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Concerted molecular decomposition of unsaturated and oxygen-containing compounds

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Abstract. Kinetic data on concerted molecular decomposition of alkenes, alcohols, ethers and esters, unsaturated acids and nitro compounds are summarized and analyzed. Experimental data are analyzed within the framework of semiempirical models treating the decomposition as (i) one-centre reaction involving transfer of hydrogen atom and (ii) two-centre reaction with simultaneous H atom transfer and cleavage of C–C, C–O or C–N bond. The effects of the molecular geometry of compounds and other factors on the activation energy of decomposition are discussed. The results of calculations of the spectrum of activation energy for concerted decomposition and the results of quantum chemical calculations of the transition-state geometries and energy characteristics are presented. The bibliography includes 59 references.

I. Introduction

Benson [1] divided the molecular decomposition reactions into the following three classes: 1) simple decomposition of a molecule into two radicals involving cleavage of a bond (molecule → 2 radicals); 2) complex decomposition involving cleavage of two or more bonds (molecule → 2 molecules); and 3) isomerization reactions involving only rearrangement of bonds and atoms in the molecule (molecule → molecule). The complex decomposition reactions are rare to occur. Much more frequently, decomposition of a molecule into two molecules proceeds by a chain mechanism *via* certain intermediate steps involving free atoms and radicals.[2, 3] For instance, molecular decomposition of ethane does not occur by the reaction

$$CH_3CH_3 \longrightarrow CH_2{=}CH_2 + H_2.$$

It proceeds as a chain process with the chain propagation steps described by the following reactions:[4]

$$H^{\bullet} + CH_3CH_3 \longrightarrow H_2 + CH_3C^{\bullet}H_2,$$

$$CH_3C^{\bullet}H_2 \longrightarrow CH_2{=}CH_2 + H^{\bullet}.$$

Gas-phase decomposition of acetaldehyde by the apparently simple reaction

$$CH_3CHO \longrightarrow CH_4 + CO$$

does not occur. The process also proceeds by a chain mechanism. Chain propagation is attained by alternating the following elementary steps:[4]

$$C^{\bullet}H_3 + CH_3CHO \longrightarrow CH_4 + CH_3C^{\bullet}O,$$

$$CH_3C^{\bullet}O \longrightarrow C^{\bullet}H_3 + CO.$$

For a reaction involving the rearrangement of bonds to proceed, it is necessary that corresponding molecular orbitals be overlapped, *i.e.*, the symmetry of the molecular orbitals involved in the rearrangement be conserved (Woodward – Hoffman rule).[2, 5] Its formulation is as follows: a reaction is said to be symmetry allowed if the symmetry of the bonds being formed matches that of the bonds being cleaved.[6] Only in this case, the overlap of the molecular orbitals necessary to form a transition state (TS) is possible.

For instance, in a hypothetical reaction

$$HCHO \longrightarrow H_2 + CO$$

the C–H bonds have the orbital symmetry a_1, the C=O bond has the symmetry b_2, while both products, H_2 and CO,

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have the symmetry a_1. Therefore, the orbital symmetry is not conserved in this reaction and it does not occur. The decomposition of formaldehyde proceeds as a chain process.[4]

In this review we will consider the molecular decomposition reactions of unsaturated and oxygen-containing compounds which involve concerted cleavage of some bonds and formation of other bonds.[1,4] Gas-phase decomposition of these compounds proceeds by the monomolecular mechanism irrespective of the reactior size and the reactor wall material. The reactions proceed *via* the formation of cyclic TS with conservation of the orbital symmetry of the bonds that are involved in the rearrangements. Two semiempirical methods[7,8] have been developed to describe and analyze such reactions. These methods were used to analyze the experimental data on concerted decomposition of alkenes, alcohols, acids, ethers and esters, as well as nitro compounds.[7–13]

II. Semiempirical models for concerted decomposition reactions

1. The oscillation model for molecular decomposition with concerted cleavage of several bonds

If concerted decomposition of a molecule involves more than one bond, the probability of localization of activation energies on these bonds depends on the number of bonds. Considering the molecule as a system of coupled oscillators, Aleksandrov[14] derived the dependence of the pre-exponent in the Arrhenius equation for this reaction on the number of bonds (n):

$$A = A_0 n 2^{1-n} \left(\frac{nRT}{\pi E}\right)^{(n-1)/2} \quad (1)$$

where $A = A_0$ at $n = 1$, E is the activation energy of concerted decomposition, R is the universal gas constant and T is the temperature (in K). For all reactions considered in this review, one has $n = 2$ and, therefore,

$$A = A_0 \sqrt{\frac{2RT}{\pi E}}. \quad (2)$$

When expressing the rate constant (k) for such a reaction in the Arrhenius form, one should keep in mind that A depends on T [see Eqn (2)] and $E = RT^2(d\ln k/dT) = E_{exp} - 0.5\,RT$ (E_{exp} is the experimental activation energy). Then, one gets:[7]

$$k = A\exp\left(-\frac{E}{RT}\right) = A_0\sqrt{\frac{2RT}{\pi E}}\exp\left(-\frac{E}{RT}\right). \quad (3)$$

2. The model for concerted decomposition as one-centre reaction involving transfer of a hydrogen atom [MIP(1)]

All reactions considered in this review involve transfer of a hydrogen atom from one C atom to some other C atom or an O atom or from an O atom to a C atom. According to quantum chemical calculations,[12] the maximum in the plot of the TS energy *vs.* reaction coordnate exactly corresponds to the maximum distance of the H atom from both atoms (C, C or C,O) of the reaction centre (Fig. 1). This gives grounds to treat the concerted decomposition of a molecule as a hydrogen abstraction reaction in which the abstraction of H atom is accompanied by simultaneous rearrangement

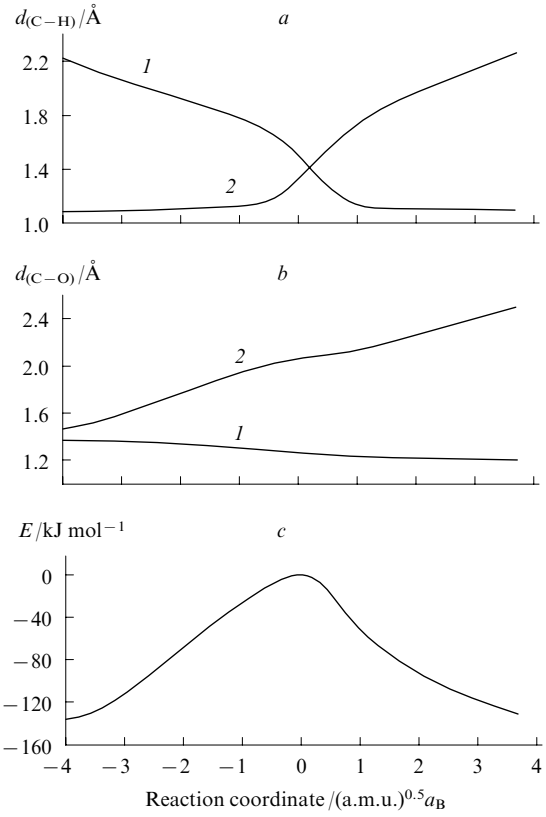


Figure 1. Changes in the C–H (*a*) and C–O (*b*) distances and in the energy (*c*) along the reaction coordinate for the decomposition of $CH_2{=}CHOEt$, calculated by the B3LYP/6-31G*.[12]
Curves (*1*) and (*2*) correspond to the bond being formed and the bond being cleaved, respectively; a_B is the Bohr radius (radius of hydrogen atom).

of other bonds. As a consequence, the semiempirical model of intersecting parabolas [MIP(1)][15,16] can be used.

Within the framework of the MIP(1) model, a radical abstraction reaction

$$R^{\bullet} + HY \longrightarrow RH + Y^{\bullet}$$

is characterized by the following parameters.[15]

1. The classical enthalpy (ΔH_e), which is related to the enthalpy of reaction [$\Delta H = \Delta H(298\ K)$]:

$$\Delta H_e = \Delta H + 0.5\,hN_A(\nu_{Y-H} - \nu_{C-H}), \quad (4)$$

where ν_{Y-H} and ν_{C-H} are the stretching vibration frequencies of the reacting bonds (Y = C or O), h is the Planck constant and N_A is the Avogadro constant.

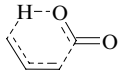
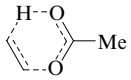
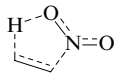
2. The classical potential barrier (E_e) which includes the activation energy, the zero-point vibrational energy of the bond being cleaved and the average kinetic energy of H atom; the parameter E_e is related to the activation energy E as follows:

$$E_e = E + 0.5\,hN_A\nu_{C-H} - 0.5\,RT. \quad (5)$$

3. The distance r_e which characterizes the elongation of the reacting bonds in the TS.

4. The parameters b ($2b^2$ is the force constant of the bond being cleaved) and b_f ($2b_f^2$ is the force constant bond being formed), as well as the coefficient $\alpha = b/b_f$.

Table 1. Transition-state geometries and kinetic parameters of molecular decomposition reactions of unsaturated compounds and nitro compounds used in the MIP(1) model.[15,16]

Decomposition reaction	Transition state	α	$b \times 10^{11}$ (see [a])	$0.5hN_Av$ (see [b])	$\Delta\Delta H_e$ (see [b])
$CH_2{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHMe$		1.00	3.743	17.4	0
$CH_2{=}CHOEt \longrightarrow CH_2{=}CH_2 + MeCHO$		1.00	3.743	17.4	0
$CH_2{=}CH(CH_2)_2OH \longrightarrow CH_2{=}CHMe + HCHO$		1.255	4.698	21.7	4.3
$CH_2{=}CHCH_2CO_2H \longrightarrow CH_2{=}CHMe + CO_2$		1.299	4.600	21.2	3.8
$MeCO_2Et \longrightarrow CH_2{=}CH_2 + MeCO_2H$		0.814	3.743	17.4	−3.8
$EtNO_2 \longrightarrow CH_2{=}CH_2 + HONO$		0.812	3.743	17.4	−4.0

[a] In $kJ^{1/2}\,mol^{-1/2}\,m^{-1}$. [b] In $kJ\,mol^{-1}$.

5. The activation energy E is determined from the equation

$$E = RT\left[\frac{\ln nA_0(2RT/\pi E)^{1/2}}{k}\right], \tag{6}$$

where A_0 is the pre-exponent per reacting bond (a constant for reactions of the same class); k is the empirical rate constant for the reaction; n is the number of equireactive C−H bonds involved in the reaction ($n = 3$ for methyl group and 2 for methylene unit).

Numerical values of the parameters α, b, $0.5hN_Av$, ΔH_e characterizing molecular decomposition of six classes of compounds are listed in Table 1.[15] The available experimental data (enthalpies and activation energies of reaction) allow one to estimate the parameter br_e:[15]

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}, \tag{7}$$

which in turn allows the activation energies of other reactions belonging to a given class to be calculated from the relation

$$E = B^2\left\{1 - \alpha\sqrt{1 - \frac{\Delta H_e}{B\,br_e}}\right\}^2 - 0.5\,(hN_Av_{Y-H} - RT), \tag{8}$$

where $B = br_e/(1 - \alpha^2)$.

The reactions involving transfer of H atom between carbon atoms are characterized by $\alpha = 1$, and the activation energy is given by

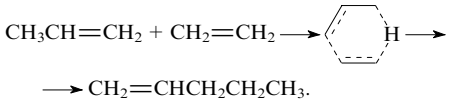
$$E = \left\{\frac{br_e}{2} + \frac{\Delta H}{2\,br_e}\right\}^2 - 0.5\,(hN_Av_{C-H} - RT). \tag{9}$$

The rate constant for concerted decomposition is calculated from Eqn (3) provided that the enthalpy of reaction, the parameter br_e and the pre-exponent A_0 are known. The parameter br_e also allows one to estimate yet another important parameter, *viz*., the classical potential barrier to thermally neutral reaction $E_{e0} = E_e$ (at $\Delta H_e = 0$) for a given class of reactions:

$$E_{e0} = (br_e)^2(1 + \alpha)^{-2}. \tag{10}$$

3. Calculations of kinetic parameters of concerted association of two molecules

Considering concerted decomposition (cd) of molecules as the forward reaction, concerted association (ca) of molecules resulting in a single molecule formed from two reactant molecules is the reverse reaction. The association reactions proceed *via* the same six-membered TS as the decomposition reactions. An example is provided by the association of two alkenes:



The results obtained using the MIP method for the concerted decomposition reactions make it possible to calculate the kinetic parameters of the reverse bimolecular reactions of association of two molecules. The decomposition reactions are endothermic, whereas the reverse (association) reactions are exothermic ($\Delta H_{ca} = -\Delta H_{cd}$) and the activation energy of association is $E_{ca} = E_{cd} - |\Delta H_{cd}|$. The pre-exponent of the association reaction (A_{ca}) is calculated using the corresponding equilibrium constant (K). Since

$$K = \exp\left(\frac{\Delta S_{ca}}{R}\right)\exp\left(\frac{\Delta H_{cd}}{RT}\right) = \frac{k_{ca}}{k_{cd}} = \frac{A_{ca}}{A_{cd}}\exp\left(\frac{E_{cd} - E_{ca}}{RT}\right), \tag{11}$$

the pre-exponent is $A_{ca} = A_{cd}\exp(\Delta S_{ca}/R)$.

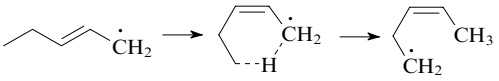
4. Concerted decomposition as two-centre reaction [MIP(2)]

Within the framework of this model, a decomposition reaction, *e.g*., decomposition of pent-1-ene

$$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3 \longrightarrow \overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H_2 + \overset{4}{C}H_2{=}\overset{5}{C}H_2,$$

is considered as a result of two elementary steps that simultaneously occur in the TS, namely, (1) transfer of hydrogen atom from the C(5) to the C(1) atom and (2) cleavage of the C(3)–C(4) bond with the formation of ethylene and propylene.[8]

Transfer of H atom is modelled by the intramolecular transfer of hydrogen atom in a structurally similar free radical which proceeds *via* the formation of a cyclic six-membered TS:



The process is characterized by the enthalpy (ΔH_{abs}) and activation energy (E_{abs}). Such isomerization reactions have been analyzed earlier [17] and some expressions describing the activation energy as function of the enthalpy of reaction have been derived. The activation energy E_{abs} is calculated using Eqns (8) and (9). In this model, the enthalpy of abstraction equals the difference between the bond dissociation (formation) energies:

$$\Delta H = D_{Y-H} - D_{C-H},$$

where Y = C or O. In addition of abstraction of H atom, concerted decomposition involves cleavage of the C(3)–C(4) bond accompanied by the formation of a new C=C π-bond, for example:†

$$\overset{1}{C^{\bullet}}H_2\overset{2}{C}H_2-\overset{3}{C}H_2\overset{4}{C}H_2R \longrightarrow \overset{1}{C}H_2=\overset{2}{C}H_2 + \overset{3}{C^{\bullet}}H_2\overset{4}{C}H_2R.$$

As a result of the decomposition, the σ-bond C(2)–C(3) is cleaved and the σ-bond C(1)–C(2) is transformed to ethylene π-bond. This step is characterized by the enthalpy ΔH_d and the activation energy E_d. The dependence of activation energy on the enthalpy of the radical decomposition reaction is correctly described by the model of three intersecting parabolas [MIP(2) model].[18] Owing to the energy conservation law the enthalpy of concerted bond cleavage (dissociation) is

$$\Delta H_d = \Delta H - \Delta H_{abs}, \qquad (12)$$

where ΔH is the enthalpy of concerted decomposition of the molecule calculated as the difference between the enthalpies of formation of products and reactants.

