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Ester Decomposition as a Two-Center Synchronous Reaction

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Abstract—Experimental data on the molecular decomposition of esters with various structures into an olefin and the corresponding acid in the gas phase are analyzed in terms of the intersecting parabolas method. Enthalpies and kinetic parameters characterizing this decomposition have been calculated for 33 reactions. Ester decomposition is a concerted two-center reaction characterized by a very high classical potential barrier of thermoneutral reaction (148–206 kJ/mol). The totality of reactions examined is divided into eight classes. Activation energies and rate constants have been calculated for 38 reactions using the kinetic parameters obtained. The activation energies and rate constants of the reverse bimolecular reaction of acid addition to olefins have been calculated by the intersecting parabolas method. Factors in the activation energy of ester decomposition and formation reactions are discussed.

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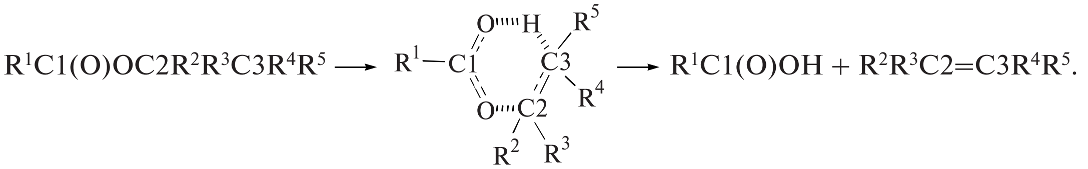
The cracking of organic compounds proceeds either as a chain reaction involving free radicals or via the decomposition of one molecule into two molecules or more [1, 2]. In our earlier works, we analyzed the decomposition of various radicals [3, 4] and the molecular decomposition of alcohols [5] and unsaturated acids [6] using the intersecting parabolas (IP) method [7–9] and determined the factors in the activation energy of these reactions. Here, we analyze experimental data concerning the decomposition of esters with various structures into an olefin and the corresponding acid. This decomposition is monomolecular, is not accompanied by the formation of free radicals, and is not accelerated by the wall of the reactor [2]. Experimental ester decomposition data are analyzed within the IP method [7–9]. Parameters describing the activation energy of the decomposition reactions as a function of their enthalpy are obtained and are used to calculate the activation energies and rate constants for the decomposition of esters with various structures and for the reverse bimolecular reactions of acid addition to olefins.

COMPUTATIONAL METHOD

Ester decomposition in the gas phase at $T \geq 500$ K proceeds monomolecularly by a concerted bond rearrangement via a six-membered transition state [2]:



$$R^1C1(O)OC2R^2R^3C3R^4R^5 \longrightarrow \quad \longrightarrow R^1C1(O)OH + R^2R^3C2{=}C3R^4R^5. \qquad \text{(I)}$$

The following changes take place in the transition state of this reaction: the C3–H and C2–O bonds break, an O–H bond forms, the π-C–O bond moves from the carbonyl oxygen to the ester oxygen, and the double bond C2=C3 forms. It was demonstrated earlier [10] that, within the IP method, the transition state can be viewed as the intersection of any pair of changing bonds. We will treat this decomposition reaction in terms of the intersection of the parabolic potential curves for the breaking C3–H bond in the ester and the forming O–H bond in the acid.

In the IP method, monomolecular ester decomposition is characterized by the following parameters [8, 9]:

(1) classical enthalpy (ΔH_e), which is related to the enthalpy of reaction (ΔH) as $\Delta H_e = \Delta H + \Delta\Delta H_e$, $\Delta\Delta H_e = 0.5hN_A(\nu_{C-H} - \nu_{O-H})$, where h is the Planck constant, N_A is Avogadro's number, and ν_{C-H} and ν_{O-H} are the stretching frequencies of the breaking and forming bonds;

(2) classical potential barrier E_e, which includes the activation energy of the reaction, the zero point energy of the breaking bond, and the mean kinetic energy of

Table 1. Kinetic parameters (k_{exp}, E, br_{e}) and ΔH of carboxylic acid ester decomposition reactions ($\alpha = 0.815$, $\Delta\Delta H_e = -3.8$ kJ/mol, $\Delta E_{\mathrm{e}} = 14.9$ kJ/mol, $A_1 = 3.2 \times 10^{12}\ \mathrm{s}^{-1}$, n is the number of equireactive bonds)

