 | −1.3 | |
| $C_6H_5CH_2$ | 370.3 | 370.7 | | 363.8 | 0.4 | | −6.5 |
| $CH_2CHCH_2$ | 369.0 | 369.3 | | 381.3 | 0.3 | | 12.3 |
| $CH_3CH{=}CHCH_2$ | 358.2 | 367.9 | | | 9.7 | | |
| $C_8H_7CH_2$ | 360.2 | 367.4 | | | 7.2 | | |
| $CH_3CHCH{=}CH_2$ | 375.0 | | | 378.7 | | | 3.7 |
| $CH_2{=}CH(CH_3)CH_2$ | 373.0 | 366.0 | | | −7.0 | | |
| $CH_2CHCHCHCH_2$ | 349.7 | 353.5 | | | 3.8 | | |
| $C_{14}H_9CH_2$ | 351.9 | 363.6 | | | 11.7 | | |
| $C_6H_5CHCH_3$ | 360.7 | | | 388.9 | | | 28.2 |
| $(C_6H_5)_2CH$ | 353.5 | 351.8 | | 348.6 | −1.7 | | −4.9 |
| $(C_6H_5)_3C$ | 338.9 | 353.3 | | 345.6 | 14.4 | | |

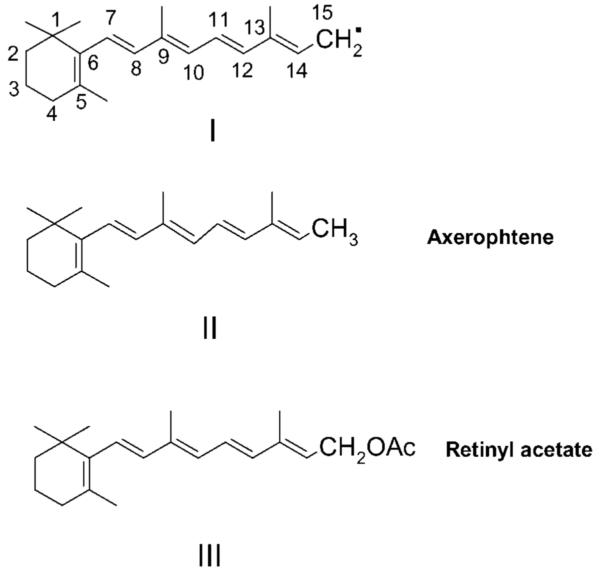
[a] Accepted.

**Table 5.** Values of $E_s(R^\bullet)$ and bond energies (kJ $mol^{-1}$) calculated from experimental data

| Compound | Bond | $\nu$ ($cm^{-1}$) | $R^\bullet$ | $E_s(R^\bullet)$ | $D$(R—H) |
|---|---|---|---|---|---|
| <br>Menadione | $CH_2$—H | 2925 |  | 63 | 376 |
| $(C_2H_5)_3COH$<br>3-Ethylpentan-3-ol | O—H | 3617[23] | $(C_2H_5)_3C$ | 34 | 405 |
| <br>3-Methylpent-2-en-4-yn-1-ol | C—O | 1008 |  | 99 | 340 |
| <br>Menthol | O—H | 3628 |  | 25 | 414 |
| <br>Retinol | C—O | 994 |  | 116.5 | 322.5 |

experimental values for unsaturated than for saturated compounds may be explained by two reasons. First, the number of $D$(R—H) determinations for saturated hydrocarbons is overwhelmingly greater than for unsaturated hydrocarbons. As a result, the validity and accuracy of $D$(C—H) values for unsaturated compounds are significantly lower than those for saturated compounds. Hence the accuracy of recommended $D(CH_2$—H) values for propylene and toluene is 8.8 and 6.3 kJ $mol^{-1}$, respectively, compared with 1.7 kJ $mol^{-1}$ for saturated hydrocarbons.[8] Second, the gas-phase values of $\nu^{iso}$(C—H) were determined for propylene, toluene and isobutene only (Table 2). For the other unsaturated compounds the $\nu$(C—H) values used in this work are the average values with correction to the gas phase (see footnote to Table 2), which introduces an additional uncertainty. Nevertheless, for all the compounds under consideration the difference between the experimental values and those calculated by Eqn. (11) does not exceed the accuracy of the experiment.[8] Some larger differences between experiment and calculation for Eqn. (12) (Table 4, column 7) may be due to the larger uncertainty of $\nu$(O—H) values than for $\nu^{iso}$(C—H).[34] About the same differences hold when using $D$(R—H)-$\nu$(C—O) relations [Eqns (13) and (14)] with the exception of ethylbenzene for unknown reason. Thus, the equations listed in Table 3 may be used to find unknown values of $D$(C—H) from different $\nu$(C—X) values measured by infrared or Raman spectroscopy.

