Physical Chemistry

Estimation of dissociation energies of C—H bonds in oxygen-containing compounds from kinetic data for radical abstraction reactions

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The C—H bond dissociation energies were calculated on the basis of the parabolic model from the rate constants of free radical reactions for more than 160 oxygen-containing compounds. The enthalpies of formation of free radicals formed from these compounds were calculated. The method was modified taking into account the influence of functional groups on the partial rate constant and for the case when the reference reaction in the reaction series belongs to another class of structurally similar reactions.

Key words: activation energy, bond dissociation energy, enthalpy of formation, radicals, parabolic model of transition state, reaction rate constants, oxygen-containing compounds.

Dissociation energies of the C—H bonds are widely used in analysis of the reactivity of oxygen-containing compounds in various reactions. The C—H bond dissociation energies are known for the series of these compounds.[1—4] The representative set of experimental rate constants of reactions for radical abstraction reactions in the liquid phase is available, involving alcohols, ketones, aldehydes, acids, esters, and ethers.[5] Statistical processing and analysis of this set make it possible to extend substantially the scope of compounds for which the C—H bond dissociation energy can be estimated.

In this work we determined the C—H bond dissociation energies for more than 160 oxygen-containing compounds using the method of estimation of the bond dissociation energies from the rate constants of the radical abstraction reactions based on the empirical parabolic model of transition state.[6] The data obtained are in good accord with the published values. The recommended C—H bond dissociation energies and enthalpies of radical formation are presented for the compounds considered. The method was modified to take into account the influence of functional groups of esters on the reaction rate constant.

The C—H bond dissociation energies in alcohols have been published elsewhere.[7]

Methods of estimation of the bond dissociation energy from rate constants of radical reactions

Basic method of calculation. The main formula for the empirical parabolic model for the simple reaction $R^{\bullet} + R'H \rightarrow RH + R'^{\bullet}$ has the following form[6]:

$$br_e = \alpha(E_{ei} - \Delta H_e)^{0.5} + E_{ei}^{0.5},$$

where (1) $\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f)$ is the enthalpy of the reaction; ν_i and ν_f are the frequencies of stretching vibrations of the cleaved and formed bonds, respectively;

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h is the Planck constant; L is Avogadro´s number; D_i and D_f are the dissociation energies of the cleaved and formed bonds, respectively; (2) activation energy $E_{ei} = E_i + 0.5(hL\nu_i - RT)$ is measured from the minimum in the potential curve of the cleaved bond energy to the minimum of the transition state; R is the universal gas constant, T is the absolute temperature (K); E_i is the experimental activation energy of the radical reaction; (3) r_e is the distance between the peaks of the potential curves in the coordinates amplitude of stretching vibrations of atoms—potential energy; (4) coefficients $b = \pi(2\mu_i)^{1/2}\nu_i$ and $b_f = \pi(2\mu_f)^{1/2}\nu_f$ describe the dependence of the potential energy on the amplitude of vibrations of atoms along the cleaved (i) and formed (f) valence bond; $2b^2$ is the bond force constant; μ_i and μ_f are the reduced weights of atoms for the cleaved and formed bonds, respectively; and (5) $\alpha = b/b_f$.

The method of calculation of the bond dissociation energy is based on the experimental fact[4,6] that for structurally similar reactions (in the same reaction series) the kinetic parameter $br_e \simeq$ const if the enthalpy of the reactions lies within the interval $\Delta H_e^{min} < \Delta H_{e1} < \Delta H_e^{max}$. When calculations are performed in the reaction series, the "reference" reaction $R^{\bullet} + R'H \rightarrow RH + R'^{\bullet}$, whose all kinetic and thermodynamic parameters are known, and the reactions $R^{\bullet} + R^iH \rightarrow RH + R^{i\bullet}$, whose cleaved bond dissociation energy D_{ei} is the subject of estimation, are distinguished.

The algorithm of calculations is the following. After the characteristics of the class of reactions, *viz.*, br_e, A_0, μ_i, ν_i, μ_f, and ν_f, were determined, the critical enthalpies of the class of the following reactions are calculated taking into account the thermochemical data:

$$\Delta H_e^{min} = -(br_e/\alpha)^2 + 2br_e\alpha^{-2}(0.5hL\nu_i)^{0.5} - 0.5(1-\alpha^2)hL\nu_i, \quad (2)$$

$$\Delta H_e^{max} = (br_e)^2 - 2br_e\alpha(0.5hL\nu_f)^{0.5} - 0.5(1-\alpha^2)hL\nu_f. \quad (3)$$

Then the enthalpies of the reference reaction are estimated

$$\Delta H_{e1} = D_{i1} - D_{f1} + 0.5(hL\nu_i - hL\nu_f). \quad (4)$$

When $\Delta H_e^{min} < \Delta H_{e1} < \Delta H_e^{max}$, D_i is calculated. The rate constants of two different reactions (1 and i) obtained by the same method are used to enhance the accuracy of calculation. The pre-exponential factor A_0 per the reacting bond remains unchanged within the same reaction series. Therefore, the difference in the activation energies ΔE_i of the reactions involving the R´H and R^iH reactants is the following:

$$\Delta E_i = -RT\ln[k_i n_1/(k_1 n_i)], \quad (5)$$

where k_i is the rate constant of the ith reaction, k_1 is the rate constant of the reference reaction, and n_i and n_1 are the numbers of the equivalent attacked bonds in the ith and reference reactions of the same reaction series. Formula (1) for the reference and ith reactions gives the following relation between the difference of the bond strengths $\Delta D_i = D_i - D_f$ and ΔE_i:

$$E_{e1}^{0.5} = br_e\{1 - \alpha[1 - (1-\alpha^2)\Delta H_{e1}/(br_e)^2]^{0.5}\}/(1-\alpha^2), \quad (6)$$

$$E_{ei} = E_{e1} + \Delta E_i, \quad (7)$$

$$\Delta D_i = 2br_e(E_{ei}^{0.5} - E_{e1}^{0.5})/\alpha^2 - (\alpha^{-2} - 1)\Delta E_i. \quad (8)$$