The decomposition of a molecule is modelled by the decomposition of a radical

$$XYZ^{\bullet} \longrightarrow X^{\bullet} + Y=Z.$$

In this model, the transition state is associated with the intersection point of the parabola describing the stretching vibration of the X···Y bond being cleaved and the parabola describing transformation of the σ-bond Y–Z to the π-bond Y=Z. The latter parabola is a superposition of two parabolas responsible for the stretching vibrations of the bonds Y–Z and Y=Z. The expression for the classical enthalpy of such a decomposition has the form [18]

$$\Delta H_e = \Delta H + 0.5\,hN_A(\nu_{X-Y} + \nu_{Y-Z} - \nu_{Y=Z}), \qquad (13)$$

† Hereafter, R is an alkyl substituent including a polymer radical.

and the classical potential barrier is:

$$E_e = E_d + 0.5\,hN_A\nu_{X-Y} - 0.5\,RT. \qquad (14)$$

The decomposition reacion is also characterized by elongation of the bonds in the TS, namely, $r_e = r^{\neq}_{X-Y} + r^{\neq}_{Y-Z} - r^{\neq}_{Y=Z}$, the parameter br_e and the coefficients $\alpha = b_{Y=Z}/b_{X-Y}$ and $\gamma = (b_{Y=Z} - b_{Y-Z})/b_{Y-Z}$.

The activation energy (E) is calculated from the equation [18]

$$E = B^2\left\{\alpha - \gamma\sqrt{1 - \frac{\Delta H_e}{B\,br_e}}\right\}^2 - 0.5(hN_A\nu_{Y=Z} - RT), \qquad (15)$$

where $B = b_{Y=Z}\,r_e/(\alpha^2 - \gamma^2)$. The parameters necessary to calculate the E values are listed in Table 2.

Since concerted decomposition of a molecule is also accompanied by redistribution of the π-bond electron density, displacement of π-electrons can be characterized by the activation energy E_π. Thus, the activation energy of concerted decomposition of a molecule can be represented by the sum [8]

$$E = E_{abs} + E_d + E_\pi, \qquad (16)$$

where E_{abs} characterizes activation of H atom transfer , E_d characterizes activation of the C–C or C–O bond cleavage and E_π characterizes activation of transformation of the π-bonds. This model allows one to assign a partial activation energy to each step of the rearrangement of bonds and thus to obtain the so-called spectrum of activation energies of concerted decomposition.

III. Decomposition of alkenes

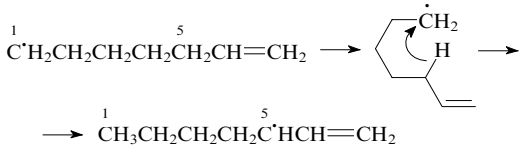
1. Experimental data

Molecular decomposition of alkenes was studied taking three compounds, *viz*., pent-1-ene, 4,4-dimethylpent-1-ene and 2,4-dimethylhex-1-ene as examples.[19–22] Table 3 presents the reaction conditions, the enthalpies of reactions and the kinetic characteristics.

From the data in Table 3 it follows that molecular decomposition of an alkene into two unsaturated compounds is endothermic ($\Delta H > 0$; more exactly, ΔH is in the range from 61 to 88 kJ mol^{-1}) and has a high activation energy (from 221 to 240 kJ mol^{-1}).

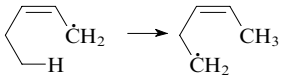
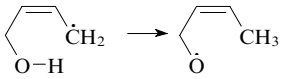
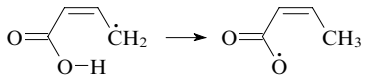
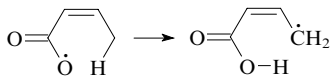
2. One-centre model for alkene decomposition

The classical potential barrier to a thermally neutral alkene decomposition reaction calculated [9] using Eqn (10) within the framework of the MIP(1) model is E_{e0} = 197.4 kJ mol^{-1} (*cf.* E_{e0} = 78.6 kJ mol^{-1} reported [17] for the isomerization of allyl radicals involving H atom transfer *via* the formation of a structurally similar six-membered TS)



Such a large difference between the E_{e0} values for the two types of reactions is a specific feature of concerted decomposition.

Table 2. MIP(1) parameters for reactions involving H atom transfer and MIP(2) parameters for reactions involving bond dissociation.[8, 11, 17]

No.	Reaction class	α	γ	br_e (see [a])	$0.5hN_Av$ (see [b])	$0.5hN_A\Delta v$ (see [b])
Reactions involving transfer of hydrogen atom						
1		1.00	—	15.73	17.4	0.0
2		1.255	—	17.78	21.7	4.3
3		1.229	—	17.41	21.2	3.8
4		0.814	—	14.17	17.4	−3.8
5		0.812	—	13.38	17.4	− 4.0
Reactions involving bond dissociation						
6	$MeC^{\bullet}HCH_2R \longrightarrow CH_2{=}CHMe + R^{\bullet}$	1.202	0.202	14.70	8.2	6.5
7	$RCH_2O^{\bullet} \longrightarrow R^{\bullet} + HCHO$	1.336	0.528	12.66	8.2	4.6
8	$MeC^{\bullet}HOR \longrightarrow MeCHO + R^{\bullet}$	1.528	0.528	20.73	6.7	3.1
9	$RCO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2$	1.826	1.088	21.78	8.2	0.9
10	$C^{\bullet}H_2CH_2OR \longrightarrow CH_2{=}CH_2 + RO^{\bullet}$	1.374	0.202	15.55	6.7	5.0
11	$C^{\bullet}H_2CH_2NO_2 \longrightarrow CH_2{=}CH_2 + N^{\bullet}O_2$	1.544	0.202	13.06	5.1	3.4

[a] In $kJ^{1/2}\ mol^{-1/2}$. [b] In $kJ\ mol^{-1}$.

Table 3. Experimental thermodynamic and kinetic parameters of alkene decomposition reactions (T = 670–1200 K).

Reaction	ΔH	E_{exp}	k_{exp} (T/K)	Ref.
$CH_2{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHMe$	87.7	239.5	12.7 (1100)	19
$CH_2{=}CHCH_2Bu^t \longrightarrow CH_2{=}CMe_2 + CH_2{=}CHMe$	82.3	237.6	3.0×10^{-5} (710)	20
$CH_2{=}CMeCH_2Bu^s \longrightarrow CH_2{=}CMe_2 + MeCH{=}CHMe$	61.0	220.7	16.5 (1040)	21

Note. Hereafter, the parameters ΔH and E_{exp} are given in kJ mol^{-1} and k_{exp} values are given in s^{-1}.

Table 4. Thermodynamic and kinetic parameters of concerted decomposition of alkenes and corresponding reverse (association) reaction calculated by the MIP(1) method.[9]

Reaction	ΔH	E_{cd}	k_{cd} (see [a])	E_{ca}	$k_{ca}\times10^{-2}$ (see [a])
$CH_2{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHMe$	87.7	230.9	19.8	143.2	6.2
$CH_2{=}CHCH_2Bu^t \longrightarrow CH_2{=}CMe_2 + CH_2{=}CHMe$	82.3	226.2	1.0×10^{-4} (see [b])	143.9	5.7
$CH_2{=}CMeCH_2Bu^s \longrightarrow CH_2{=}CMe_2 + MeCH{=}CHMe$	61.0	216.0	16.7 [c]	155.0	1.7
$CH_2{=}CHBu^n \longrightarrow 2\,CH_2{=}CHMe$	74.5	223.6	29.9	149.1	3.2
$CH_2{=}CMePr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CMe_2$	81.0	227.2	29.8	146.2	8.9
$CH_2{=}CHBu^s \longrightarrow CH_2{=}CH_2 + cis\text{-}MeCH{=}CHMe$	75.6	224.2	41.8	148.6	3.4
$CH_2{=}CHBu^s \longrightarrow CH_2{=}CH_2 + trans\text{-}MeCH{=}CHMe$	74.4	223.5	45.2	149.1	3.2
$MeCH{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHEt$	101.6	238.6	5.6	137.0	8.1
$Me_2C{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHPr^i$	98.6	237.0	10.0	138.4	3.5
$Me_2C{=}CMePr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CMePr^i$	90.2	232.3	16.9	142.1	2.3
$CH_2{=}CHBu^i \longrightarrow 2\,CH_2{=}CHMe$	80.3	226.8	62.5	146.5	4.3
$MeCH{=}CHBu^n \longrightarrow CH_2{=}CHMe + CH_2{=}CHEt$	85.6	229.7	15.1	144.1	3.7
$MeCH{=}CHBu^i \longrightarrow CH_2{=}CHMe + CH_2{=}CHEt$	94.0	234.4	26.8	140.0	5.8
$Me_2C{=}CMeBu^n \longrightarrow CH_2{=}CHMe + CH_2{=}CMePr^i$	78.8	226.0	22.7	147.2	1.3
$CH_2{=}CMeCH_2Bu^t \longrightarrow 2\,CH_2{=}CMe_2$	67.7	219.9	202.5	152.2	4.6

Note. Hereafter, the E_{cd} and E_{ca} values are given in kJ mol^{-1}, the k_{cd} values (monomolecular reaction) are given in s^{-1} and the k_{ca} values (bimolecular reaction) are given in litre $mol^{-1}\ s^{-1}$. [a] At 1100 K; [b] at 740 K; [c] at 1040 K.

The parameters of concerted decomposition of alkenes ($br_e = 28.10$ kJ$^{1/2}$ mol$^{-1/2}$, $A_0 = 3.83 \times 10^{12}$ s^{-1}) determined using the experimental data taken from Table 3 made it possible to calculate the activation energies and rate constants for the decomposition of unsaturated compounds of different structure.[9] The results of calculations are listed in Table 4; they are in good agreement with the experimental values (root-mean-square error is $\Delta E = 8.2 \pm 2.7$ kJ mol^{-1}). Table 4 also presents the activation energies and rate constants for the reverse reaction, namely, concerted association of the correponding alkenes. As can be seen, the reverse reaction, although being exothermic, proceeds with a very low rate constant. This is due to the high value $E_{e0} = 197.4$ kJ mol^{-1}, on the one hand, and to the high negative activation entropy of the association of two molecules ($\Delta S_{ca} = -132$ J mol^{-1} K^{-1}, on the other hand).

3. Quantum chemical calculations

Quantum chemical calculations of concerted decomposition of six alkenes were carried out using different methods within the framework of the density functional theory and the GAUSSIAN 98 program.[9, 23] The results obtained are listed in Table 5, which also presents the results of calculations by the MIP(1) method taken from Table 4 (they are shown for comparison). It follows that the results of CCSD(T) and B3LYP/6-31G* calculations and those obtained by the MIP method are in good agreement. Namely, the ΔH and E values differ by 12 and 8 kJ mol^{-1} on the average, respectively. The transition-state geometries for the reactions under study are shown in Fig. 2.

For all reactions in question, the C···H···C fragment of the cyclic six-membered TS is almost symmetric. The vibration with imaginary frequency in the TS is in the range 1147–1251 cm^{-1} and has a small reduced mass of the order of 1.5. This suggests that passage of the system through the potential barrier is associated with the motion of just hydrogen atom from the methyl group to methylene

Table 5. The enthalpies and activation energies of alkene decomposition reactions calculated by different methods ($T = 298$ K).[9]

Parameter	MIP(1)	CCSD(T)/6-311++G**//B3LYP/6-31G*	B3LYP/6-311++G**//B3LYP/6-31G*
	$CH_2{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHMe$		
ΔH	87.7	93.7	70.2
E	230.9	236.2	214.5
	$CH_2{=}CHBu^s \longrightarrow CH_2{=}CH_2 + cis\text{-}MeCH{=}CHMe$		
ΔH	75.6	94.5	61.3
E	224.2	237.7	216.1
	$CH_2{=}CHBu^s \longrightarrow CH_2{=}CH_2 + trans\text{-}MeCH{=}CHMe$		
ΔH	74.4	89.7	55.6
E	223.5	230.4	203.8
	$CH_2{=}CMePr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CMe_2$		
ΔH	81.0	90.1	62.6
E	227.2	228.6	208.8
	$CH_2{=}CHBu^n \longrightarrow 2\,CH_2{=}CHMe$		
ΔH	74.5	84.4	54.9
E	223.6	232.0	213.5
	$CH_2{=}CHBu^i \longrightarrow 2\,CH_2{=}CHMe$		
ΔH	80.3	94.7	58.6
E	226.8	240.1	214.7

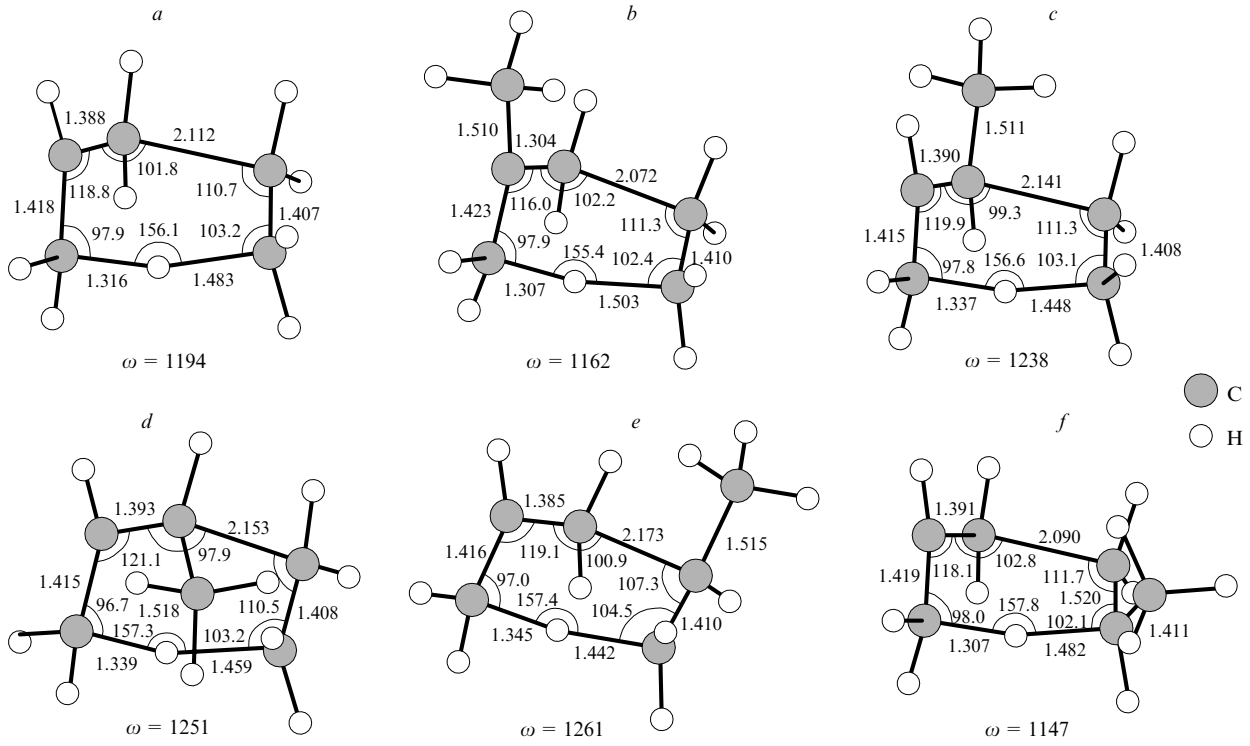


Figure 2. Transition-state geometries for the decomposition of pent-1-ene (*a*), 2-methylpent-1-ene (*b*), 3-methylpent-1-ene resulting in *trans*- (*c*) and *cis*-but-2-ene (*d*), 4-methylpent-1-ene (*e*) and hex-1-ene (*f*).[9]
From this point on, the distances are given in Ångströms and the angles are reported in degrees; the wavenumbers (in cm^{-1}) refer to imaginary vibrational frequencies in the corresponding transition states.

unit. Therefore, within the framework of the MIP method, such reactions can quite correctly be described by the intersection of parabolas corresponding to the C—H bonds being cleaved and being formed [MIP(1) model]. The transition-state geometries for the decomposition of pent-1-ene and its homologues are very similar. It is noteworthy that the sum of the corresponding C—H distances in the TS is almost constant and varies to a lesser extent than the individual C—H bond lengths. The lengths of the double bonds being formed in the TS for all systems vary to even smaller extent.