The equations were applied to estimate unknown $E_s(R^\bullet)$ and $D$(R—H) values in some compounds including ones of medical and biological interest. The results are presented in Table 5. The obtained values of $E_s(R^\bullet)$ and $D$(C—H) seem to be reasonable compared with the data in Table 2 for compounds of similar structure. Radicals formed from menadione, 3-ethylpentan-3-ol and 3-methylpent-2-en-4-yn-1-ol may be compared with those from methylnaphthalene, *tert*-butane and pentadiene. The $E_s(R^\bullet)$ value estimated from the $\nu$(C—O) of retinol (126 kJ $mol^{-1}$, Table 5) is referred to the radical **I** (Scheme 1). Thus the strength of the primary C-15—H bond in axerophtene (**II**) calculated by Eqn. (11) (Table 3) is 323 kJ $mol^{-1}$, i.e. about 47 kJ $mol^{-1}$ stronger than the secondary C-15—H bond in retinyl acetate (**III**), for which a value of 276 kJ $mol^{-1}$ was previously found.[5] For 1-methyl-4-isopropylcyclohexane $D$(C-3—H) = 414 kJ $mol^{-1}$. It is interesting to compare the value with that of cyclohexane itself. For the latter compound two different values of $D$(C—H) have been published,[1,17] 400 and 416 kJ $mol^{-1}$. Also, two different $\nu^{iso}$ (C—H) values for cyclohexane have been reported,[25] 2891 and 2922 $cm^{-1}$ for axial and equatorial vibrations, respectively. According to Eqn. (10) (Table 3), one obtains 406 and 416 kJ $mol^{-1}$ for axial and equatorial C—H bond strengths. It may be concluded that in chemical reactions on which the values listed in Refs 1 and 17 are based (namely bromination of cyclohexane[1] and decomposition of *tert*-butylcyclohexane[17,40]), different types of C—H bonds (axial or equatorial) are involved. Thus, the $D$(C—H) calculations based on spectral data not only lead to the correct bond strengths but also permit the determination of the molecular conformation. For example, it follows from the data in Table 5 that the C—O bond in menthol is equatorial, in agreement with the established structure of the compound.[41]



**Scheme 1**

Let us consider now the use of $E_s(R^{\bullet})$ for kinetic purposes. For the abstraction of an H-atom by peroxy radicals, the following equation was found:[7]

$$3 + \log k_{abstr} = -(1.49 \pm 0.46) + (0.048 \pm 0.004)E_s(R\cdot) \qquad r = 0.958 \qquad (17)$$

From this equation, the expected rate constant for H-atom abstraction from the C-15 position of axerophtene (**II**, Scheme 1) should be $\sim 56\ l\,mol^{-1}\ s^{-1}$.

The propagation rate constant calculated in a similar manner for the autoxidation of triethylmethane is $k_{abstr} = 0.0024\ l\,mol^{-1}\ s^{-1}$. The value is comparable to that for isobutane ($0.003\ l\,mol^{-1}\ s^{-1}$) found under similar conditions.[42]

Not only the rate constants of peroxy radical attack on the C—H bonds depend on the $E_s(R^{\bullet})$ values of the radicals formed. The published data[43] for H-atom abstraction from conjugated compounds (α-methylnaphthalene, ethylbenzene, cumene, diphenylmethane, triphenylmethane and cyclohexa-1,3-diene) by $CH_3$ radicals (liquid phase, 65 °C) fit the following equation:

$$\log k = (0.84 \pm 0.44) + (0.026 \pm 0.004)E_s(R\cdot) \qquad r = 0.952 \qquad (18)$$

From this equation, the value of the rate constant of H-atom abstraction by methyl radicals from the C-15 carbon atom of axerophtene was estimated to be $\sim 1.6 \times 10^4$ $l\,mol\,s^{-1}$. This value lies between those for triphenylmethane and cyclohexa-1,3-diene.[43]

To investigators of the autoxidation of organic compounds, the correlations such as Eqns (5) and (6) for peroxy radicals are of special interest. The IR spectra of several peroxy radicals were published and collected in a review article.[39] The data presented in Fig. 4 and Table 3 [Eqn. (15)] show the excellent correlation of the $\nu$(C—O) frequencies of radicals with the corresponding $E_s(R^{\bullet})$ values. The possibility of calculations of $\nu$(C—O) frequencies of different radicals from known $E_s(R^{\bullet})$ values and vice versa is obvious.

From all the data presented one may conclude that the stabilization energy of the radicals and C—H bond strengths of many organic compounds could be estimated from the vibrational (infrared and Raman) spectra. $E_s(R^{\bullet})$ itself is a useful quantity for predicting kinetic and spectral properties of organic compounds.

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