In the method proposed, the dissociation energy of the cleaved bond (D_i) is calculated using the formula

$$D_i = \Delta D_i + D_1. \quad (9)$$

If different radicals with the same atom bearing the free valence lead the radical attack in the reaction series (*i.e.*, $D_{ef} \neq$ const), then the correction is introduced into formula (9), and the latter takes the form

$$D_i = \Delta D_i + D_1 - D_f^1 + D_{fj}, \quad (10)$$

where D_f^1 is the energy of the formed bond in the reference reaction, and D_{fj} is the dissociation energy of the formed bond in the jth reaction of the considered series.

Analysis of the accuracy in determination of ΔD_i of this method shows[4] that the maximum error does not exceed 2.5—4.0 kJ mol^{-1}.

Modification of the method of calculation for the case when the reference reaction belongs to another class of reactions. Sometimes the reference compound R´H from the given class of reactions is absent from the specific reaction series but is present in another class, and its thermochemical parameters are known. Since the kinetic parameter br_e differs, the calculation formulas should be modified. Based on Eq. (1) and assumed that the α parameter is the same for the both classes and D_f = const in the series considered, we get the following formula for calculation of ΔD_i:

$$\Delta D_i = 2br_{e1}(E_{ei}^{0.5} - E_{e1}^{0.5} - \Delta br_e)/\alpha^2 + \Delta br_e(2E_{ei}^{0.5} - \Delta br_e)/\alpha^2 - (\alpha^{-2} - 1)\Delta E_i, \quad (11)$$

where br_{e1} is the kinetic parameter of the reference reaction, and $\Delta br_e = br_e - br_{e1}$.

In this case, formula (5) for the calculation of ΔE_{ei} takes the form

$$\Delta E_{ei} = -RT\ln(A_1/A_i). \quad (12)$$

The dissociation energies of the C—H bonds in the α-position to the double bond in acids were calculated using formulas (11) and (12) (Table 1).

Taking account of functional groups in calculation of the dissociation bond energy. For some compounds, in particular, esters, the reactivities of primary bonds in the acid residue and secondary bonds in the alcohol residue

Table 1. Dissociation energies (D_i) of the C—H bonds in acids calculated from the kinetic data

Compound	R´H	D_1[a]	ΔD_i[b]	D_i	$-\Delta H(RH)$[c]	$-\Delta H(R^{\bullet})$[c]	Refs.
		kJ mol^{-1}					
C{—H}(O)OH	Malonic acid	400.1	−7.422	392.68	378.8	**204.1**	8
CH_2{—H}C(O)OH	Cyclohexane	408.8	5.277	414.08	432.2	**236.1**	9
MeCH{—H}C(O)OH	Cyclohexane	408.8	−9.920	398.88	447.7	**266.8**	9
Me_2C{—H}C(O)OH	Decane	413	−24.188	388.81	—	—	10
	Cyclohexane	408.8	−20.284	388.52	—	—	9
	Propionic acid	398.9	−11.263	387.64	—	—	11
				388.3±0.6[d]	481.2	**310.9**	
$MeCH_2$CH{—H}C(O)OH	Decane	413	−15.257	397.74	—	—	10
	Cyclohexane	408.8	−9.081	399.72	—	—	9
				398.7	472.8	**292.1**	9
$Me_2(CH_2${—H})CC(O)OH	Decane	413	2.172	415.17	510.4	**313.2**	10
$Me(CH_2)_2$CH{—H}C(O)OH	Cyclohexane	408.8	−9.362	399.44	489.5	**308.1**	9
$Me(CH_2)_3$CH{—H}C(O)OH	Decane	413	−15.884	397.12	513.8	**334.7**	10
$Me(CH_2)_4$CH{—H}C(O)OH	Pentanoic acid	399.4	−0.344	399.06	538.2	**357.1**	12
$Me(CH_2)_7$CH{—H}C(O)OH	Pentanoic acid	399.4	−0.444	398.96	600.1	**419.1**	12
CH{—H}(OH)C(O)OH	Propionic acid	398.9	−1.124	397.78	**572.7**	**392.9**	11
MeC{—H}(OH)C(O)OH	Propionic acid	398.9	−13.120	385.78	—	—	11
			−12.606	386.29	468.8	**300.8**	13
CH{—H}$[C(O)OH]_2$	Butanoic acid	398.7	1.477	400.1	811.5	**629.4**	14
HO(O)CCH{—H}CH_2C(O)OH	Acetic acid	414.1	−16.288	397.83	830.3	**650.5**	14
$[C${—H}(OH)C(O)OH$]_2$	Propionic acid	398.9	−6.278	392.68	859.1	**684.4**	13
cyclo-[C{—H}(C(O)OH)$(CH_2)_3$]	Propionic acid	398.9	−7.895	399.01	355.6	**174.6**	8
cyclo-[C{—H}(C(O)OH)$(CH_2)_5$]	Cyclohexane	408.8	−20.663	388.17	396.9	**226.7**	9
C_6H_5CH{—H}C(O)OH	Toluene	375	−8.800	367.0	318.0	**169.0**	15
CH{—H}ClC(O)OH	Propionic acid	398.9	0	398.9	435.1	**254.2**	11
NCCH{—H}C(O)OH	Malonic acid	400.1	−1.748	398.35	—	—	8
MeC(O)NHCH{—H}C(O)OH	Propionic acid	398.9	3.266	402.17	602.5	**418.3**	13
MeC(O)NHC{—H}(Me)C(O)OH	Propionic acid	398.9	−5.883	393.02	627.6	**452.6**	13
cyclo-[C(C(O)OH)=CHCH{—H}$(CH_2)_2$]	Isopropyl alcohol	390.5	−30.665	359.84	—	—	8
cis-cyclo-[C(C(O)OH)=C(C(O)OH)— —CH{—H}$(CH_2)_3$]	Isopropyl alcohol	390.5	−20.496	370.00	—	—	8