4. Decomposition of alkenes as concerted two-centre reaction

As shown above, decomposition of alkenes proceeds *via* the formation of the six-membered TS. For instance, in the case of pent-1-ene, a hydrogen atom is transferred between the C(5) and C(1) atoms; the process is modelled by the reaction No. 1 (see Table 2). This is accompanied by cleavage of strong C—H bond in the methyl group $C(5)H_3$ (D_{C-H} = 422 kJ mol^{-1}) and the formation of a weaker propylene allylic bond C(1)—H (D_{C-H} = 368 kJ mol^{-1}). The rearrangement of bonds is an endothermic process with the enthalpy

$$\Delta H_{abs} = 422 - 368 = 54 \text{ kJ mol}^{-1}.$$

Calculations using Eqn (9) give E_{abs} = 78.6 kJ mol^{-1}. Simultaneously, the decomposition of pent-1-ene is accompanied by cleavage of the σ-bond C—C; dissociation of this bond is partly compensated by the formation of the π-bond C=C. Equation (12) gives the value ΔH_d = 39.4 kJ mol^{-1} for the enthalpy of cleavage and E_d = 113.3 kJ mol^{-1} for the activation energy of bond cleavage.[8] Correspondingly, the activation energy of migration of σ—π-bonds is E_π = 43 kJ mol^{-1}. Figure 3 shows the spectra of activation energies (E_{abs}, E_d and E_π) for the three reactions of concerted decomposition of alkenes. As can be seen, the activation energies E_{abs} (73—79 kJ mol^{-1}) and E_d (112 ± 1 kJ mol^{-1}) are very close and the rearrangement of σ—π-bonds appears to be most sensitive to the molecular structure (E_π varies in the range from 32 to 43 kJ mol^{-1}).[8]

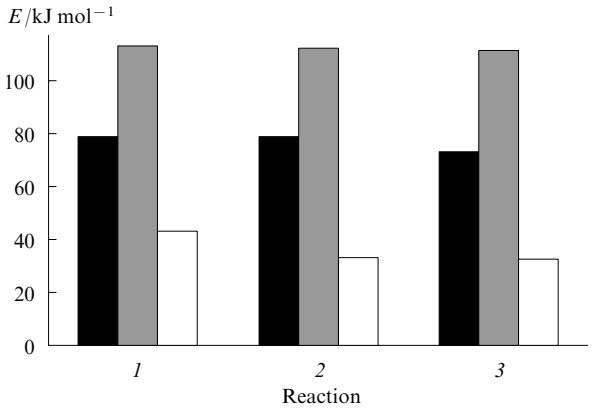


Figure 3. Energy spectra of reactions:[8]
$CH_2{=}CHPr^n \longrightarrow CH_2{=}CH_2 + CH_2{=}CHMe$ (*1*),
$CH_2{=}CHCH_2Bu^t \longrightarrow CH_2{=}CMe_2 + CH_2{=}CHMe$ (*2*),
$CH_2{=}CMeCH_2Bu^s \longrightarrow CH_2{=}CMe_2 + MeCH{=}CHMe$ (*3*).
Black column is E_{abs}, gray column is E_d and white column is E_π.

IV. Decomposition of aliphatic alcohols

1. Experimental data

Gas-phase decomposition of aliphatic alcohols into alkene and water ($T \geqslant 800$ K) proceeds by the monomolecular mechanism involving concerted rearrangement of bonds *via* formation of a four-membered TS:[22]

$$R^1R^2CHCR^3R^4OH \longrightarrow R^1R^2C{=}CR^3R^4 + H_2O.$$

As a result, the σ-bonds C—H and C—OH are cleaved and the bonds σ-H—OH and π-C=C are respectively formed. Concerted decomposition of aliphatic alcohols is an endothermic process ($\Delta H > 0$; more exactly, ΔH is in the range from 47 to 54 kJ mol^{-1}) and requires high activation energies to proceed (E = 263—283 kJ mol^{-1}, Table 6).[22, 24–28]

2. One-centre model for decomposition of aliphatic alcohols

An analysis of experimental data within the framework of the MIP(1) model suggests the effect of the structure of the alkyl residue on the activation energy of decomposition.[7] The decomposition of secondary alcohols (R_2CHOH) is characterized by the parameters br_e = 28.14 kJ$^{1/2}$ mol$^{-1/2}$, $A_0 = 1.6 \times 10^{14}$ s^{-1}, E_{e0} = 253.0 kJ mol^{-1} [*cf.* br_e = 29.04 kJ$^{1/2}$ mol$^{-1/2}$, $A_0 = 5.0 \times 10^{14}$ s^{-1} and E_{e0} = 269.5 kJ mol^{-1} for the decomposition of tertiary alcohols (R_3COH)]; *i.e.*, the R_3C group causes the activation barrier to increase by 16.5 kJ mol^{-1}. Probably, this can be due to higher strain in the four-membered TS owing to the presence of substituents.[22]

The values of the parameters br_e and A_0 for the decomposition of alcohols into alkenes and water calculated using the experimental data were used to determine the activation energies [Eqn (8)] and rate constants for some individual reactions belonging to these classes. The results of calculations are summarized in Table 7.

As can be seen from Tables 6 and 7, the calculated activation energy values for the decomposition of the secondary and tertiary alcohols are close to the experimental values (root-mean-square error is 3.2 ± 1.6 kJ mol^{-1}).

Table 6. Experimental thermodynamic and kinetic parameters of decomposition of aliphatic alcohols.

Reaction	ΔH	E_{exp}	k_{exp} (800 K)	Ref.
$Pr^iOH \longrightarrow CH_2{=}CHMe + H_2O$	50.7	262.6	1.47×10^{-3}	24
$Bu^tOH \longrightarrow CH_2{=}CMe_2 + H_2O$	54.0	282.0	3.58×10^{-4}	22
	54.0	277.7	6.77×10^{-4}	25
	54.0	282.6	3.26×10^{-4}	26
	54.0	281.6	3.76×10^{-4}	27
$Pr^iCMe_2OH \longrightarrow CH_2{=}CMePr^i + H_2O$	52.9	278.5	4.03×10^{-4}	28
$Pr^iCMe_2OH \longrightarrow Me_2C{=}CMe_2 + H_2O$	46.6	277.4	7.93×10^{-5}	28

Table 7. Thermodynamic and kinetic parameters of decomposition and formation reactions of aliphatic alcohols calculated by the MIP(1) method.[7]

Reaction	ΔH	E_{cd}	k_{cd} (800 K)	E_{ca}	k_{ca} (800 K)
EtOH ⟶ CH_2=CH_2 + H_2O	45.2	256.8	3.3×10^{-3}	211.6	4.7×10^{-8}
Pr^iOH ⟶ CH_2=CHMe + H_2O	50.7	259.3	4.5×10^{-3}	208.6	7.4×10^{-8}
Pr^nOH ⟶ CH_2=CHMe + H_2O	33.1	251.3	5.1×10^{-3}	218.2	1.8×10^{-8}
Bu^iOH ⟶ CH_2=CMe_2 + H_2O	25.2	247.8	4.3×10^{-3}	222.6	9.1×10^{-9}
Bu^sOH ⟶ MeCH=CHMe + H_2O	41.1	254.9	2.9×10^{-3}	213.8	3.4×10^{-8}
Bu^sOH ⟶ CH_2=CHEt + H_2O	52.8	260.2	2.0×10^{-3}	207.4	8.9×10^{-8}
$Pr^iCHMeOH$ ⟶ Me_2C=CHMe + H_2O	31.4	250.5	2.9×10^{-3}	219.1	1.5×10^{-8}
$Pr^iCHMeOH$ ⟶ CH_2=$CHPr^i$ + H_2O	46.5	257.4	3.0×10^{-3}	210.9	5.3×10^{-8}
$Bu^tCHMeOH$ ⟶ CH_2=$CHBu^t$ + H_2O	47.9	258.0	2.7×10^{-3}	210.1	5.9×10^{-8}
$Pr^nCHMeOH$ ⟶ EtCH=CHMe + H_2O	40.6	254.7	3.0×10^{-3}	214.1	3.2×10^{-8}
$Pr^nCHMeOH$ ⟶ CH_2=$CHPr^n$ + H_2O	50.7	259.3	2.3×10^{-3}	208.6	7.4×10^{-8}
Bu^tOH ⟶ CH_2=CMe_2 + H_2O	54.0	277.2	4.4×10^{-4}	223.2	8.3×10^{-9}
Pr^iCMe_2OH ⟶ Me_2C=CMe_2 + H_2O	46.6	273.8	8.2×10^{-5}	227.2	4.5×10^{-9}
Pr^iCMe_2OH ⟶ CH_2=$CMePr^i$ + H_2O	52.9	276.7	3.2×10^{-4}	223.8	7.6×10^{-9}

3. The addition of water to alkenes

A concerted association of alkene and water, like the decomposition of the corresponding alcohol, proceeds *via* the formation of the same TS:

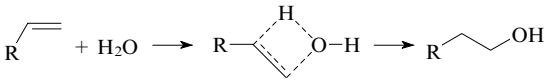


Table 7 presents the activation energy and the rate constant values for the reverse reaction, namely, the addition of water to alkenes.[7] This reaction, although being exothermic, proceeds with a very low rate constant. This is due to high E_{e0} value (253.0 and 269.5 kJ mol^{-1} for the formation of secondary and tertiary alcohols, respectively) and to high negative entropy of activation of the association of two molecules (for instance, the entropy of the reaction

$$CH_2{=}CHMe + H_2O \rightleftharpoons Pr^iOH$$

is -143.9 J mol^{-1} K^{-1}).[7, 29]

4. Quantum chemical calculations

Quantum chemical calculations were carried out for the following decomposition reactions of alcohols:[7]

$$EtOH \longrightarrow CH_2{=}CH_2 + H_2O,$$

$$Bu^tOH \longrightarrow Me_2C{=}CH_2 + H_2O.$$

In these cases, decomposition proceeds *via* the formation of a four-membered TS (Fig. 4 *a*,*c*). In the presence of an additional water molecule, the formation of a six-membered TS is possible as in, *e.g.*, the reaction (see Fig. 4 *b*)

$$EtOH + H_2O \longrightarrow CH_2{=}CH_2 + 2\,H_2O.$$

The results of quantum chemical calculations are in good agreement with the results obtained for the decomposition of alcohols by the MIP(1) method (Table 8).

From the data in Table 8 it follows that the energy profiles based on the structures mentioned above and optimized by the quantum chemical methods CCD and B3LYP almost match each other provided that the energy of the system was calculated by the coupled cluster method CCSD(T)/6-311++G**. Alternative calculations within the framework of the density functional theory (B3LYP/6-

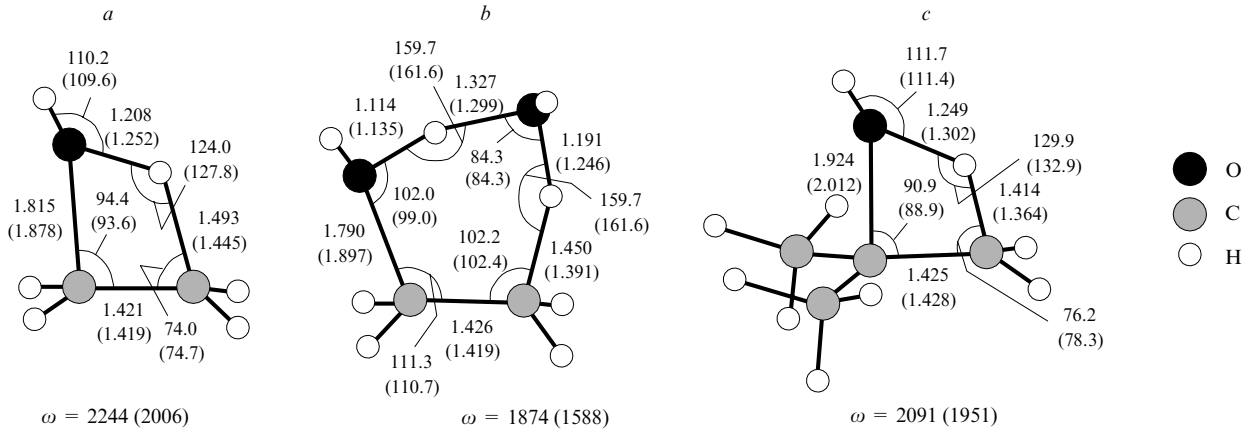


Figure 4. Transition-state geometries for the decomposition of alcohols resulting in alkenes: EtOH (*a*), EtOH involving an additional water molecule (*b*) and Bu^tOH (*c*).[7]
Calculations were carried out by the CCD/6-31G* and B3LYP/6-31G* (numbers in parentheses) methods.

Table 8. A comparison of the results of calculations of the enthalpies and activation energies for decomposition of alcohols (T = 298 K).[7]

Parameter	MIP(1)	CCSD(T)/6-311++G**//CCD/6-31G*	CCSD(T)/6-311++G**//B3LYP/6-31G*	B3LYP/6-311++G**//B3LYP/6-31G*
EtOH ⟶ CH_2=CH_2 + H_2O				
ΔH	45.2	44.5	44.6	41.9
E	256.8	283.0	283.2	260.9
EtOH + H_2O ⟶ CH_2=CH_2 + 2H_2O				
ΔH	–	44.5	44.6	41.9
E	–	226.0	225.8	191.6
Bu^tOH ⟶ CH_2=CMe_2 + H_2O				
ΔH	54.0	59.0	60.9	38.7
E	277.2	276.9	277.6	245.5

311++G**//B3LYP/6-31G*) give somewhat different results and usually underestimate the activation energy values. The theoretical values of the enthalpy of reaction differ insignificantly from the experimental results and the theoretical values of the activation energy differ slightly from the values determined using the MIP(1) approach. The decomposition of ethanol *via* the formation of the six-membered TS due to the involvement of the additional water molecule is accompanied by a significant decrease in the activation energy (by about 60 kJ mol^{-1}). This makes it possible to decide between two mechanisms based on the experimental activation energy value. The fact that this value agrees with the results obtained theoretically for the four-membered TS suggests the lack of conditions for autocatalysis by water (decomposition product) in the experiment.

V. Decomposition of unsaturated alcohols

1. Experimental data

Concerted decomposition of unsaturated alcohols bearing an OH group in the β-position relative to the C=C bond proceeds in the gas phase at 600–700 K by the monomolecular mechanism:[22, 30]

$$R^1R^2C{=}CHCH_2CR^3R^4OH \longrightarrow R^1R^2CHCH{=}CH_2 + R^3R^4CO.$$

The corresponding experimental data are listed in Table 9.

Decomposition of unsaturated as well as aliphatic alcohols is an endothermic process ($\Delta H > 0$; more exactly, ΔH varies from 30 to 102 kJ mol^{-1}). The activation energy is very high and varies between 163 and 182 kJ mol^{-1}; however, these values are about 100 kJ mol^{-1} lower than those characterizing the decomposition of corresponding aliphatic alcohols into alkene and water (see Tables 6 and 7).