Reaction	T, K	n	k_{exp}(600 K), s^{-1}	E, kJ/mol	ΔH, kJ/mol	br_{e}^*	Reference
$\mathrm{MeCOOEt \longrightarrow CH_2{=}CH_2 + MeCOOH}$	782–884	3	1.21×10^{-5}	205.4	62.7	25.21	[14]
	648–697	3	8.78×10^{-6}	207.2	62.7	25.31	[15]
	679–737	3	9.91×10^{-6}	206.6	62.7	25.28	[16]
$\mathrm{MeCOOPr \longrightarrow MeCH{=}CH_2 + MeCOOH}$	650–700	2	9.67×10^{-6}	204.7	51.1	25.52	[17]
	725–810	2	1.06×10^{-5}	204.2	51.1	25.49	[18]
$\mathrm{MeCOOBu}^n \longrightarrow \mathrm{EtCH{=}CH_2 + MeCOOH}$	668–741	2	1.48×10^{-5}	202.6	52.1	25.35	[19]
$\mathrm{MeCOOCH_2Bu}^n \longrightarrow \mathrm{PrCH{=}CH_2 + MeCOOH}$	725–810	2	2.76×10^{-5}	199.5	51.7	25.16	[18]
$\mathrm{MeCOO(CH_2)_2CHMe_2 \longrightarrow CH_2{=}CHCHMe_2 + MeCOOH}$	660–712	2	1.22×10^{-5}	203.5	50.2	25.47	[20]
	633–693	2	1.26×10^{-5}	203.4	50.2	25.46	[21]
$\mathrm{MeCOO(CH_2)_2Ph \longrightarrow CH_2{=}CHPh + MeCOOH}$	642–702	2	6.25×10^{-5}	195.4	44.6	25.11	[17]
	616–682	2	6.09×10^{-5}	195.5	44.6	25.12	[22]
$\mathrm{HCOOEt \longrightarrow CH_2{=}CH_2 + HCOOH}$	810–920	3	1.77×10^{-5}	203.7	58.6	25.22	[14]
$\mathrm{EtCOOEt \longrightarrow CH_2{=}CH_2 + EtCOOH}$	913–1100	3	1.12×10^{-5}	206.0	60.1	25.32	[23]
$\mathrm{PrCOOEt \longrightarrow CH_2{=}CH_2 + PrCOOH}$	633–693	3	1.28×10^{-5}	205.3	65.0	25.12	[24]
$\mathrm{PhCH_2COOEt \longrightarrow CH_2{=}CH_2 + PhCH_2COOH}$	650–700	3	1.57×10^{-5}	204.3	63.2	25.09	[25]
						$br_{\mathrm{e}} = 25.28 \pm 0.14$	
$\mathrm{MeCOOCH_2CHMe_2 \longrightarrow CH_2{=}CMe_2 + MeCOOH}$	725–810	1	4.98×10^{-6}	204.5	42.4	25.77	[18]
$\mathrm{MeCOOCH_2CHMeEt \longrightarrow CH_2{=}CMeEt + MeCOOH}$	725–810	1	2.89×10^{-6}	207.3	42.5	25.95	[18]
$\mathrm{MeCOO(CH_2)_2OMe \longrightarrow CH_2{=}CHOMe + MeCOOH}$	653–708	2	2.01×10^{-6}	212.5	46.2	26.16	[26]
	825–810	2	1.76×10^{-6}	213.2	46.2	26.21	[18]
$\mathrm{MeCOO(CH_2)_2OEt \longrightarrow CH_2{=}CHOEt + MeCOOH}$	725–810	2	2.19×10^{-6}	212.1	46.3	26.14	[18]
						$br_{\mathrm{e}} = 26.05 \pm 0.16$	
$\mathrm{MeCOOCHMe_2 \longrightarrow CH_2{=}CHMe + MeCOOH}$	609–668	6	3.58×10^{-4}	192.2	68.3	24.12	[27]
$\mathrm{MeCOOCHMeEt \longrightarrow CH_2{=}CHEt + MeCOOH}$	600	3	1.44×10^{-4}	193.2	68.9	24.17	[2]
$\mathrm{MeCOOCHMePr \longrightarrow CH_2{=}CHPr + MeCOOH}$	600	3	3.98×10^{-4}	188.2	68.3	23.85	[2]
$\mathrm{MeCOOCHMeCHMeEt \longrightarrow CH_2{=}CHCHMeEt + MeCOOH}$	600	3	5.89×10^{-4}	186.2	63.9	23.86	[2]
$\mathrm{MeCOOCHMeCH_2Bu \longrightarrow CH_2{=}CHCH_2Bu + MeCOOH}$	600	3	6.03×10^{-4}	186.1	68.3	23.70	[2]
$\mathrm{MeCOOCHMeCH_2Bu \longrightarrow MeCH{=}CHBu + MeCOOH}$	600	2	2.81×10^{-4}	187.9	68.3	23.83	[2]
$\mathrm{MeCOOCHEtBu \longrightarrow EtCH{=}CHPr + MeCOOH}$	600	2	5.01×10^{-4}	185.0	56.9	24.01	[2]
$\mathrm{MeCOOCHEtBu \longrightarrow MeCH{=}CHBu + MeCOOH}$	600	2	5.62×10^{-4}	184.4	56.7	23.98	[2]
$\mathrm{MeCOOCHMeCH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH_2CH{=}CH_2 + MeCOOH}$	600	3	2.51×10^{-4}	190.4	70.0	23.94	[2]