[a] Bond dissociation energy of the reference reaction.
[b] Increase in the bond dissociation energy.
[c] The enthalpies of radicals obtained in this work are given by bold.
[d] Mean D_1 value.

are comparable. In such cases, the additivity rule of the reactivities of groups (presentation of the reaction rate constant as the sum of the partial rate constants for the reacting groups) should be used for the calculation of the bond dissociation energies in the CH_2OCOR groups of esters, which also contain the MeO groups. The reaction rate constant k for the molecule containing m MeO groups and m_1 CH_2OCOR groups is presented as the sum

$$k = 3mk(\mathrm{MeO}) + 2m_1k(\mathrm{CH_2OCOR}). \qquad (13)$$

In our case, the experimental rate constants for dimethyl oxalate were known,[8] and the partial rate constant for the CH_2OCOR group of the corresponding ester were inserted instead of k_i into formula (5).

Results and Discussion

The initial data and results of calculation of the C—H bond dissociation energies in the oxygen-containing compounds are presented in Tables 1—5. The details of calculation are presented in Table 2, and the results of calculation are presented in Tables 1 and 3—5. For all classes of oxygen-containing compounds the kinetic parameter br_e was taken as 17.3 kJ$^{0.5}$ mol$^{-0.5}$ for the reactions $R^{\bullet}$ + RH and 14.5 kJ$^{0.5}$ mol$^{-0.5}$ for the reactions $H^{\bullet}$ + RH.[6] In the calculation using formulas (11) and (12) for the reference reaction the kinetic parameter was used as that for the reaction of the $Me^{\bullet}$ radical with alcohol, *i.e.*, br_e = 15.8 kJ mol$^{-0.5}$.[6] The pre-exponential

factors per reacting bond for the reactions of R˙ + RH and H˙ + RH are $1 \cdot 10^9$ and $1 \cdot 10^{11}$ L mol^{-1} s^{-1}, respectively.

The bond dissociation energies in cyclic esters and some linear ethers (for the radical attack to the secondary C—H bond), except for those of 1,4-dioxane and

Table 2. Dissociation energies (D_i) of the C—H bonds in ketones calculated from the kinetic data

Compound	R´H	T/K	k_i/k_1[a]	n_1/n_i[b]	D_1[c]	ΔE_i[d]	ΔD_i[e]	D_i	$-\Delta H$(R—H)	ΔH(R˙)[f]	Refs.
					kJ mol^{-1}						
MeC(O)CH$_2${—H}	Isooctane	347	0.772	0.17	400	5.915	12.486	412.49	—	—	16
	Cyclohexane	347	0.509	1	408.8	1.948	4.047	412.85	—	—	16
	Ethanol	403	0.767	0.33	399.8	4.560	10.33	410.13	—	—	17
								411.8±1.5[g]	−217.1	**−23.3**	
MeC(O)CH{—H}Me	Pentan-3-one	296	0.900	2	396.5	−1.447	−3.909	392.59	−240.6	**−66.0**	18
MeC(O)C{—H}Me$_2$	Diisopropyl ketone	296	0.857	2	387.6	−1.327	−3.764	383.80	−262.3	**−96.5**	18
MeC(O)CH{—H}CH$_2$Me	Pentan-3-one	296	0.450	2	396.5	0.259	0.692	397.19	−259.0	**−79.8**	18
MeCH{—H}C(O)CH$_2$Me	Cyclooctane	333	0.446	4	401.9	−1.6	−4.06	397.84	—	—	19
	Cycloheptane	333	0.564	3.5	403.9	−1.885	−4.71	399.19	—	—	19
	Acetone	333	7.628	1.5	411.8	−6.748	−17.973	393.83	—	—	19
								396.5±2.8[g]	−258.2	**−79.7**	
MeCH$_2$CH{—H}— —C(O)(CH$_2$)$_2$Me	Pentan-3-one	333	0.972	1	396.5	0.079	0.185	397.39	—	—	20
		343	1.302	1		−0.752	−1.762	395.44	—	—	20
		353	2.453	1		−2.633	−6.221	390.98	—	—	20
								394.6±3.3[g]	**−302.1**	**−125.5**	
Me(CH$_2$)$_2$CH{—H}— —C(O)(CH$_2$)$_3$Me	Pentan-3-one	333	0.835	1	396.5	0.5	1.163	398.36	—	—	20
		343	1.292	1		−0.732	−1.713	395.49	—	—	20
		353	1.697	1		−1.554	−3.653	393.55	—	—	20
								395.8±2.4[g]	**−343.4**	**−165.6**	
MeC(O)CH$_2$C{—H}Me$_2$	Acetone	296	0.800	4	411.8	−2.863	−7.818	388.68	−288.7	**−118.0**	18
Me$_2$C{—H}C(O)CHMe$_2$	Acetone	333	7.628	3	411.8	−8.667	−23.342	388.46	—	—	19
	Pentan-3-one	343	1.58	2	396.5	−3.282	−7.776	389.42	—	—	20
		353	2.123	2		−4.243	−10.102	387.10	—	—	20
		363	2.712	2		−5.104	−12.200	385.00	—	—	20
								387.5±1.9[g]	−311.3	**−141.8**	
cyclo-[C(O)CH{—H}(CH$_2$)$_3$]	Pentan-3-one	333	0.300	1	396.5	3.338	7.675	404.88	—	—	20
		343	0.453	1		2.259	5.220	402.42	—	—	20
		353	1.580	1		1.166	2.707	399.91	—	—	20
		363	0.969	1		0.094	0.219	397.42	—	—	20
								401.2±3.2[g]	−194.8	**−11.6**	
cyclo-[C(O)CH{—H}(CH$_2$)$_4$]	Pentan-3-one	296	1.450	0.5	396.5	−0.914	−2.460	394.1	−225.9	**−49.8**	18
CH$_2${—H}C(O)C(O)Me	Acetylacetone	319	0.47	3	399.1	4.916	12.539	411.63	−327.2	**−133.6**	8
MeC(O)CH{—H}C(O)Me	Cyclooctane	333	0.165	8	401.9	−0.767	−1.93	399.97	—	—	19
	Acetone	333	2.823	3	411.8	−5.915	−15.68	396.12	—	—	19
	Cycloheptane	333	0.209	7	403.9	−1.052	−2.61	401.29	—	—	19
								399.1±2.7[g]	−380.6	**−199.5**	
MeC(O)CH{—H}— —C(O)OCH$_2$Me	Acetylacetone	319	1.45	1	399.1	−0.986	−2.617	396.48	**−606.8**	**−428.3**	8
PhC(O)CH$_2${—H}	Decane	373	1.379	5.33	413	−6.189	−13.055	399.95	—	—	10
	Pentan-3-one	343	0.171	0.67	396.5	4.216	9.658	406.86	—	—	10
		363	0.394	0.67		1.944	4.494	401.70	—	—	10
								402.8±3.6[g]	−106.5	**78.3**	
PhC(O)CH{—H}Me	Decane	373	2.086	8	413	−8.730	−8.598	394.40	−128.4	**48.0**	10
PhC(O)C{—H}Me$_2$	Decane	373	3.862	16	1413	−2.79	−27.692	385.31	**−153.6**	**13.7**	10