2. One-centre model for the decomposition of unsaturated alcohols

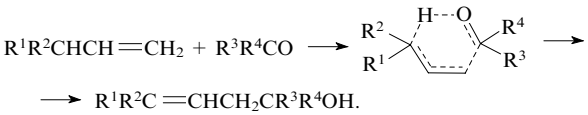
Within the framework of the one-centre model, the TS of decomposition was treated as a result of the rearrangement of two bonds, *viz*., the O–H bond being cleaved and the C–H bond being formed. Treatment of experimental data within the framework of the MIP(1) model allowed one to divide the concerted decomposition reactions into three classes depending on the structure of the initial unsaturated alcohols (hereafter, the br_e parameter is given in kJ$^{1/2}$ mol$^{-1/2}$, E_{e0} is given in kJ mol^{-1} and A_0 is given in s^{-1}):[7]

Compound	br_e	E_{e0}	$A_0 \times 10^{-12}$
CH_2=$CHCH_2CH_2OH$	27.53	149.0	2.8
CH_2=$CHCH_2CR_2OH$	28.60	160.9	2.8
PhCH=$CHCH_2CH_2OH$ or CH_2=$CPhCH_2CH_2OH$	26.42	137.3	2.8

The values of the br_e parameters calculated from experimental data were used within the framework of one-centre MIP(1) model to determine the activation energies [Eqn (8)] and rate constants of some reactions belonging to the three classes mentioned above. The results of these calculations are listed in Table 10. The data in Tables 9 and 10 show that the theoretically calculated activation energy values of decomposition of unsaturated alcohols are in good agreement with the experimental data (root-mean-square error is $\Delta E = 2.9 \pm 2.4$ kJ mol^{-1}).

3. The addition of carbonyl compounds to alkenes

The addition of carbonyl compounds to alkenes is the reverse reaction with respect to the decomposition of unsaturated alcohols. Both reactions proceed *via* a structurally similar six-membered TS:



The kinetic parameters of such reactions are unavailable in the literature. Table 10 lists the kinetic parameters of the reactions of concerted association of corresponding alkenes and carbonyl compounds, which were calculated using the parameters characterizing the decomposition of alcohols.[7] Decomposition reactions of unsaturated alcohols are endo-

Table 9. Experimental parameters[22, 30] and the spectrum of activation energies for concerted decomposition of unsaturated alcohols (T = 600–700 K).[8]

Reaction	ΔH	E_{exp}	k_{exp} (650 K)	E_{abs}	E_d	E_π	Ref.
CH_2=$CH(CH_2)_2OH$ ⟶ CH_2=CHMe + HCHO	61.9	173.6	7.37×10^{-3}	85.5	41.3	44.1	22
CH_2=$CMe(CH_2)_2OH$ ⟶ CH_2=CMe_2 + HCHO	60.3	168.5	1.89×10^{-2}	92.5	38.1	35.2	30
CH_2=$CHCH_2CHMeOH$ ⟶ CH_2=CHMe + MeCHO	42.7	169.7	1.51×10^{-2}	85.5	36.2	45.3	22
CH_2=$CHCH_2CMe_2OH$ ⟶ CH_2=CHMe + Me_2CO	30.3	166.3	2.85×10^{-2}	87.6	32.5	43.5	30
CH_2=$CPh(CH_2)_2OH$ ⟶ CH_2=CMePh + HCHO	62.1	163.0	5.21×10^{-2}	93.0	38.4	28.9	30
PhCH=$CH(CH_2)_2OH$ ⟶ CH_2=CHBn + HCHO	102.2	182.1	1.54×10^{-3}	103.2	46.0	30.2	30

Note. Hereafter, E_{abs}, E_d and E_p are given in kJ mol^{-1}.

Table 10. Thermodynamic and kinetic parameters of decomposition and formation reactions of unsaturated alcohols calculated by the MIP(1) method.[7]

Reaction	ΔH	E_{cd}	k_{cd} (650 K)	E_{ca}	k_{ca} (650 K)
$CH_2{=}CH(CH_2)_2OH \longrightarrow CH_2{=}CHMe + HCHO$	61.9	168.6	1.1×10^{-2}	106.7	1.75×10^{-3}
$CH_2{=}CMe(CH_2)_2OH \longrightarrow CH_2{=}CMe_2 + HCHO$	60.3	167.7	1.3×10^{-2}	107.4	3.08×10^{-3}
$MeCH{=}CH(CH_2)_2OH \longrightarrow CH_2{=}CHEt + HCHO$	72.2	175.0	3.8×10^{-3}	102.8	2.41×10^{-3}
$Me_2C{=}CH(CH_2)_2OH \longrightarrow CH_2{=}CHPr^i + HCHO$	80.9	180.4	1.2×10^{-3}	99.5	2.21×10^{-3}
$Me_2C{=}CMe(CH_2)_2OH \longrightarrow CH_2{=}CMePr^i + HCHO$	62.1	168.8	1.1×10^{-2}	106.7	5.85×10^{-4}
$CH_2{=}CHCH_2CHMeOH \longrightarrow CH_2{=}CHMe + MeCHO$	42.7	168.9	1.1×10^{-2}	126.2	4.85×10^{-5}
$CH_2{=}CHCHMeCHMeOH \longrightarrow MeCH{=}CHMe + MeCHO$	39.4	166.9	1.5×10^{-2}	127.5	3.74×10^{-5}
$MeCH{=}CHCH_2CHMeOH \longrightarrow CH_2{=}CHEt + MeCHO$	55.5	176.5	2.6×10^{-3}	121.0	8.30×10^{-5}
$Me_2C{=}CHCH_2CHMeOH \longrightarrow CH_2{=}CHPr^i + MeCHO$	58.6	178.3	1.8×10^{-3}	119.7	5.28×10^{-5}
$Me_2C{=}CMeCH_2CHMeOH \longrightarrow CH_2{=}CMePr^i + MeCHO$	47.7	171.9	6.1×10^{-3}	124.2	2.29×10^{-5}
$MeCH{=}CHCHMeCHMeOH \longrightarrow MeCH_2CH{=}CHMe + MeCHO$	54.4	175.8	2.9×10^{-3}	121.4	7.71×10^{-5}
$CH_2{=}CHCH_2CMe_2OH \longrightarrow CH_2{=}CHMe + Me_2CO$	30.3	161.6	4.23×10^{-2}	131.3	1.85×10^{-5}
$CH_2{=}CMeCH_2CMe_2OH \longrightarrow CH_2{=}CMe_2 + Me_2CO$	27.9	160.2	5.5×10^{-2}	132.3	3.08×10^{-5}
$MeCH{=}CHCH_2CMe_2OH \longrightarrow CH_2{=}CHEt + Me_2CO$	49.2	172.7	5.2×10^{-3}	123.5	5.23×10^{-5}
$CH_2{=}CPh(CH_2)_2OH \longrightarrow CH_2{=}CMePh + HCHO$	62.1	157.1	9.8×10^{-2}	95.0	1.02×10^{-2}
$PhCH{=}CH(CH_2)_2OH \longrightarrow CH_2{=}CHBn + HCHO$	102.2	182.4	8.4×10^{-4}	80.2	2.40×10^{-1}

thermic (see Table 10); consequently, reactions of their formation should be exothermic. The latter are characterized by high negative entropy of activation, the pre-exponent is $A_{0(ca)} = 2.0\times10^6$ litre mol^{-1} s^{-1}. As follows from the data in Table 10, the addition of carbonyl compounds to alkenes proceeds with high activation energy (80–132 kJ mol^{-1}) and the rate constants vary from 0.2 to 3.1×10^5 litre mol^{-1} s^{-1}. Substituents in the alkene and carbonyl compound affect the activation energy value in different manner. For the same carbonyl compound (*e.g.*, formaldehyde), the introduction of substituents into alkene molecule causes the activation energy of the addition reaction to decrease (106.7 *vs.* 99.5 kJ mol^{-1}, see Table 10). As the structure of the carbonyl compound becomes more complicated, the activation energy of the addition to propylene increases as follows: formaldehyde (106.7 kJ mol^{-1}) < acetaldehyde (126.2 kJ mol^{-1}) < acetone (131.3 kJ mol^{-1}).

4. Results of quantum chemical calculations

The results of analysis of the decomposition of unsaturated alcohols within the framework of the MIP(1) model agree well with the results of quantum chemical calculations.[7] Below we present the calculated values of the energy parameters (in kJ mol^{-1}) of the reaction

$$CH_2{=}CHCH_2CH_2OH \longrightarrow CH_2{=}CHMe + HCHO.$$

Parameter	MIP(1)	CCSD(T)/6-311++G**//CCD/6-31G*	CCSD(T)/6-311++G**//B3LYP/6-31G*	B3LYP/6-311++G**//B3LYP/6-31G*
ΔH	61.9	53.3	53.8	39.2
E	168.6	175.1	174.0	149.5

As can be seen, the energy profiles obtained for the structures mentioned above and optimized by the quantum chemical methods CCD and B3LYP almost match each other provided that the energy of the system is calculated by the CCSD(T)/6-311++G** method. Theoretical values of the enthalpy of reaction differ insignificantly from the experimental values while the theoretical activation energy values are in reasonable agreement with the values obtained using the MIP(1) model. The corresponding TS geometry is shown in Fig. 5.

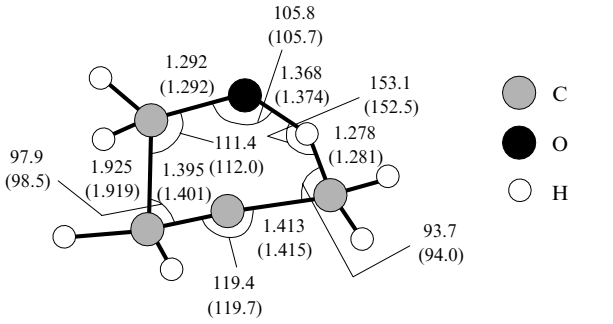


Figure 5. Geometry of six-membered transition state of $CH_2{=}CH(CH_2)_2OH$ decomposition from the results of CCD/6-31G* and B3LYP/6-31G* (numbers in parentheses) calculations.[7]

5. The two-centre model for decomposition of unsaturated alcohols

According to this model, the decomposition reaction involves three concerted steps, *viz.*,[8] 1) transfer of H atom from the O atom to the C atom (this step is modelled by the radical reaction No. 2 (see Table 2); 2) cleavage of the C–C bond with the formation of carbonyl group in the carbonyl compound molecule (this step is modelled by the reaction No. 7); and 3) migration of π-bonds:

$$R^1R^2C{=}CHCH_2CR^3R^4OH \longrightarrow \text{(H···O, } R^1, R^2, R^3, R^4\text{)} \longrightarrow$$

$$\longrightarrow R^1R^2CH{-}CH{=}CH_2 + R^3R^4CO.$$

Transfer of H atom is an endothermic reaction because it is accompanied by cleavage of the strong alcohol O–H bond (D_{O-H} = 432 kJ mol^{-1}) and a weak propylene allylic C–H bond (D_{C-H} = 368 kJ mol^{-1}) is formed.[31] The enthalpy of H atom transfer (ΔH_{abs}) varies in the range 64–89 kJ mol^{-1} (Ref. 8). From Table 9 it follows that the

Table 11. Experimental parameters [22, 32–35] and the spectrum of activation energies for concerted decomposition of vinyl ethers (T = 600–850 K).[12]

Reaction	ΔH	E_{exp}	k_{exp} (600 K)	E_{abs}	E_d	E_π	Ref.
$CH_2{=}CHOEt \longrightarrow CH_2{=}CH_2 + MeCHO$	25.0	187.9	3.02×10^{-5}	61.6	97.5	26.3	22
$CH_2{=}CHOPr^n \longrightarrow CH_2{=}CHMe + MeCHO$	13.9	184.1	4.29×10^{-5}	56.1	97.2	28.3	32
$CH_2{=}CHOBu^n \longrightarrow CH_2{=}CHEt + MeCHO$	14.6	183.1	5.20×10^{-5}	56.1	97.4	26.0	22
	14.6	182.0	6.57×10^{-5}	56.1	97.4	26.0	33
$CH_2{=}CMeOEt \longrightarrow CH_2{=}CH_2 + Me_2CO$	9.3	176.8	2.74×10^{-4}	61.6	91.2	21.5	22
$CH_2{=}CHOPr^i \longrightarrow CH_2{=}CHMe + MeCHO$	27.9	177.1	5.21×10^{-4}	61.6	93.6	20.3	22
	27.9	178.0	4.35×10^{-4}	61.6	93.6	20.3	33
	27.9	178.2	4.20×10^{-4}	61.6	93.6	20.3	34
$CH_2{=}CHOBu^t \longrightarrow CH_2{=}CMe_2 + MeCHO$	−0.7	165.6	7.80×10^{-3}	61.6	91.2	3.2	33
	−0.7	163.7	1.15×10^{-2}	61.6	98.3	3.2	35

activation energy of H atom transfer is rather high, namely, $85 < E_{abs} < 103$ kJ mol^{-1}. The activation energy of decomposition (E_d) is low and varies in the range from 32 to 46 kJ mol^{-1}, while the activation energy of π-bond rearrangement varies from 29 to 45 kJ mol^{-1}.

VI. Decomposition of ethers

1. Experimental data

Concerted gas-phase decomposition of vinyl ethers at 500 K proceeds by the monomolecular mechanism and results in alkene and carbonyl compound:[22]

$$R^1R^2\overset{1}{C}{=}\overset{2}{C}R^3O\overset{3}{C}R^4R^5\overset{4}{C}HR^6R^7 \longrightarrow$$
$$\longrightarrow R^1R^2\overset{1}{C}H\overset{2}{C}(O)R^3 + R^4R^5\overset{3}{C}{=}\overset{4}{C}R^6R^7$$

Experimental results on the decomposition of ethers are listed in Table 11.[22, 32–35] As can be seen, most decomposition reactions are endothermic and their enthalpies vary in the range from 0 to 28 kJ mol^{-1}. The activation energies of decomposition of ethers are very high (from 164 to 188 kJ mol^{-1}).

2. One-centre model for decomposition of ethers

Within the framework of one-centre model the TS of concerted decomposition of vinyl ethers can be interpreted as a result of intersection of the potential energy curves of the stretching vibrations of two bonds, the ether C(4)−H bond being cleaved and the C(1)−H bond being formed in the carbonyl compound.[12] An analysis of experimental data within the framework of this model showed that the decomposition reactions of vinyl ethers can be divided into two classes according to the substituents in structurally similar ethers. These classes of reactions are characterized by the following br_e and E_{e0} values:[12]

Compound	br_e	E_{e0}	$A_0\times10^{-13}$
$R^1R^2C{=}CR^3OCH_2CHR^4R^5$ (R^1, R^2, R^3, R^4, R^5 = H or Alk)	27.37	187.3	1.12
$R^1R^2C{=}CR^3OCR^4R^5CHR^6R^7$ (R^1, R^2, R^3, R^6, R^7 = H or Alk; R^4, R^5 = Alk)	26.57	176.5	1.12

As can be seen, even in thermally neutral conditions ($\Delta H_e = 0$), the activation barrier to decomposition of ethers depends on the nature of substituents at carbons. The br_e values calculated from experimental data for the decomposition of two classes of vinyl ethers were used to determine the activation energies and rate constants of some individual reactions.[12] The results of calculations are listed in Table 12. A comparison reveals reasonable agreement with experimental data (root-mean-square error is 2.2 ± 1.5 kJ mol^{-1}).