(*to be continued*)

Table 2 (*continued*)

Compound	R´H	T/K	k_i/k_1[a]	n_1/n_i[b]	D_1[c]	ΔE_i[d]	ΔD_i[e]	D_i	$-\Delta H$(R—H)	$\Delta H(R^{\bullet})$[f]	Refs.
					kJ mol^{-1}						
PhC(O)CH{—H}CH_2Me	Decane	373	2.107	8	413	−8.76	−18.663	394.33	**−149.0**	**27.3**	10
PhC(O)CCH_2{—H}Me_2	Decane	373	0.534	1.78	413	0.158	0.327	413.33	**−167.2**	**28.1**	10
PhC(O)CH_2C{—H}Me_2	Pentan-3-one	353	1.377	2	396.5	−5.009	−16.968	385.23	**−171.8**	**−4.6**	20
PhC(O)CH{—H}$(CH_2)_7$Me	Decane	373	2.131	8	413	−8.795	−18.741	394.26	**−272.8**	**−95.6**	10

[a] Dissociation bond energy of the reference reaction.
[b] k_i is the reaction rate constant, and k_1 is the rate constant of the reference reaction.
[c] n_1 and n_i is the number of the attacked bonds in the reference and studied reactants.
[d] The difference between the activation energies of the reactions.
[e] ΔD_i is the increase in the bond dissociation energies.
[f] The enthalpies of molecules and radicals obtained in this work are given by bold.
[g] Mean D_1 value.

Table 3. Dissociation energies (D_i) of the C—H bonds in aldehydes calculated from the kinetic data