Table 12. Thermodynamic and kinetic parameters of decomposition and formation reactions of vinyl ethers calculated by the MIP(1) method.[12]

Reaction	ΔH	E_{cd}	k_{cd} (600 K)	E_{ca}	k_{ca} (600 K)
$CH_2{=}CHOEt \longrightarrow CH_2{=}CH_2 + MeCHO$	25.0	185.1	3.11×10^{-5}	160.1	1.34×10^{-9}
$CH_2{=}CHOPr^n \longrightarrow CH_2{=}CHMe + MeCHO$	13.9	179.4	6.59×10^{-5}	165.5	5.16×10^{-10}
$CH_2{=}CHOBu^n \longrightarrow CH_2{=}CHEt + MeCHO$	14.6	179.8	6.08×10^{-5}	165.2	5.46×10^{-10}
$CH_2{=}CMeOEt \longrightarrow CH_2{=}CH_2 + Me_2CO$	9.3	177.1	1.58×10^{-4}	167.8	6.48×10^{-10}
$MeCH{=}CHOEt \longrightarrow CH_2{=}CH_2 + EtCHO$	36.9	179.7	9.15×10^{-5}	142.8	3.26×10^{-8}
$MeCH{=}CMeOEt \longrightarrow CH_2{=}CH_2 + EtC(O)Me$	18.1	181.5	6.46×10^{-5}	163.4	5.24×10^{-10}
$Me_2C{=}CHOEt \longrightarrow CH_2{=}CH_2 + Pr^iCHO$	43.3	194.7	4.42×10^{-6}	151.4	2.90×10^{-9}
$Me_2C{=}CMeOEt \longrightarrow CH_2{=}CH_2 + Pr^iC(O)Me$	30.9	188.1	1.69×10^{-5}	157.2	9.06×10^{-10}
$CH_2{=}CHOPr^i \longrightarrow CH_2{=}CHMe + MeCHO$	27.9	175.8	4.11×10^{-4}	147.9	1.75×10^{-8}
$CH_2{=}CHOBu^t \longrightarrow CH_2{=}CMe_2 + MeCHO$	−0.7	161.3	1.17×10^{-2}	162.0	1.02×10^{-9}
$MeCH{=}CHOPr^i \longrightarrow CH_2{=}CHMe + EtCHO$	42.3	183.4	7.93×10^{-5}	141.1	4.58×10^{-8}
$MeCH{=}CHOBu^s \longrightarrow MeCH{=}CHMe + EtCHO$	33.8	178.9	7.30×10^{-4}	145.1	2.04×10^{-8}
$MeCH{=}CHOBu^s \longrightarrow CH_2{=}CHEt + EtCHO$	43.1	183.8	4.04×10^{-5}	140.7	4.96×10^{-8}
$MeCH{=}CHOCMe_2Et \longrightarrow Me_2C{=}CHMe + EtCHO$	14.8	169.1	5.35×10^{-4}	154.3	3.24×10^{-9}
$MeCH{=}CHOCMe_2Et \longrightarrow CH_2{=}CMeEt + EtCHO$	21.3	172.4	8.21×10^{-4}	151.1	6.16×10^{-9}
$MeCH{=}CHOCMe_2Pr^i \longrightarrow Me_2C{=}CMe_2 + EtCHO$	14.3	168.8	2.84×10^{-4}	154.5	3.12×10^{-9}
$MeCH{=}CHOCMe_2Pr^i \longrightarrow CH_2{=}CMePr^i + EtCHO$	20.6	172.1	8.72×10^{-4}	151.5	5.68×10^{-9}

The reverse reaction, *viz*., the addition of a carbonyl compound to alkene, is exothermic and proceeds very slowly with high activation energy owing to high negative entropy of activation ($\Delta S = -128.5$ J mol^{-1} K^{-1})[12] (see Table 12).

3. Quantum chemical calculations of molecular decomposition of vinyl ethers

Quantum chemical calculations were carried out for two decomposition reactions of vinyl ethers.[12]

The calculated enthalpy and activation energy values of these reactions are compared below with the corresponding values obtained using the MIP(1) model ($T = 298$ K).

Parameter	MIP(1)	CCSD(T)/6-311++G**//CCD/6-311++G**	CCSD(T)/6-311++G**//B3LYP/6-31G*	B3LYP/6-311++G**//B3LYP/6-31G*
$CH_2{=}CHOEt \longrightarrow CH_2{=}CH_2 + MeCHO$				
ΔH	25.0	15.8	16.5	8.6
E	185.1	195.1	192.6	174.1
$CH_2{=}CMeOEt \longrightarrow CH_2{=}CH_2 + Me_2CO$				
ΔH	9.3	11.1	13.1	1.5
E	177.1	–	190.5	173.5

The results of calculations are sufficiently close to the experimental values. Figure 6 presents the transition-state geometries for these reactions.

All the reactions in question are endothermic and, in accordance with Hammond's postulate, their TS are 'late' in character with respect to cleavage of the C–O bond. At the same time, the C···H···C fragment of the cyclic TS is almost symmetric (see Fig. 6). The vibration with imaginary frequency has a small reduced mass, namely, 1.46 for both reactions. This suggests that passage through the potential barrier mainly involves the motion of hydrogen atom from methyl group to methylene unit. Cleavage of the C–O bond occurs in the preliminary step in the ascending region of the potential curve (see Fig. 1).

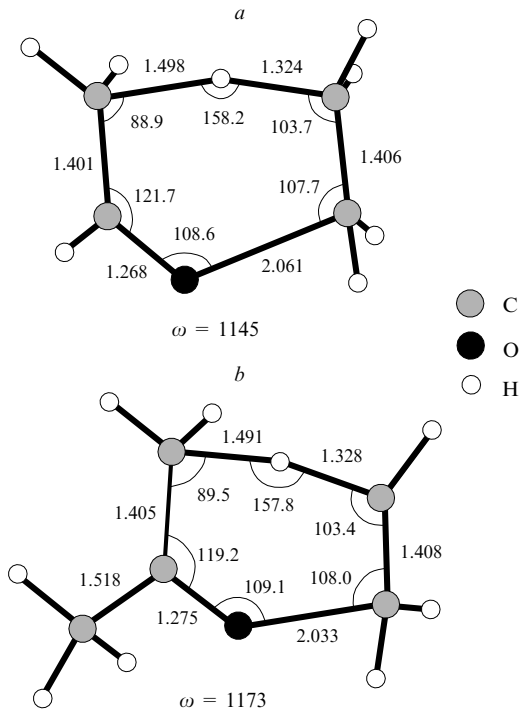
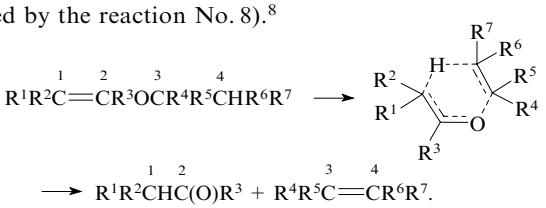


Figure 6. Transition-state geometries for decomposition of ethers $CH_2{=}CROEt$: R = H (*a*) and R = Me (*b*). Obtained from B3LYP/6-31G* calculations.[12]

4. Two-centre model for decomposition of ethers

Processes occurring in the TS of concerted decomposition of ethers include 1) transfer of H atom between the C(4) and C(1) atoms (this is modelled by reaction No. 1, see Table 2) and 2) cleavage of the C(3)–O bond followed by the formation of alkene and carbonyl compound (this is modelled by the reaction No. 8).[8]



Transfer of H atom is an endothermic reaction ($\Delta H_{abs} = 18-28$ kJ mol^{-1}).[8] Contrary to this, cleavage of the C–O bond is exothermic because it is compensated by the formation of carbonyl π-bond ($\Delta H_d = -18-0$ kJ mol^{-1}).[8] The activation energies of H atom transfer, C–O bond dissociation and of π-bond displacement vary from 56 to 62, from 91 to 98 and from 19 to 34 kJ mol^{-1}, respectively (see Table 11).

VII. Decarboxylation of acids

1. Experimental data

At high temperatures, unsaturated acids decompose into alkenes and carbon dioxide:[22]

$$R^1R^2C{=}CR^3CR^4R^5CO_2H \longrightarrow R^1R^2CHCR^3{=}CR^4R^5 + CO_2.$$

Such a concerted decomposition is exothermic (its enthalpy varies from 16 to 34 kJ mol^{-1}) but requires high activation energies (130–165 kJ mol^{-1}) to proceed at high temperatures (Table 13).[22,36]

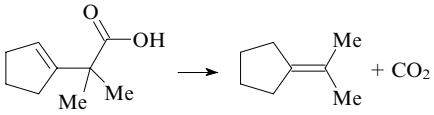
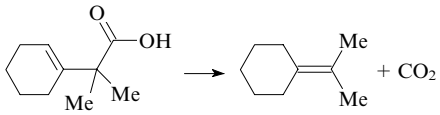
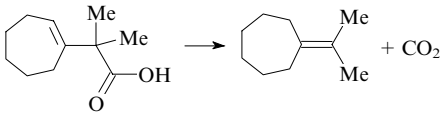
2. One-centre model for molecular decarboxylation of acids

The experimental data presented in Table 13 were analyzed within the framework of the one-centre model [MIP(1)][10] which treats transfer of H atom from the carboxyl group to the carbon atom as the rate-limiting step. Substituents in the carboxylic acid affect the activation energy of decomposition; therefore, all reactions studied were divided into three groups depending on the structures of initial compounds.

The first group comprises acids containing only hydrogen atom as substituent in the β-position ($br_e = 31.37$ kJ$^{1/2}$ mol$^{-1/2}$ and $E_{e0} = 186.2$ kJ mol^{-1}) and various substituents (Alk, Ar and H) in all other positions.

The second and third groups include acids containing alkyl and aryl substituents in the β-position, respectively; all other positions can be occupied by various functional groups. Decomposition of the second group of acids is characterized by $br_e = 30.10$ kJ$^{1/2}$ mol$^{-1/2}$ and $E_{e0} = 171.3$ kJ mol^{-1}. The decomposition of $CH_2{=}CPhCH_2CO_2H$ is characterized by smaller br_e and E_{e0} values (28.65 kJ$^{1/2}$ mol$^{-1/2}$ and 155.3 kJ mol^{-1}, respectively). As can be seen, the acids bearing substituents in the

Table 13. Experimental parameters [22, 36] and the spectrum of activation energies for concerted decomposition of acids (T = 450 – 600 K).[8]

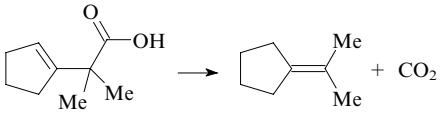
Reaction	ΔH	E_{exp}	k_{exp} (500 K)	E_{abs}	E_d	E_π	Ref.
$CH_2{=}CHCH_2CO_2H \longrightarrow CH_2{=}CHMe + CO_2$	−17.9	163.5	1.66×10^{-6}	89.9	23.3	48.6	22
	−17.9	163.9	1.50×10^{-6}	89.9	23.3	48.6	36
$CH_2{=}CHCMe_2CO_2H \longrightarrow MeCH{=}CMe_2 + CO_2$	−33.9	155.1	1.25×10^{-5}	95.5	18.1	39.4	36
$MeCH{=}CHCMe_2CO_2H \longrightarrow Me_2C{=}CHEt + CO_2$	−23.8	163.4	1.68×10^{-6}	115.9	14.7	30.7	22
$PhCH{=}CHCMe_2CO_2H \longrightarrow PhCH_2CH{=}CMe_2 + CO_2$	−18.6	165.1	1.13×10^{-6}	112.9	16.4	33.7	22
	−32.9	148.1	6.75×10^{-5}	102.6	16.4	27.0	22
	−29.2	151.4	3.05×10^{-5}	102.6	17.1	29.6	22
	−29.1	146.5	1.00×10^{-4}	–	–	–	22
$CH_2{=}CMeCMe_2CO_2H \longrightarrow Me_2C{=}CMe_2 + CO_2$	−24.9	142.2	2.78×10^{-4}	102.6	17.9	19.6	22
	−24.9	142.0	2.94×10^{-4}	102.6	17.9	19.6	36
$MeCH{=}CEtCMe_2CO_2H \longrightarrow Me_2C{=}CEt_2 + CO_2$	−16.5	148.9	5.58×10^{-5}	109.8	17.7	19.3	22
$CH_2{=}CPhCMe_2CO_2H \longrightarrow PhMeC{=}CMe_2 + CO_2$	−32.6	138.7	6.53×10^{-4}	102.6	16.4	16.7	22
	−32.6	137.2	3.79×10^{-5}	102.6	16.4	16.7	36
$CH_2{=}CPhCH_2CO_2H \longrightarrow CH_2{=}CMePh + CO_2$	−18.2	129.8	2.72×10^{-4}	97.5	20.8	17.0	36

β-position are characterized by lower classical barriers to thermally neutral reaction (E_{e0}) compared to the acids unsubstituted at this position.

The br_e values for the decomposition of these classes of acids calculated from experimental data were used to determine the activation energies and rate constants for a number of individual decarboxylation reactions ($A_0 = 9.1\times10^{11}$ s^{-1}). The results of calculations are listed in Table 14.[10]

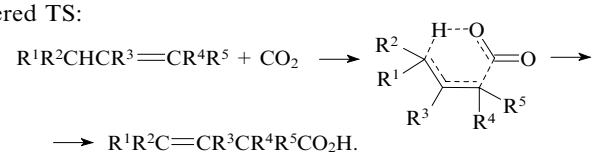
The data of Table 14 show that the calculated values of the activation energy of decomposition of unsaturated acids are close to the experimental values (root-mean-square error is 2.0 ± 3.7 kJ mol^{-1}).

Table 14. Thermodynamic and kinetic parameters of decomposition and formation reactions of acids calculated by the MIP(1) method.[10]

Reaction	ΔH	E_{cd}	k_{cd} (500 K)	E_{ca}	k_{ca} (500 K)
$CH_2{=}CHCH_2CO_2H \longrightarrow CH_2{=}CHMe + CO_2$	−17.9	159.2	2.73×10^{-6}	177.1	4.48×10^{-16}
$MeCH{=}CHCH_2CO_2H \longrightarrow CH_2{=}CHEt + CO_2$	−9.0	164.2	8.09×10^{-7}	173.2	7.63×10^{-16}
$Bu^tCH{=}CHCH_2CO_2H \longrightarrow CH_2{=}CHCH_2Bu^t + CO_2$	−13.2	161.8	1.45×10^{-6}	175.0	4.95×10^{-16}
$Me_2C{=}CHCH_2CO_2H \longrightarrow CH_2{=}CHPr^i + CO_2$	−3.5	167.3	3.80×10^{-7}	170.8	6.82×10^{-16}
$CH_2{=}CHCMe_2CO_2H \longrightarrow MeCH{=}CMe_2 + CO_2$	−33.9	150.4	2.33×10^{-5}	184.3	7.93×10^{-17}
$MeCH{=}CHCMe_2CO_2H \longrightarrow EtCH{=}CMe_2 + CO_2$	−23.8	155.9	6.12×10^{-6}	179.7	1.59×10^{-16}
$Me_2C{=}CHCMe_2CO_2H \longrightarrow Pr^iCH{=}CMe_2 + CO_2$	−18.6	158.8	3.01×10^{-6}	177.4	1.39×10^{-16}
$PhCH{=}CHCMe_2CO_2H \longrightarrow PhCH_2CH{=}CMe_2 + CO_2$	−18.6	158.8	3.01×10^{-6}	177.4	2.78×10^{-16}
$PhMeC{=}CHCMe_2CO_2H \longrightarrow PhMeCHCH{=}CMe_2 + CO_2$	−17.6	159.4	2.61×10^{-6}	177.0	1.53×10^{-16}
	−32.9	150.9	2.07×10^{-5}	183.8	5.96×10^{-17}
$CH_2{=}CMeCH_2CO_2H \longrightarrow CH_2{=}CMe_2 + CO_2$	−18.5	144.1	1.09×10^{-4}	162.6	2.93×10^{-14}
$MeCH{=}CMeCH_2CO_2H \longrightarrow CH_2{=}CMeEt + CO_2$	−11.9	147.8	4.41×10^{-5}	159.7	1.96×10^{-14}
$CH_2{=}CMeCMe_2CO_2H \longrightarrow Me_2C{=}CMe_2 + CO_2$	−24.9	140.6	2.56×10^{-4}	165.5	1.46×10^{-14}
$CH_2{=}CBu^tCMe_2CO_2H \longrightarrow Bu^tMeC{=}CMe_2 + CO_2$	−12.8	147.3	9.97×10^{-5}	160.1	2.67×10^{-14}
$CH_2{=}CPhCMe_2CO_2H \longrightarrow PhMeC{=}CMe_2 + CO_2$	−32.6	136.3	7.30×10^{-4}	168.9	3.22×10^{-15}
$MeCH{=}CMeCMe_2CO_2H \longrightarrow EtMeC{=}CMe_2 + CO_2$	−19.5	143.5	1.26×10^{-4}	163.0	8.88×10^{-15}
$Bu^tCH{=}CMeCMe_2CO_2H \longrightarrow Bu^tCH_2CMe{=}CMe_2 + CO_2$	−26.1	139.9	3.03×10^{-4}	166.0	4.31×10^{-15}
$PhCH{=}CMeCMe_2CO_2H \longrightarrow PhCH_2CMe{=}CMe_2 + CO_2$	10.6	160.5	1.99×10^{-6}	149.9	2.07×10^{-13}
$MeCH{=}CPhCMe_2CO_2H \longrightarrow PhEtC{=}CMe_2 + CO_2$	−7.2	150.3	2.40×10^{-5}	157.5	3.33×10^{-14}

3. The addition of CO_2 to alkenes

The reverse, with respect to the decomposition reactions of unsaturated acids, are the addition reactions of carbon dioxide to alkenes, which proceed *via* the same six-membered TS:



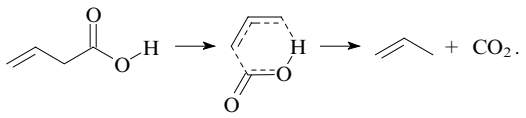
$$R^1R^2CHCR^3{=}CR^4R^5 + CO_2 \longrightarrow \longrightarrow R^1R^2C{=}CR^3CR^4R^5CO_2H.$$

Published data on the kinetic parameters of such reactions are unavailable. The parameters obtained for the decomposition of acids were used to calculate the kinetic parameters of the reactions of formation of acids by adding CO_2 to alkenes.[10] The decomposition reactions of unsaturated acids are exothermic (see above); therefore, the corresponding formation reactions are endothermic with the pre-exponent $A_{ca} = 4.5 \times 10^2$ litre mol^{-1} s^{-1}. The results of calculations are listed in Table 14.