Compound	R´H	D_1[a]	ΔD_i[b]	D_i	$-\Delta H$(RH)[c]	$\Delta H(R^{\bullet})$[c]	Refs.
		kJ mol^{-1}					
HC{—H}(O)	—	—	—	377.8	108.6	**51.2**	4
CH_2{—H}CH(O)	—	—	—	394.3	165.8	10.5	21
MeC{—H}(O)	—	—	—	373.8	165.8	−10.0	21
C{—H}(O)C(O)OH	Ethanal	373.8	1.520	375.32	**389.1**	**−231.9**	8
$Me(CH_2)_2$C{—H}(O)	Ethanal	373.8	−2.565	371.23	207.5	**−54.3**	15
$Me(CH_2)_3$C{—H}(O)	Butanal	371.2	0.831	372.03	230.5	**−76.5**	22
Me_2CHC{—H}(O)	The same	371.2	−6.659	364.54	215.5	**−69.0**	22
Me_2CHCH_2C{—H}(O)	»	371.2	−8.590	362.61	238.5	**−93.9**	22
$MeCH_2$CH(Me)C{—H}(O)	»	371.2	−10.38	360.82	**229.8**	**−87.0**	22
Me_3CC{—H}(O)	»	371.2	3.932	375.13	242.7	**−85.6**	22
$(MeCH_2)_2$CHC{—H}(O)	»	371.2	−4.016	367.18	255.2	**−106.0**	22
$Me(CH_2)_8$C{—H}(O)	Decane	413	−39.714	373.26	**322.9**	**−176.6**	10
$CH_2(OH)(CHOH)_3$C{—H}(O)	Ethanal	373.8	−3.764	370.04	—	—	8
$CH_2(OH)(CHOH)_4$C{—H}(O)	D-Ribose	370.0	1.402	371.4	—	—	23
$CH_2OH(CHOH)_4$C{—H}(O)	D-Ribose	370.0	−0.160	369.84	—	—	23
PhC{—H}(O)	—	—	—	348.0	37.7	**92.3**	4
$PhCH_2$C{—H}(O)	Butanal	371.2	−9.222	361.98	54.4	**89.6**	22
$PhCMe_2$C{—H}(O)	Ethanal	373.8	−10.932	362.87	**96.2**	**48.7**	24
3-$NO_2C_6H_4$C{—H}(O)	Benzaldehyde	348.0	−4.285	343.72	—	—	24
4-$NO_2C_6H_4$C{—H}(O)	The same	348.0	−7.099	340.36	50.2	**72.2**	24
4-$CMe_3C_6H_4$C{—H}(O)	»	348.0	−10.874	337.13	—	—	24
4-$CMe_3C_6H_4$C{—H}(O)	»	348.0	−2.503	345.42	—	—	25
4-MeC_6H_4C{—H}(O)	»	348.0	−2.231	345.77	75.3	**52.5**	25
3-MeC_6H_4C{—H}(O)	»	348.0	−1.026	346.97	—	—	25
4-$OMeC_6H_4$C{—H}(O)	»	348.0	−1.605	346.40	205.0	**−76.6**	25
3-$OMeC_6H_4$C{—H}(O)	»	348.0	2.933	350.93	—	—	25
4-$OC_6H_5C_6H_4$C{—H}(O)	»	348.0	−0.803	347.12	—	—	25
4-ClC_6H_4C{—H}(O)	»	348.0	4.272	352.27	66.9	**67.4**	25
3-ClC_6H_4C{—H}(O)	»	348.0	5.546	353.55	—	—	25
3-BrC_6H_4C{—H}(O)	»	348.0	5.826	353.83	—	—	25

[a] Bond dissociation energy of the reference reaction.
[b] Increase in the bond dissociation energy.
[c] The enthalpies of molecules and radicals obtained in this work are given by bold.

Table 4. Dissociation energies (D_i) of the C—H bonds in ethers calculated from the kinetic data

Compound	R´H	D_1[a]	ΔD_i[b]	D_i	ΔH(R—H)[c]	ΔH(R$^\bullet$)[c]	Refs.
		kJ mol^{-1}					
$MeOCH_2${—H}	Cyclohexane	408.8	4.591	413.4	—	—	19
	Cyclooctane	401.9	9.76	411.7	—	—	19
	Methanol	411	−0.49	410.5	—	—	19
				411.9±1.2 [d]	−184.1	**9.8**	
MeCH{—H}OCH_2Me	Cyclohexane	408.8	−9.52	399.3	—	—	13
	Cyclopentane	408.4	−8.39	400	—	—	13
	Cyclopropane	429	−26.7	402.3	—	—	13
	Ethane	422	−19.7	402.3	—	—	13
	Ethanol	399.75	0.635	400.4	—	—	13
	Isopropyl alcohol	390.5	11.7	402.2	—	—	26
	2,3-Dimethylbutane	396.4	−0.75	395.6	—	—	27
	2,4-Dimethylbutane	400	−3.6	396.4	—	—	27
	2,5-Dimethylhexane	400	−0.16	399.8	—	—	27
	Methanol	411	−14.3	396.7	—	—	27
	Nonane	413	−13.5	399.5	—	—	27
				399.5±2.4 [d]	−251.5	**−70.0**	
Me_2CHOC{—H}Me_2	2,3-Dimethylbutane	396.4	−6	390.4	—	—	27
	Isopropyl alcohol	390.5	0.446	390.9	—	—	27
	Methanol	411	−20.9	390.1	—	—	27
	2,3-Dimethylbutane	396.4	−5.32	391.1	—	—	28
	Ethanol	399.8	−9.75	390	—	—	28
				390.8±0.9 [d]	−318.8	**−146.0**	
$Me(CH_2)_3OCH${—H}$(CH_2)_2Me$	1-Decanol	395.6	−3.464	392.14	—	—	10
	1-Nonanol	395.8	−3.578	392.22	—	—	10
				392.2 [d]	−334.7	**−160.5**	
CH{—H}$(OCH_2Me)_2$	Tetrahydrofuran	391.6	−1.467	390.13	—	**−200.3**	29
CH{—H}$[O(CH_2)_2Me]_2$	Tetrahydrofuran	391.6	−0.374	391.23	—	—	29
	Diethoxymethane	391.2	1.088	392.29	—	—	30
				391.8 [d]	**−413.7**	**−239.9**	
CH{—H}$[O(CH_2)_3Me]_2$	Tetrahydrofuran	391.6	−1.944	389.66	—	—	29
	Diethoxymethane	391.2	−0.475	390.73	—	—	30
				390.2 [d]	**−454.9**	**−282.7**	
MeC{—H}$(OMe)_2$	Tetrahydrofuran	391.6	−2.241	389.36	—	—	30
	Diethoxymethane	391.2	−6.184	385.02	—	—	30
				387.2 [d]	−389.5	**−220.3**	
$Me_3COCMe_2CH_2${—H}	Dibutyl ether	392.2	9.872	402.07	−364.0	**−179.9**	31
cyclo-[$O(CH_2)_3CH${—H}]	2,3-Dimethylbutane	396.4	−4.72	391.7	—	—	27
	Isopropyl alcohol	390.5	1.714	392.2	—	—	27
	Methanol	411	−19.6	391.4	—	—	27
	2,3-Dimethylbutane	396.4	−4.98	391.4	—	—	28
	Isopropyl alcohol	390.5	0.902	391.4	—	—	32
				391.6±0.4 [d]	−184.1	**−10.5**	
cyclo-[OC{—H}$Me(CH_2)_3$]	Isopropyl alcohol	390.5	−6.4	384.1 [d]	−220.1	**−54.0**	33
cyclo-[$O(CH_2)_2OCH${—H}CH_2]	Cyclohexane	408.8	−1.07	407.7	—	—	27
	Methanol	411	−5.79	405.2	—	—	27
	Cyclohexane	408.8	−0.89	407.9	—	—	16
	Methanol	411	−6.72	404.3	—	—	13
	2,3-Dimethylbutane	396.4	7.358	403.8	—	—	28
	2,4-Dimethylpentane	308		404.5	—	—	28
	Methanol	411	−6.27	404.7	—	—	28
				405.4±0.7 [d]	−315.3	**−127.9**	

(*to be continued*)

Table 4 (*continued*)

Compound	R´H	D_1[a]	ΔD_i[b]	D_i	ΔH(R—H)[c]	ΔH(R•)[c]	Refs.
		kJ mol^{-1}					
cyclo-[OC{—H}(Me)$(CH_2)_2$CH(Me)]	Tetrahydrofuran	391.6	−4.085	387.52	—	—	31
cyclo-[O$(CH_2)_4$CH{—H}]	The same	391.6	10.109	401.71	—	—	31
cyclo-[OCH{—H}O$(CH_2)_4$]	»	391.6	1.924	393.5	—	—	30
cyclo-[OCH{—H}O$(CH_2)_3$]	Diethoxymethane	391.2	−0.548	390.85	—	—	30
	The same	391.2	0.435	391.64	—	—	30
				391.2 [d]	—	—	
cyclo-[OCH{—H}OCMe$_2(CH_2)_2$]	»	391.2	3.649	394.85	—	—	30
1,5-Dioxyspiro[5.5]undecane	»	391.2	5.022	396.22	—	—	30
cyclo-[O$(CH_2)_2$C{—H}(Me)OCH(Me)]	»	391.2	−18.19	373.01	—	—	30
cyclo-{OC{—H}[$(CH_2)_2$Me]O$(CH_2)_3$}	»	391.2	−13.48	377.72	—	—	30
cyclo-[O$(CH_2)_2$OC{—H}(Me)]	»	391.2	−12.327	378.87	—	—	30
	Dipropoxymethane	390.2	−14.843	375.34	—	—	34
	2-Methyl-1,3-dioxolane	378.9	0.000	378.9	—	—	35
				377.1 [d]	—	—	
cyclo-[OC{—H}(CHMe$_2$)OCH$_2$CMe$_2$CH$_2$]	Dipropoxymethane	390.2	−8.219	381.98	—	—	34
cyclo-[OC{—H}(CHMe$_2$)O$(CH_2)_4$]	The same	390.2	−12.039	378.16	—	—	34
cyclo-[OC{—H}($(CH_2)_2$Me)OCH$_2$CMe$_2$CH$_2$]	»	390.2	−24.47	365.73	—	—	34
cyclo-[OC{—H}(Me)O$(CH_2)_2$]	»	390.2	−30.61	359.59	—	—	34
cyclo-[OC{—H}(Me)CH$_2$]	2-Methyl-1,3-dioxolane	378.9	−2.875	376.03	—	—	35
cyclo-[OC(CH$_2$Me)(Me)OCH{—H}CH$_2$]	The same	378.9	2.836	381.74	—	—	35
cyclo-[OCMe$_2$CH{—H}C(O)$(CH_2)_2$]	»	378.9	10.714	389.61	—	—	35
3-ClC_6H_4CH{—H}OMe	Ethylbenzene	364.1	−3.31	360.8	—	—	36
	The same	364.1	−3.08	361.0	—	—	37
				360.9 [d]	—	—	
(3-Cl$C_6H_4)_2$C{—H}OMe	»	364.1	−11.7	352.4	—	—	38
4-ClC_6H_4CH{—H}OMe	»	364.1	−4.69	359.4	—	—	36
	»	364.1	−4.5	359.6	—	—	37
				359.5 [d]	—	—	
4-ClC_6H_4C{—H}$(OMe)_2$	»	364.1	−9.76	354.3	—	—	38
4-BrC_6H_4CH{—H}OMe	Ethylbenzene	364.1	−6.22	357.9	—	—	37
4-BrC_6H_4C{—H}$(OMe)_2$	The same	364.1	−9.76	354.3	—	—	38
(4-Br$C_6H_4)_2$C{—H}OMe	»	364.1	−14	350.1	—	—	38
C_6H_4C{—H}$(OMe)_2$	»	364.1	−10.2	353.9	—	—	38
4-CH{—H}OMeC_6H_4OMe	»	364.1	−9.64	354.5	—	—	37
4-CH{—H}$(OMe)_2C_6H_4$OMe	»	364.1	−10.9	353.2	—	—	38
4-CH{—H}OMe$C_6H_4(CH_2)_3$Me	»	364.1	−6.42	357.7	—	—	36
4-CMe$_3C_6H_4$C{—H}$(OMe)_2$	»	364.1	−11	353.1	—	—	38
(4-OMeC_6H_4CH{—H})$_2$O	»	364.1	−14.1	350.0	—	—	38
(4-OMe$C_6H_4)_2$C{—H}OMe	»	364.1	−21.3	342.8	—	—	38
4-C(O)OMeC_6H_4C{—H}$(OMe)_2$	»	364.1	−8.9	355.2	—	—	38
[4-C(O)OMe$C_6H_4]_2$C{—H}OMe	»	364.1	−10.6	353.5	—	—	38
4-CH{—H}OMeC_6H_4Me	»	364.1	−6.85	357.2	—	—	36
	»	364.1	−6.62	357.5	—	—	37
				357.3 [d]	—	—	
(4-Me$C_6H_4)_2$C{—H}OMe	»	364.1	−17.5	346.6	—	—	38
(4-CMe$_3C_6H_4)_2$C{—H}OMe	»	364.1	−16.5	347.6	—	—	38