From the data in Table 14 it follows that the addition of CO_2 to alkenes is almost impossible at their decomposition temperatures (T = 500 K). The activation energies of such addition reactions vary in the range 150 – 184 kJ mol^{-1}.

4. Two-centre MIP model for decomposition of unsaturated acids

The decomposition of unsaturated acids proceeds *via* the formation of a six-membered TS, for instance:



Transfer of H atom is accompanied by cleavage of strong O – H bond in the carboxyl group (D_{O-H} = 441 kJ mol^{-1}) and the formation of a weak propylene allylic bond C – H (D_{C-H} = 368 kJ mol^{-1}).[31] Therefore, the process is endothermic and is modelled by the reaction No. 3 (see Table 2). Cleavage of the C – C bond is modelled by the reaction No. 9 in Table 2. The parameters ΔH_{abs} and ΔH_{abs} for the decomposition of ten unsaturated acids are as follows: $73 < \Delta H_{abs} < 109$ kJ mol^{-1} and $90 < E_{abs} < 116$ kJ mol^{-1} (see Table 13).[8] On the contrary, cleavage of the C – C bond is an exothermic process characterized by the enthalpy varying from –91 to –133 kJ mol^{-1}; the energy E_π also varies over a wide range from 17 to 49 kJ mol^{-1}.

VIII. Decomposition of esters

1. Experimental data

Decomposition of an ester into the acid and alkene [22]

$$R^1CO_2CH_2CH_2R^2 \longrightarrow R^1CO_2H + CH_2{=}CHR^2$$

is endothermic ($\Delta H > 0$; more exactly, ΔH is in the range from 26 to 80 kJ mol^{-1}) and has a very high activation energy (from 166 to 213 kJ mol^{-1}). The rate constants for decomposition vary between 9.7×10^{-2} and 1.8×10^{-6} s^{-1} (T = 600 K). Large scatter of numerical values of the kinetic parameters is due to the variety of ester structures (Table 15).[22, 37 – 51]

2. One-centre model for molecular decomposition of esters

Ester decomposition reactions are divided into eight classes. Each class includes the decomposition reactions of structur-

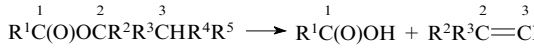
Table 15. Experimental parameters [22, 37 – 51] and the spectrum of activation energies for concerted decomposition of carboxylic acid esters (T = 650 – 900 K).[13]

Reaction	ΔH	E_{exp}	k_{exp} (600 K)	E_{abs}	E_d	E_π	Ref.
$MeCO_2Et \longrightarrow CH_2{=}CH_2 + MeCO_2H$	62.7	205.4	1.21×10^{-5}	25.7	100.2	77.0	22
	62.7	207.2	8.78×10^{-6}	25.7	100.2	77.0	37
	62.7	206.6	9.91×10^{-6}	25.7	100.2	77.0	38
$MeCO_2Pr^n \longrightarrow CH_2{=}CHMe + MeCO_2H$	51.1	204.7	9.67×10^{-6}	22.3	97.0	82.9	39
	51.1	204.2	1.06×10^{-5}	22.3	97.0	82.9	22
$MeCO_2Bu^n \longrightarrow CH_2{=}CHEt + MeCO_2H$	52.1	202.6	1.48×10^{-5}	22.3	97.1	80.7	40
$MeCO_2C_5H_{11}$-n $\longrightarrow CH_2{=}CHPr^n + MeCO_2H$	51.7	199.5	2.76×10^{-5}	–	–	–	22
$MeCO_2C_5H_{11}$-iso $\longrightarrow CH_2{=}CHPr^i + MeCO_2H$	50.2	203.5	1.22×10^{-5}	–	–	–	41
	50.2	203.4	1.26×10^{-5}	–	–	–	42
$MeCO_2(CH_2)_2Ph \longrightarrow CH_2{=}CHPh + MeCO_2H$	44.6	195.4	6.25×10^{-5}	6.5	89.9	96.6	39
	44.6	195.5	6.09×10^{-5}	6.5	89.9	96.6	22
$HCO_2Et \longrightarrow CH_2{=}CH_2 + HCO_2H$	58.6	203.7	1.77×10^{-5}	25.7	99.6	75.9	22
$EtCO_2Et \longrightarrow CH_2{=}CH_2 + EtCO_2H$	60.1	206.0	1.12×10^{-5}	25.7	99.8	78.0	43
$Pr^nCO_2Et \longrightarrow CH_2{=}CH_2 + Pr^nCO_2H$	65.0	205.3	1.28×10^{-5}	–	–	–	44
$PhCH_2CO_2Et \longrightarrow CH_2{=}CH_2 + PhCH_2CO_2H$	63.2	204.3	1.57×10^{-5}	23.0	99.2	79.6	45
$MeCO_2Bu^i \longrightarrow CH_2{=}CMe_2 + MeCO_2H$	42.4	204.5	4.98×10^{-6}	17.6	94.0	90.4	22
$MeCO_2CH_2CHMeEt \longrightarrow CH_2{=}CMeEt + MeCO_2H$	42.5	207.3	2.89×10^{-6}	17.6	94.0	93.2	22
$MeCO_2(CH_2)_2OMe \longrightarrow CH_2{=}CHOMe + MeCO_2H$	46.2	213.2	1.76×10^{-6}	17.4	94.4	98.9	22
	46.2	212.5	2.01×10^{-6}	17.4	94.4	98.9	46
$MeCO_2(CH_2)_2OEt \longrightarrow CH_2{=}CHOEt + MeCO_2H$	46.3	212.1	2.19×10^{-6}	–	–	–	22
$MeCO_2Pr^i \longrightarrow CH_2{=}CHMe + MeCO_2H$	68.3	192.2	3.58×10^{-4}	25.7	101.2	62.8	47
$MeCO_2Bu^s \longrightarrow CH_2{=}CHEt + MeCO_2H$	68.9	193.2	1.44×10^{-4}	25.7	101.3	63.7	22
$MeCO_2CHMePr^n \longrightarrow CH_2{=}CHPr^n + MeCO_2H$	68.3	188.2	3.98×10^{-4}	–	–	–	22
$MeCO_2CHMeBu^s \longrightarrow CH_2{=}CHBu^s + MeCO_2H$	63.9	186.2	5.89×10^{-4}	–	–	–	22
$MeCO_2CHMeC_5H_{11}$-n $\longrightarrow CH_2{=}CHC_5H_{11}$-n + $MeCO_2H$	68.3	186.1	6.03×10^{-4}	22.3	99.7	61.6	22
$MeCO_2CHMeC_5H_{11}$-n $\longrightarrow MeCH{=}CHBu^n + MeCO_2H$	68.3	187.9	2.81×10^{-4}	22.3	99.7	61.6	22
$MeCO_2CHEtBu^n \longrightarrow EtCH{=}CHPr + MeCO_2H$	56.9	185.0	5.01×10^{-4}	22.3	97.9	62.3	22
$MeCO_2CHEtBu^n \longrightarrow MeCH{=}CHBu^n + MeCO_2H$	56.7	184.4	5.62×10^{-4}	22.3	97.9	62.3	22
$MeCO_2CHMeCH_2CH{=}CH_2 \longrightarrow$ $\longrightarrow CH_2{=}CHCH_2CH{=}CH_2 + MeCO_2H$	70.0	190.4	2.51×10^{-4}	25.7	101.5	60.7	22

Table 15 (continued).

Reaction	ΔH	E_{exp}	k_{exp} (600 K)	E_{abs}	E_d	E_π	Ref.
$MeCO_2$(cyclo-C_6H_{11}) ⟶ cyclo-C_6H_{10} + $MeCO_2H$	56.8	182.9	7.67×10^{-4}	–	–	–	22
$MeCO_2CHMeCH_2C(O)Me$ ⟶ $MeC(O)CH{=}CHMe$ + $MeCO_2H$	25.7	167.2	1.79×10^{-2}	15.1	91.0	58.6	22
$MeCO_2CHMeCH_2NMe_2$ ⟶ $CH_2{=}CHCH_2NMe_2$ + $MeCO_2H$	67.1	189.2	3.23×10^{-4}	–	–	–	22
$MeCO_2CHMePh$ ⟶ $CH_2{=}CHPh$ + $MeCO_2H$	71.8	189.5	3.02×10^{-4}	–	–	–	22
$MeCO_2CHPhCH_2Ph$ ⟶ $PhCH{=}CHPh$ + $MeCO_2H$	46.2	178.4	1.87×10^{-3}	6.5	90.0	79.4	22
$EtCO_2Pr^i$ ⟶ $CH_2{=}CHMe$ + $EtCO_2H$	69.4	192.5	3.37×10^{-4}	–	–	–	48
$MeCO_2Bu^t$ ⟶ $CH_2{=}CMe_2$ + $MeCO_2H$	71.2	170.9	3.83×10^{-2}	25.7	101.7	41.0	22
$MeCO_2Bu^s$ ⟶ $CH_2{=}CMeEt$ + $MeCO_2H$	59.2	168.7	3.98×10^{-2}	22.3	101.9	41.0	22
$MeCO_2CMe_2Et$ ⟶ $MeCH{=}CMe_2$ + $MeCO_2H$	67.0	168.4	1.41×10^{-2}	22.3	101.9	41.0	22
HCO_2Bu^t ⟶ $CH_2{=}CMe_2$ + HCO_2H	72.3	171.9	3.10×10^{-2}	–	–	–	22
$EtCO_2Bu^t$ ⟶ $CH_2{=}CMe_2$ + $EtCO_2H$	72.3	171.1	3.64×10^{-2}	25.7	101.9	41.0	47
$Pr^nCO_2Bu^t$ ⟶ $CH_2{=}CMe_2$ + Pr^nCO_2H	72.3	171.8	3.16×10^{-2}	–	–	–	49
$PhCO_2Et$ ⟶ $CH_2{=}CH_2$ + $PhCO_2H$	80.5	202.3	2.10×10^{-5}	–	–	–	45
	80.5	206.6	9.90×10^{-6}	–	–	–	50
$PhCO_2Pr^i$ ⟶ $CH_2{=}CHMe$ + $PhCO_2H$	77.7	188.4	7.49×10^{-4}	–	–	–	51
	77.7	188.4	7.49×10^{-4}	–	–	–	49
$PhCO_2Bu^t$ ⟶ $CH_2{=}CMe_2$ + $PhCO_2H$	72.3	166.2	9.73×10^{-2}	–	–	–	45
$MeCO_2CHMeCH_2Cl$ ⟶ $ClCH{=}CHMe$ + $MeCO_2H$	63.8	200.5	2.23×10^{-5}	–	–	–	22
$MeCO_2CHMeCH_2Cl$ ⟶ $CH_2{=}CHCH_2Cl$ + $MeCO_2H$	70.5	199.0	4.52×10^{-5}	–	–	–	22

ally similar esters characterized by br_e = const. Each group of compounds is characterized by a particular value of the energy E_{e0} of the classical potential barrier to thermally neutral reaction. The MIP parameters for the ester decomposition reactions are listed below.



Substituents	br_e	E_{e0}
R^1 = H, Alk; R^2 = R^3 = R^4 = H; R^5 = H, Alk, Ph	25.10	191.2
R^1 = H, Alk; R^2 = R^3 = H; R^4 = R^5 = Alk or R^4 = H, R^5 = OAlk	25.91	203.8
R^1 = H, Alk; R^2 = H; R^3 = Alk, Ph, CH_2NMe_2, All; R^4 = H; R^5 = H, Alk, Ph	23.77	171.5
R^1 = H, Alk; R^2 = R^3 = Alk; R^4 = R^5 = H or R^4 = H, R^5 = Alk	22.36	151.8
R^1 = R^2 = Me, R^3 = R^4 = H, R^5 = Cl	24.50	182.2
R^1 = Ph, R^2 = R^3 = R^4 = R^5 = H	24.38	180.4
R^1 = Ph, R^2 = Alk, R^3 = R^4 = R^5 = H	23.35	165.5
R^1 = Ph, R^2 = R^3 = Me, R^4 = R^5 = H	21.92	145.9

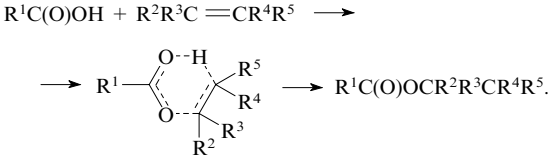
Even in thermally neutral conditions (ΔH_e = 0), decomposition of esters is characterized by very high classical potential barriers ($146 < E_{e0} < 204$ kJ mol^{-1}). This is apparently due to the presence of substituents at the carbon atoms C(1), C(2) and C(3) and to the joint effect of substituents in the TS.

The parameters br_e for the decomposition of four groups of esters were calculated from experimental data and then used to determine the activation energies E [Eqn (8)] and rate constants k [Eqn (3), $A_0 = 1.67\times10^{14}$ s^{-1}] for a number of individual reactions. The results of analysis of gas-phase decomposition of carboxylic acid esters within the framework of the MIP(1) model are listed in Table 16.

A comparison of the results of calculations with experimental data showed a a reasonable agreement (root-mean-square error is $\Delta E = 2.7 \pm 1.8$ kJ mol^{-1}).