(*to be continued*)

Table 4 (*continued*)

Compound	R´H	D_1[a]	ΔD_i[b]	D_i	ΔH(R—H)[c]	$\Delta H(R^{\bullet})$[c]	Refs.
		kJ mol^{-1}					
$PhOCH_2\{-H\}$	Ethylbenzene	364.1	20.95	385.0	−67.8	**99.2**	19
$PhCH\{-H\}OMe$	The same	364.1	−5.06	359.0	−75.3	**65.7**	37
$PhCH\{-H\}OCH_2Ph$	»	364.1	−5.06	359.0	19.5	**160.5**	37
$Ph_2C\{-H\}OMe$	»	364.1	−9.97	354.1	—	—	37
cyclo-$[OC\{-H\}(SCH_2Me)(CH_2)_4]$	Dipropoxymethane	390.2	−24.674	365.53	—	—	34
cyclo-$[OC\{-H\}(S(CH_2)_4Me)(CH_2)_4]$	The same	390.2	−25.792	364.41	—	—	34
cyclo-$[OC\{-H\}S(CH_2)_2]$	»	390.2	−9.266	380.93	—	—	34
cyclo-$[OC\{-H\}(Me)S(CH_2)_2]$	»	390.2	−12.359	377.84	—	—	34
cyclo-$[OC\{-H\}(CH_2Me)S(CH_2)_2]$	»	390.2	−12.359	377.84	—	—	34
cyclo-$[OC\{-H\}(CH(Me)_2)S(CH_2)_2]$	»	390.2	−12.201	378.0	—	—	34
cyclo-$[OCMe_2SCH\{-H\}CH_2]$	»	390.2	4.514	394.71	—	—	34

[a] Bond dissociation energy of the reference reaction.
[b] Increase in the bond dissociation energy.
[c] The enthalpies of molecules and radicals obtained in this work are given by bold.
[d] Mean value.

Table 5. Dissociation energies (D_i) of the C—H bonds in esters calculated from the kinetic data

Compound	R´H	D_1[a]	ΔD_i[b]	D_i	$-\Delta H$(R—H)[c]	$-\Delta H(R^{\bullet})$[c]	Refs.
				kJ mol^{-1}			
$MeC(O)OCH_2\{-H\}$				404.0	410.0	**224.0**	4
$MeCH_2CH\{-H\}C(O)OMe$	Decane	413	−18.068	394.93	451.9	**275.0**	8
$Me(CH_2)_2CH\{-H\}C(O)OMe$	The same	413	−18.141	394.86	471.5	**294.6**	8
$Me(CH_2)_3CH\{-H\}C(O)OMe$	»	413	−18.539	394.46	493.7	**317.2**	8
$Me(CH_2)_3C(O)OCH\{-H\}Me$	»	413	−20.715	392.29	507.1	**332.8**	8
$Me(CH_2)_3C(O)OCH\{-H\}CH_2Me$	»	413	−20.888	392.12	**527.7**	**353.6**	8
$Me(CH_2)_3C(O)OC\{-H\}Me_2$	»	413	−25.084	387.92	544.8	**374.9**	8
$Me_3CC(O)OC(CH_2\{-H\})Me_2$	»	413	2.010	415.01	**546.2**	**349.2**	8
$Me(CH_2)_3C(O)OCH\{-H\}(CH_2)_6Me$	»	413	−21.137	391.86	**630.9**	**457.0**	8
$MeOC(O)CH\{-H\}C(O)OMe$	»	413	−21.339	391.66	737.9	**564.2**	8
$MeOC(O)C(O)OCH_2\{-H\}$	»	413	−9.050	403.95	677.8	**491.8**	8
$MeOC(O)CH_2CH\{-H\}C(O)OMe$	»	413	−8.234	404.77	**780.2**	**593.6**	8
$MeOC(O)(CH_2)_2CH\{-H\}C(O)OMe$	»	413	−19.901	393.10	**801.1**	**626.0**	8
$MeOC(O)(CH_2)_4CH\{-H\}C(O)OMe$	»	413	−19.807	393.19	**842.3**	**667.1**	8
$MeOC(O)(CH_2)_6CH\{-H\}C(O)OMe$	»	413	−20.443	392.56	**883.6**	**709.0**	8
$MeCH_2OC(O)C(O)OCH\{-H\}Me$	»	413	−16.782	396.22	740.6	**562.4**	8
$Me_2CHOC(O)C(O)OC\{-H\}Me_2$	»	413	−16.760	396.24	**833.7**	**665.0**	8
$Me_2COC(O)(CH_2)_2C(O)OC\{-H\}Me_2$	»	413	−17.498	395.50	**629.7**	**451.7**	8
$Me_2CHOC(O)(CH_2)_3C(O)OC\{-H\}Me_2$	»	413	−21.262	391.74	**649.9**	**476.2**	8
$Me_2CHOC(O)(CH_2)_5C(O)OC\{-H\}Me_2$	»	413	−21.784	391.22	**691.1**	**517.9**	8
$Me_2CHOC(O)(CH_2)_8C(O)OC\{-H\}Me_2$	»	413	−21.926	391.07	**753.0**	**579.9**	8
$Me_2COC(O)CH_2CH\{-H\}C(O)OH$	»	413	−19.863	393.14	**740.5**	**565.4**	8
$Me_2COC(O)(CH_2)_2CH\{-H\}C(O)OH$	»	413	−21.912	391.03	**761.1**	**588.1**	8
$Me_2COC(O)(CH_2)_3CH\{-H\}C(O)OH$	»	413	−21.527	391.47	**781.8**	**608.3**	8
$Me_2COC(O)(CH_2)_4CH\{-H\}C(O)OH$	»	413	−21.719	391.28	802.7	**629.4**	8
$Me_2COC(O)(CH_2)_7CH\{-H\}C(O)OH$	»	413	−21.719	391.28	921.7	**748.4**	8
$PhC(O)OCH_2\{-H\}$	Cyclohexane	408.8	9.56	418.4	288.7	**88.3**	16
$PhSi(CH_2\{-H\})Me_2$	Pentane	413	−2.948	410.06	—	—	19