3. The addition of acids to alkenes

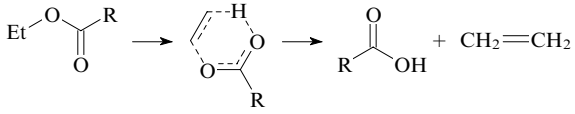
The reverse, with respect to the ester decomposition reactions, are the concerted addition reactions of acids to alkenes, which proceed *via* the same six-membered TS:[13]



No published data on the kinetics of the reverse reactions are available at the moment. The ester decomposition reactions are endothermic (see above); therefore, the reverse, ester formation reactions, will be exothermic. Table 16 presents the results of calculations of the enthalpies, activation energies (E_{ca}) and rate constants for the reactions (k_{ca}, 600 K). As can be seen, the addition of acids to alkenes should proceed with high activation energy ($94.9 < E_{ca} < 164.3$ kJ mol^{-1}). The rate constants for the reactions vary from 8.0×10^{-10} to 8.9×10^{-4} litre mol^{-1} s^{-1}. The E_{e0} energy values for the decomposition of esters determined using the MIP(1) model (see above) also characterize the corresponding reverse reactions (ester formation reactions) in thermally neutral conditions.

4. Decomposition of esters as concerted two-centre reaction

Concerted decomposition of esters treated as two-centre reaction involves[8] (1) transfer of H atom from a C atom to the carbonyl O atom of the ester group and (2) cleavage of the C–O bond and results in a carboxylic acid and alkene, for instance:



Transfer of H atom is modelled by the reaction No. 4 (see Table 2). This is an exothermic process because

Table 16. Thermodynamic and kinetic parameters of decomposition and formation reactions of esters calculated by the MIP(1) method.[13]

Reaction	ΔH	E_{cd}	k_{cd} (600 K)	E_{ca}	k_{ca} (600 K)
$MeCO_2Et \longrightarrow CH_2{=}CH_2 + MeCO_2H$	62.7	203.9	9.96×10^{-6}	141.2	8.30×10^{-8}
$MeCO_2Pr^n \longrightarrow CH_2{=}CHMe + MeCO_2H$	51.1	198.3	2.06×10^{-5}	147.2	2.49×10^{-8}
$MeCO_2Bu^n \longrightarrow CH_2{=}CHEt + MeCO_2H$	52.1	198.7	1.91×10^{-5}	146.6	2.81×10^{-8}
$MeCO_2C_5H_{11}$-n $\longrightarrow CH_2{=}CHPr^n + MeCO_2H$	51.7	198.5	1.98×10^{-5}	146.8	2.70×10^{-8}
$MeCO_2C_5H_{11}$-iso $\longrightarrow CH_2{=}CHPr^i + MeCO_2H$	50.2	197.8	2.28×10^{-5}	147.6	2.30×10^{-8}
$MeCO_2(CH_2)_2Ph \longrightarrow CH_2{=}CHPh + MeCO_2H$	44.6	195.1	3.96×10^{-5}	150.5	1.29×10^{-8}
$EtCO_2Et \longrightarrow CH_2{=}CH_2 + EtCO_2H$	60.1	202.6	1.30×10^{-5}	142.5	6.40×10^{-8}
$Pr^nCO_2Et \longrightarrow CH_2{=}CH_2 + Pr^nCO_2H$	65.0	205.0	7.95×10^{-6}	140.0	1.06×10^{-7}
$PhCH_2CO_2Et \longrightarrow CH_2{=}CH_2 + PhCH_2CO_2H$	63.2	204.1	9.54×10^{-6}	140.9	8.82×10^{-8}
$HCO_2Et \longrightarrow CH_2{=}CH_2 + HCO_2H$	58.6	201.9	1.49×10^{-5}	143.3	5.45×10^{-8}
$MeCO_2Bu^i \longrightarrow CH_2{=}CMe_2 + MeCO_2H$	42.4	206.7	5.90×10^{-6}	164.3	8.09×10^{-10}
$MeCO_2CH_2Bu^s \longrightarrow CH_2{=}CMeEt + MeCO_2H$	42.5	206.7	5.90×10^{-6}	164.2	8.26×10^{-10}
$MeCO_2(CH_2)_2OMe \longrightarrow CH_2{=}CHOMe + MeCO_2H$	46.2	208.5	2.60×10^{-6}	162.3	1.21×10^{-9}
$MeCO_2(CH_2)_2OEt \longrightarrow CH_2{=}CHOEt + MeCO_2H$	46.3	208.5	2.60×10^{-6}	164.2	8.26×10^{-10}
$MeCO_2Pr^i \longrightarrow CH_2{=}CHMe + MeCO_2H$	68.3	187.1	3.01×10^{-4}	118.8	7.40×10^{-6}
$MeCO_2Bu^s \longrightarrow CH_2{=}CHEt + MeCO_2H$	68.9	187.4	2.88×10^{-4}	118.5	7.86×10^{-6}
$MeCO_2CHMePr^n \longrightarrow CH_2{=}CHPr^n + MeCO_2H$	68.3	187.4	2.84×10^{-4}	119.1	6.97×10^{-6}
$MeCO_2CHMeBu^s \longrightarrow CH_2{=}CHBu^s + MeCO_2H$	63.9	184.9	4.71×10^{-4}	121.0	4.76×10^{-6}
$MeCO_2CHMeC_5H_{11}$-n $\longrightarrow MeCH{=}CHBu^n + MeCO_2H$	68.3	187.1	2.01×10^{-4}	118.8	7.40×10^{-6}
$MeCO_2CHEtBu^n \longrightarrow EtCH{=}CHPr^n + MeCO_2H$	56.9	181.5	6.26×10^{-4}	124.6	2.31×10^{-6}
$MeCO_2CHEtBu^n \longrightarrow MeCH{=}CHBu^n + MeCO_2H$	56.7	181.4	6.39×10^{-4}	124.7	2.26×10^{-6}
$MeCO_2CHPr^n_2 \longrightarrow EtCH{=}CHPr^n + MeCO_2H$	57.0	181.5	6.26×10^{-4}	124.5	2.36×10^{-6}
$MeCO_2CHMeCH_2CH{=}CH_2 \longrightarrow$ $\longrightarrow CH_2{=}CHCH_2CH{=}CH_2 + MeCO_2H$	70.0	187.9	2.56×10^{-4}	117.9	8.86×10^{-6}
$MeCO_2C_6H_{11}$-cyclo $\longrightarrow$ cyclo-$C_6H_{10} + MeCO_2H$	56.8	181.4	6.39×10^{-4}	124.6	2.31×10^{-6}
$MeCO_2CHMeCH_2NMe_2 \longrightarrow$ $\longrightarrow CH_2{=}CHCH_2NMe_2 + MeCO_2H$	67.1	186.5	3.40×10^{-4}	119.4	6.56×10^{-6}
$MeCO_2CHMePh \longrightarrow CH_2{=}CHPh + MeCO_2H$	71.8	188.8	2.13×10^{-4}	117.0	1.06×10^{-5}
$MeCO_2CHPhCH_2Ph \longrightarrow PhCH{=}CHPh + MeCO_2H$	46.2	176.3	1.80×10^{-3}	130.1	7.68×10^{-7}
$EtCO_2Pr^i \longrightarrow CH_2{=}CHMe + EtCO_2H$	69.4	187.6	2.72×10^{-4}	118.2	8.34×10^{-6}
$Pr^nCO_2Pr^i \longrightarrow CH_2{=}CHMe + Pr^nCO_2H$	68.4	187.2	2.95×10^{-4}	118.8	7.40×10^{-6}
$HCO_2Pr^i \longrightarrow CH_2{=}CHMe + HCO_2H$	68.5	187.2	2.95×10^{-4}	118.7	7.55×10^{-6}
$MeCO_2Bu^t \longrightarrow CH_2{=}CMe_2 + MeCO_2H$	71.2	169.0	3.74×10^{-2}	97.8	4.98×10^{-4}
$MeCO_2CMe_2Et \longrightarrow CH_2{=}CMeEt + MeCO_2H$	59.2	163.0	4.04×10^{-2}	103.8	1.50×10^{-4}
$MeCO_2C_5H_{11}$-tert $\longrightarrow MeCH{=}CMe_2 + MeCO_2H$	67.0	166.8	1.24×10^{-2}	99.8	3.33×10^{-4}
$MeCO_2CMeEt_2 \longrightarrow MeCH{=}CMeEt + MeCO_2H$	67.4	167.0	1.19×10^{-2}	99.6	3.47×10^{-4}
$MeCO_2CMeEt_2 \longrightarrow CH_2{=}CEt_2 + MeCO_2H$	77.0	171.9	6.61×10^{-3}	94.9	8.91×10^{-4}
$EtCO_2Bu^t \longrightarrow CH_2{=}CMe_2 + EtCO_2H$	72.3	169.5	1.07×10^{-2}	97.2	5.62×10^{-4}
$Pr^nCO_2Bu^t \longrightarrow CH_2{=}CMe_2 + Pr^nCO_2H$	72.3	169.5	1.07×10^{-2}	97.2	5.62×10^{-4}
$HCO_2Bu^t \longrightarrow CH_2{=}CMe_2 + HCO_2H$	72.3	169.5	1.07×10^{-2}	97.2	5.62×10^{-4}

$D_{O-H} > D_{C-H}$; its enthalpy ΔH_{abs} is from -77 to -19 kJ mol^{-1}. Cleavage of the C$-$O bond can be either exothermic or endothermic depending on the ester structure ($\Delta H_d = -32-53$ kJ mol^{-1}).[8] It is modeled by the reaction No. 10 in Table 2. Decomposition of a large number of esters was studied (see Table 15). The activation energy of H atom transfer is low (6.5–26 kJ mol^{-1}), whereas E_d is, on the contrary, high (90–102 kJ mol^{-1}). The activation energy E_π varies over a wide range from 41 to 99 kJ mol^{-1}.

IX. Decomposition of nitroalkanes

1. Experimental data

Nitroalkanes decompose into corresponding alkenes and nitrous acid:[52]

$$RCH_2CH_2NO_2 \longrightarrow CH_2{=}CHR + HONO.$$

From the data in Table 17 it follows that concerted molecular decomposition of nitroalkanes is endothermic ($\Delta H > 0$, $52 < \Delta H < 84$ kJ mol^{-1}) and has a high activation energy (from 175 to 188 kJ mol^{-1}).[52]

2. One-centre model for molecular decomposition of nitro compounds

Decomposition of aliphatic nitro compounds (RNO_2) within the framework of the MIP(1) model is characterized by different br_e values that depend on the substituent structure, being equal to 23.53 kJ$^{1/2}$ mol$^{-1/2}$ for substituents R of normal structure and to 22.33 kJ$^{1/2}$ mol$^{-1/2}$ for branched R.[11] Correspondingly, the classical potential barriers to thermally neutral reaction for these substituents are 167.9 and 151.9 kJ mol^{-1}. Thus, alkyl groups in the nitro compound affect the TS energy, *viz*., substituents in the α-position cause the classical barrier to thermally neutral reaction (E_{e0}) to decrease by 16.0 kJ mol^{-1}. The br_e values were used to calculate the activation energies [Eqn (8)] and rate constants [Eqn (3), $A_0 = 2.3\times10^{12}$ s^{-1}] for a series of decomposition reactions of nitroalkanes of different structure. The results of calculations are presented in Table 18.

From the data in Tables 17 and 18 it follows that the calculated activation energies of decomposition of nitro compounds are close to experimental values (root-mean-square error is $\Delta E = 2.6 \pm 2.4$ kJ mol^{-1}).

Table 17. Experimental parameters [53] and the spectrum of activation energies for concerted decomposition of nitroalkanes ($T = 550-650$ K).[11]

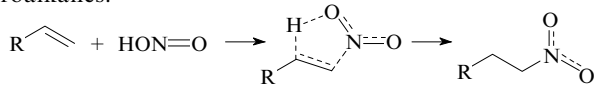
Reaction	ΔH	E_{exp}	k_{exp} (625 K)	E_{abs}	E_d	E_π
$EtNO_2 \longrightarrow CH_2{=}CH_2 + HONO$	74.9	187.6	3.18×10^{-4}	93.0	51.7	40.3
$Pr^nNO_2 \longrightarrow CH_2{=}CHMe + HONO$	64.8	186.2	2.79×10^{-4}	91.1	51.7	40.8
$Bu^nNO_2 \longrightarrow CH_2{=}CHEt + HONO$	64.5	184.2	4.09×10^{-4}	91.6	51.6	38.4
$n\text{-}C_5H_{11}NO_2 \longrightarrow CH_2{=}CHPr^n + HONO$	64.3	183.9	4.38×10^{-4}	91.6	51.5	38.2
$n\text{-}C_6H_{13}NO_2 \longrightarrow CH_2{=}CHBu^n + HONO$	64.6	183.6	4.61×10^{-4}	91.6	51.6	37.8
$iso\text{-}C_5H_{11}NO_2 \longrightarrow CH_2{=}CHPr^i + HONO$	62.5	183.9	4.33×10^{-4}	91.1	51.4	38.8
$Bu^iNO_2 \longrightarrow CH_2{=}CMe_2 + HONO$	52.2	183.1	2.54×10^{-4}	83.7	50.7	46.1
$Pr^iNO_2 \longrightarrow CH_2{=}CHMe + HONO$	79.4	179.2	3.22×10^{-3}	93.0	52.2	31.4
$Bu^sNO_2 \longrightarrow CH_2{=}CHEt + HONO$	84.2	175.0	3.59×10^{-3}	91.1	53.8	27.5

Table 18. Thermodynamic and kinetic parameters of decomposition and formation reactions of nitroalkanes calculated using the MIP(1) method.[11]

Reaction	ΔH	E_{cd}	k_{cd} (625 K)	E_{ca}	k_{ca} (625 K)
$EtNO_2 \longrightarrow CH_2{=}CH_2 + HONO$	74.9	187.5	2.0×10^{-4}	112.6	2.91×10^{-5}
$Pr^nNO_2 \longrightarrow CH_2{=}CHMe + HONO$	64.8	182.4	3.5×10^{-4}	117.6	1.11×10^{-5}
$Bu^nNO_2 \longrightarrow CH_2{=}CHEt + HON$	64.5	182.3	3.6×10^{-4}	117.8	1.07×10^{-5}
$n\text{-}C_5H_{11}NO_2 \longrightarrow CH_2{=}CHPr^n + HONO$	64.3	182.2	3.7×10^{-4}	117.9	1.05×10^{-5}
$n\text{-}C_6H_{13}NO_2 \longrightarrow CH_2{=}CHBu^n + HONO$	64.6	182.3	3.6×10^{-4}	117.7	1.09×10^{-5}
$iso\text{-}C_5H_{11}NO_2 \longrightarrow CH_2{=}CHPr^i + HONO$	62.5	181.3	4.4×10^{-4}	118.8	8.82×10^{-6}
$Bu^i(CH_2)_2NO_2 \longrightarrow CH_2{=}CHBu^i + HONO$	60.5	179.3	6.5×10^{-4}	118.8	8.82×10^{-6}
$Bu^s(CH_2)_2NO_2 \longrightarrow CH_2{=}CHBu^s + HONO$	61.3	180.7	4.9×10^{-4}	119.4	7.87×10^{-6}
$Bu^iNO_2 \longrightarrow CH_2{=}CMe_2 + HONO$	52.2	176.3	5.8×10^{-4}	124.1	3.18×10^{-6}
$Bu^sCH_2NO_2 \longrightarrow CH_2{=}CMeEt + HONO$	54.1	177.2	4.9×10^{-4}	123.1	3.86×10^{-6}
$Et_2CHCH_2NO_2 \longrightarrow CH_2{=}CEt_2 + HONO$	54.2	177.3	4.8×10^{-4}	123.1	3.86×10^{-6}
$Pr^iNO_2 \longrightarrow CH_2{=}CHMe + HONO$	79.4	173.2	6.3×10^{-3}	93.8	1.08×10^{-3}
$Bu^sNO_2 \longrightarrow CH_2{=}CHEt + HONO$	84.2	175.7	2.0×10^{-3}	91.5	1.72×10^{-3}
$Bu^sNO_2 \longrightarrow MeCH{=}CHMe + HONO$	70.7	168.8	5.0×10^{-3}	98.1	4.74×10^{-4}
$Et_2CHNO_2 \longrightarrow MeCH{=}CHEt + HONO$	78.3	172.7	4.6×10^{-3}	94.4	9.67×10^{-4}

3. The addition of alkenes to HNO_2

The kinetic parameters of decomposition obtained using the MIP(1) method (see Table 18) were used to calculate the kinetic parameters of the addition of nitrous acid to alkenes resulting in nitro compounds. The formation of nitro compounds (association reaction) proceeds *via* the same five-membered transition state as in the decomposition of nitroalkanes.