[a] Bond dissociation energy of the reference reaction.
[b] Increase in the bond dissociation energy.
[c] The enthalpies of molecules and radicals obtained in this work are given by bold.

tetrahydrofuran, were estimated from the kinetic data for the abstraction reactions $RO_2^{\bullet}$ + RH.

It has previously[39] been shown that the polar effect ΔE_μ in the reactions of $RO_2^{\bullet}$ with cyclic esters is insignificant and equals ~−3 kJ mol^{-1}. This allows one to correct the kinetic parameter for reactions of this type using the formula

$$\Delta E_\mu = \{br_e^2 - b[r_e(RH)]^2\}/(1 + \alpha^2), \quad (14)$$

where α = 0.814, br_e(RH) = 13.62 kJ$^{0.5}$ mol$^{-0.5}$, and ΔE_μ = −3 kJ mol^{-1}.[6]

Thus, the br_e value for cyclic esters in the abstraction reactions $RO_2^{\bullet}$ + RH can be accepted as 13.44 kJ$^{0.5}$ mol$^{-0.5}$, and the pre-exponential factor per reacting bond can be taken as $1 \cdot 10^8$ L mol^{-1} s^{-1}.

The bond dissociation energies for alkane molecules in the reference reactions[9] and enthalpies of formation of the molecules[40,41] have previously been published. The enthalpies of formation of the corresponding radicals were estimated using the formula

$$\Delta H(R{-}H) + D(R{-}H) = \Delta H(R^{\bullet}) + 218 \text{ kJ mol}^{-1} \quad (15)$$

according to the thermochemical equation RH = $R^{\bullet}$ + $H^{\bullet}$, where $\Delta H(H^{\bullet})$ = 218 kJ mol^{-1}.

When the α-C—H bond is cleaved in the molecule of an oxygen-containing compound, the radical formed is stabilized due to the interaction of the unpaired electron with the p-electrons of the O atom. The D(C—H) values obtained in this work make it possible to estimate the energy of the $RC^{\bullet}HX$ (X = OH, OR, COOR, OC(O)R, C(O)Ph) radical that formed as the difference in the C—H bond dissociation energies in RMe (D(C—H) = 422 kJ mol^{-1}) and XMe, RCH_2Me (D(C—H) = 413 kJ mol^{-1}) and RCH_2X, R_2CHMe (D(C—H) = 400 kJ mol^{-1}) and R_2CHX, *etc*.

It follows from the results of calculation (Table 6) that the energy of radical stabilization by the oxygen-containing group is within 7 to 20 kJ mol^{-1}. This is much lower than the stabilization caused by the Ph ring in the α-position (see Table 6).

The maximum stabilization of the radical by the same group was found for the RCH_2X fragment. The groups can be arranged in the following series by the stabilizing ability (see Table 6): RC(O)O > C(O)OR > C(O)R > > OH > COOH > OR.

Thus, the calculations allowed us to extend considerably the range of oxygen-containing compounds, whose fundamental characteristic of the molecule, *viz*., bond dissociation energy, is presently known, and to refine its values for almost all compounds with the known C—H bond dissociation energies. The use of the kinetic data provides the consistent scale of D(C—H) values for a wide range of oxygen-containing compounds. The bond dissociation energies for several ketones, aldehydes, acids, and cyclic ethers were estimated for the first time.

Table 6. Decrease in the C—H bond strength (ΔD) due to the introduction of the X group into the hydrocarbon molecule

X	ΔD/kJ mol^{-1}				
	MeX	RCH_2X	R_2CHX	$RCHX_2$	CH_2X_2
OH	11.0	16.0±1.6	9.9±0.6	—	—
OR	10.1±1.2	13.5±2.4	9.2±0.9	12.8±3.1	21.3±1.0
HOOC—	7.9	14.3±0.8	11.7±0.6	14.0	12.9
RC(O)O—	18.0	20.8±0.1	8.7±0.3	—	—
ROOC—	7.0	18.2±0.2	—	—	21.3
R(O)C—	10.2±1.5	17.4±1.0	13.3±2.6	—	13.9±2.7
Ph(O)C—	19.2	18.6	14.7	—	—
Ph	47.0	47.9	45.3	49.0	55.2

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