If the decomposition of nitro compounds is an endothermic reaction, the reverse reaction resulting in nitro compounds is an exothermic process. The pre-exponent for the reactions leading to nitroalkanes [$A_{0(ca)} = 7.5\times10^4$ litre mol^{-1} s^{-1}] was calculated [11] using the equilibrium constant (K) of the reaction:

$$CH_2{=}CHMe + HONO \rightleftharpoons Pr^nNO_2.$$

Small value of the pre-exponent is due to the entropy change in the addition reaction, *viz*., $\Delta S = -161.1$ J mol^{-1} K^{-1}. The results of calculations of the enthalpies (ΔH_{ca}), activation energies (E_{ca}) and rate constants for the formation of some nitro compounds from alkenes and nitrous acid are presented in Table 18. The addition of HONO to alkenes is characterized by high activation energy ($E_{ca} = 91-124$ kJ mol^{-1}, see Table 18). The rate constants for the reaction vary from 1.7×10^{-3} to 3.2×10^{-6} litre mol^{-1} s^{-1}.

4. Decomposition of nitroalkanes as concerted two-centre reaction

The results of calculations of the partial activation energies using the two-centre model [MIP(2)] are presented in Table 17. As can be seen, hydrogen abstraction in the reactions of concerted decomposition of nitro compounds is an endothermic step (enthalpy of abstraction reaction varies from 94.4 to 72.4 kJ mol^{-1}), whereas the decomposition with cleavage of the C—N bond is exothermic owing to compensation through the formation of the C=C π-bond (enthalpy of decomposition varies from 0 to −21.9 kJ mol^{-1}).[11] Hydrogen abstraction requires an activation energy lying in the range from 83.7 to 93.0 kJ mol^{-1}. The activation energy of C—N bond dissociation in the compounds in question varies from 50.7 to 53.8 kJ mol^{-1}, being in all cases lower than the energy of hydrogen abstraction. This agrees well with the results of quantum chemical calculations for related reactions.[54,55] The activation energy E_π characterizing the electron density redistribution in the TS varies from 27.5 to 46.1 kJ mol^{-1} (Ref. 11).

X. Conclusion

Using both, MIP(1) and MIP(2), versions of the parabolic model, one can not only calculate the kinetic parameters of numerous reactions of concerted decomposition of unsaturated compounds, esters and nitro compounds from experimental data, but also highlight the factors affecting the activation energies of the decomposition reactions in question.[56] The most important factors are considered below.

1. The enthalpy of reaction

The enthalpy of reaction strongly affects the activation energy.[16] Within the framework of the MIP(1) model this dependence can be expressed analytically. Transformation of Eqn. (8) at $\Delta H_e \ll B\,br_e$ gives the following expression for the activation energy as function of ΔH:

$$\frac{dE}{dH} = \frac{\alpha}{1+\alpha} + \frac{\alpha^2 \Delta H_e}{2(br_e)^2}. \qquad (17)$$

An analysis of this equation shows that an increase in E with an increase in ΔH_e is governed by the coefficient α (force constant ratio of the bond being cleaved to the bond being formed) and parameter br_e, *i.e.*, E_{e0} [see Eqn (10)]. The MIP(1) model parameters describing the dependence of the activation energy of a reaction on enthalpy its for concerted decomposition of molecules are given below.

For the decomposition reactions studied, the coefficient $\alpha(1+\alpha)^{-1}$ varies from 0.45 to 0.56 and the term $0.5\alpha^2(br_e)^{-2}$ varies in a wider range from 5.06×10^{-4} to 40.4×10^{-4} kJ mol^{-1}.

Compound	α	br_e	$\alpha/(1+\alpha)$	$10^4\alpha^2/2(br_e)^2$
$CH_2{=}CHR$	1.000	28.10	0.50	6.34
$CH_2{=}CHCH_2CH_2OH$	1.255	27.53	0.56	10.40
$CH_2{=}CHOCH_2CH_2R$	1.000	27.56	0.50	6.56
$CH_2{=}CHCH_2CO_2H$	1.299	31.37	0.56	8.56
$MeCO_2CH_2CH_2R$	0.814	25.10	0.45	5.24
$RCH_2CH_2NO_2$	0.812	25.53	0.45	5.06

At small ΔH values, the dependence of E on ΔH is governed by the coefficient $\alpha(1+\alpha)^{-1}$. All reactions considered here, except decarboxylation of acids, are endothermic.

2. The effect of substituents

The substituents in reactant molecules influence E and k in dual manner, namely, through the change in the enthalpy of reaction and through the corresponding dependences of E_{e0}. The latter is of particular interest. Shown below are the E_{e0} values (in kJ mol^{-1}) calculated by the MIP(1) method for linear (R = H) and substituted (R = Me, Ph) esters, ethers, alcohols, acids and nitroalkanes.

Compounds	Formula	E_{e0}			ΔE_π
		R = H	R = Me	R = Ph	
1	$CH_2{=}CHOCHMeR$	187.3	176.5	–	10.8
2	$RCH{=}CHCH_2CH_2OH$	149.0	–	137.3	11.7
3	$CH_2{=}CHCH_2CR_2OH$	149.0	160.9	–	11.9
4	$CH_2{=}CHCR_2CO_2H$	186.2	171.4	–	14.8
5	$CH_2{=}CRCH_2CO_2H$	186.2	–	155.3	30.9
6	$MeCO_2CHRCHR_2$	191.2	171.5	–	19.7
7	$MeCO_2CR_2CHR_2$	191.2	151.8	–	39.4
8	RCO_2Et	–	191.2	180.4	10.8
9	RCO_2Bu^t	–	151.8	145.9	5.9
10	$PhCO_2CHMeR$	180.4	165.5	–	14.9
11	$PhCO_2CMe_2R$	165.5	145.9	–	19.6
12	$RMeCHNO_2$	168.5	151.9	–	16.7

From the E_{e0} values presented it follows that for most compounds under consideration, the methyl and phenyl substituents reduce the activation energy of thermally neutral concerted decomposition. Since $E_{e0(abs)}$ and $E_{e0(d)}$ are independent of substituents,[15,16] this effect should be attributed to the change in $E_{e0(\pi)}$. The benzene ring (owing to the conjugation effect) and methyl group (owing to the inductive effect) cause the electron density in the cyclic TS to increase. Probably, a decrease in $E_{e0(\pi)}$ is also due to just this effect of substituent on the electron density and energy characteristics of the TS. A comparison of the E_{e0} values for alcohols **2** and **3** shows that the alkyl substituents near the alcohol group cause the activation energy to increase by 11.9 kJ mol^{-1}, which is apparently due to steric hindranes produced by them in the TS.

3. Effect of the ring strain energy in the transition state

The activation energies of decomposition of aliphatic and unsaturated alcohols are influenced by the strain in the cyclic TS (n is the ring size)[7] (see also Tables 7–10).

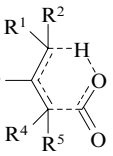
Reaction	n	E_e (see [a])	E_{e0} (see [a])
$EtOH \rightarrow CH_2{=}CH_2 + H_2O$	4	256.8	253.0
$CH_2{=}CHCH_2CH_2OH \rightarrow$ $\rightarrow CH_2{=}CHMe + HCHO$	6	168.6	149.0

[a] In kJ mol^{-1}.

As can be seen, the activation energy (E_e) and the classical potential barrier (E_{e0}) to thermally neutral decomposition of unsaturated alcohols are about 100 kJ mol^{-1} lower than the corresponding decomposition energies of aliphatic alcohols. This is due to the fact that decomposition of unsaturated alcohols proceeds concertedly *via* the formation of a six-membered TS, whereas the decomposition of alkanols proceeds *via* the formation of a TS containing a strained four-membered ring. The energy of ring strain in cyclobutane is 111 kJ mol^{-1} (Ref. 57). The results of quantum chemical calculations (see Table 8) show that on going from the four-membered to the six-membered TS of the ethanol decomposition reaction the activation energy also significantly decreases (by about 60 kJ mol^{-1}) due to the involvement of an additional water molecule.

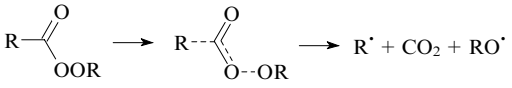
4. The spectrum of activation energies

As shown earlier,[7–13] all molecular decomposition reactions are characterized by high potential barriers to thermally neutral reaction ($E_{e0} > 151.9$ kJ mol^{-1}). This is due to simultaneous concentration of energy on two reaction centres (see transition structures in Table 1) and the energy consumed for redistribution of electrons in the bonds of the molecule being decomposed. The dependence of the potential barrier to thermally neutral reaction on the number of reacting bonds is clearly seen when comparing the decarboxylation reactions. Previously, we analyzed the decarboxylation reactions of carboxyl radicals and peroxy esters within the framework of the MIP model.[58,59] All three types of decarboxylation reactions differ in the number of bonds involved in the rearrangement, on the one hand, and in the activation energies of thermally neutral reactions (E_{e0}), on the other hand. The E_{e0} values for these reactions are compared below.

Reaction	TS	E_{e0} (see [a])	n_b	E_{e0}/n_b (see [a])
$CH_2{=}CHCH_2CO_2H \rightarrow$ $\rightarrow CH_2{=}CHMe + CO_2$		186.2	5	37.2
$Me_3CC(O)OOCMe_3 \rightarrow$ $\rightarrow CO_2 + Me_3C^{\bullet} + Me_3CO^{\bullet}$	C···C(O)−O···O	96.2	3	32.1
$Me_3CCO_2^{\bullet} \rightarrow$ $\rightarrow CO_2 + Me_3C^{\bullet}$	C···C(O)−O	45.1	1.5	30.1

[a] In kJ mol^{-1}.

As can be seen from these data, the decomposition of $RCO_2^{\bullet}$ radical involves cleavage of only one bond and the formation of CO_2 [the total number of bonds involved in the rearrangement (n_b) is 1.5] and $E_{e0} = 45$ kJ mol^{-1}. Concerted decomposition of the peroxy ester involves cleavage of two bonds:



namely, C−C and O−O, and the formation of CO_2 (3 bonds being rearranged). Therefore, the activation energy of this thermally neutral decomposition is higher (E_{e0} = 96 kJ mol^{-1}). Decomposition of β,γ-unsaturated acids considered in this review is accompanied by rearrangements of five bonds, *viz*., the O−H and C−C bonds are cleaved, the C−H bond and CO_2 molecule are formed and the π-C=C bond migrates. The activation energy of such a thermally neutral decomposition is even higher (186.2 kJ mol^{-1}). As can be seen, the larger the number of bonds participating in the decarboxylation of a species the higher the activation barrier to thermally neutral decomposition. However, from the rightmost column it follows that the ratio of E_{e0} to the number of bonds being rearranged remains nearly constant and equal to 33.1 ± 2.9 kJ mol^{-1}. Thus, the three types of decarboxylation reactions are characterized by nearly the same activation barrier to thermally neutral decomposition calculated per reacting bond.

The MIP(2) method allows one to assess the activation energy distribution between two reaction centres in the TS of concerted molecular decomposition. This distribution is shown in Fig. 3 and presented in Tables 9, 11, 13, 15, 17 for individual reactions. But each reaction is characterized by its own enthalpy value. To compare the spectrum of activation energies of reactions from different classes, the activation energies should be normalized to the same enthalpy value (optimally, to $\Delta H_e = 0$). This can be done by comparing the results obtained using the MIP(1) and MIP(2) models. Namely, the former model allows one to calculate $E_{e0} = E_e$ (at $\Delta H_e = 0$) from experimental data [see Eqn (10)] while the latter helps to determine the spectrum of activation energies [see Eqn (16)]. For instance, concerted decomposition of linear alkenes is characterized by E_{e0} = 197.4 kJ mol^{-1}; hydrogen abstraction is characterized by $E_{e0(abs)}$ = 61.9 kJ mol^{-1} and cleavage of C−C bond is characterized by $E_{e0(d)}$ = 109.6 kJ mol^{-1}. Having compared

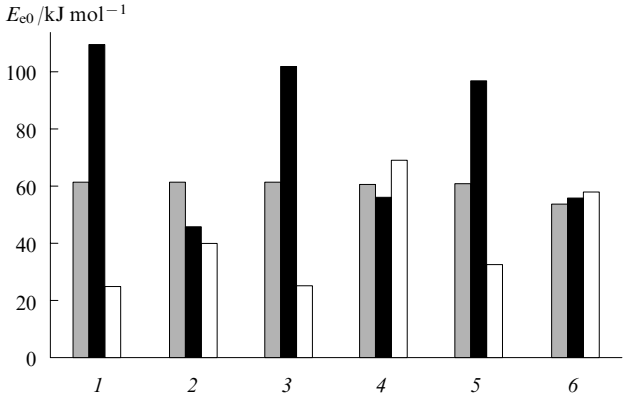


Figure 7. Activation spectra for thermally neutral reactions of concerted decomposition of alkenes (*1*), unsaturated alcohols (*2*), vinyl ethers (*3*), unsaturated acids (*4*), esters (*5*) and nitroalkanes (*6*).
Black column is $E_{e0(abs)}$, gray column is $E_{e0(d)}$ and white column is $E_{e0(\pi)}$.[8, 11]

E_{e0}[MIP(1)] with $E_{e0(abs)}$ and $E_{e0(d)}$, one gets [see Eqn (16)] $E_{e0(\pi)}$ = 25.9 kJ mol^{-1}. Figure 7 presents the spectrum of activation energies for six classes of concerted decomposition reactions.

The diagram shows that for five classes of concerted decomposition reactions, transfer of H atom between the C and C, C and O, or O and C atoms is characterized by nearly the same activation energy $E_{e0(abs)}$ = 61−62 kJ mol^{-1} (Ref. 8). Only for transfer of H atom from the C atom towards NO_2 group it is somewhat lower, *viz*., 54 kJ mol^{-1} (Ref. 8). The range of changes in $E_{e0(d)}$ is much wider, namely, E_{e0} = 110 (alkenes), 102 (vinyl ethers), 97 (esters), 56 (acids and nitroalkanes) and 46 kJ mol^{-1} (alcohols).[8] The $E_{e0(\pi)}$ values also vary over a wide range (kJ mol^{-1}), *viz*., $E_{e0(\pi)}$ = 26 (alkenes and vinyl ethers), 33 (esters), 41 (unsaturated alcohols), 58 (nitroalkanes) and 69 (unsaturated acids). The maximum E_{e0} value obtained using the MIP approach is 197 kJ mol^{-1}, being characteristic of the decomposition of alkeness. The minimum value (149 kJ mol^{-1}) is characteristic of the decomposition of unsaturated alcohols.

Summing up, by combining experimental research with calculations using the MIP(1) and MIP(2) models one can determine the kinetic parameters of molecular decomposition reactions and establish the factors affecting the activation energies of such reactions. These factors include the enthalpy of reaction, the inductive effect of substituents, the presence of aryl substituents near the reaction centre, steric hindranes and the effect of ring strain in the transition state. Using the two-centre model for concerted decomposition of different classes of organic compounds, the energy spectrum of the process was calculated and the contributions of the activation energies of H atom transfer, bond dissociation and π-bond migration to the overall activation of decomposition of each molecule were determined.

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