Table 1. (Contd.)

Reaction	T, K	n	k_{exp}(600 K), s^{-1}	E, kJ/mol	ΔH, kJ/mol	br_{e}^{*}	Reference
$MeCOO\text{-}(cyclo\text{-}C_6H_{11}) \longrightarrow \text{-}(cyclo\text{-}C_6H_{10}) + MeCOOH$	623–773	2	7.67×10^{-4}	182.9	56.8	23.87	[28]
$MeCOOCHMeCH_2C(O)Me \longrightarrow MeC(O)CH{=}CHMe + MeCOOH$	529–570	2	1.79×10^{-2}	167.2	25.7	23.81	[29]
$MeCOOCHMeCH_2NMe_2 \longrightarrow CH_2{=}CHCH_2NMe_2 + MeCOOH$	600	3	3.23×10^{-4}	189.2	67.1	23.96	[2]
$MeCOOCHMePh \longrightarrow CH_2{=}CHPh + MeCOOH$	585–641	3	3.02×10^{-4}	189.5	71.8	23.82	[22]
$MeCOOCHPhCH_2Ph \longrightarrow PhCH{=}CHPh + MeCOOH$	575–625	2	1.87×10^{-3}	178.4	46.2	23.91	[30]
$EtCOOCHMe_2 \longrightarrow MeCH{=}CH_2 + EtCOOH$	563–623	6	3.37×10^{-4}	192.5	69.4	24.11	[31]
						$br_{\mathrm{e}} = 23.93 \pm 0.13$	
$MeCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + MeCOOH$	516–576	9	3.83×10^{-2}	170.9	71.2	22.50	[32]
	514–564	9	3.76×10^{-2}	171.0	71.2	22.51	[33]
$MeCOOCMe_2Et \longrightarrow CH_2{=}CMeEt + MeCOOH$	600	6	3.98×10^{-2}	168.7	59.2	22.78	[2]
$MeCOOCMe_2Et \longrightarrow MeCH{=}CMe_2 + MeCOOH$	600	2	1.41×10^{-2}	168.4	67.0	22.47	[2]
$HCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + HCOOH$	503–573	9	3.1×10^{-2}	171.9	72.3	22.53	[34]
$EtCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + EtCOOH$	543–620	9	3.64×10^{-2}	171.1	72.3	22.47	[27]
$PrCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + PrCOOH$	513–563	9	3.16×10^{-2}	171.8	72.3	22.52	[35]
						$br_{\mathrm{e}} = 22.54 \pm 0.10$	

* $(\mathrm{kJ/mol})^{1/2}$.

the particle and is related to the experimentally determinable activation energy as $E_{\mathrm{e}} = E + \Delta E_{\mathrm{e}}$, $\Delta E_{\mathrm{e}} = 0.5hN_{\mathrm{A}}\nu_{\mathrm{C-H}} - 0.5RT$, where R is the gas constant and T is temperature (K);

(3) parameter r_{e}, which is the total extension of the two reacting bonds (C–H and O–H) in the transition state;

(4) parameter b ($2b^2$ is the force constant of the breaking bond), b_{f} ($2b_{\mathrm{f}}^2$ is the force constant of the forming bond), and coefficient $\alpha = b/b_{\mathrm{f}}$;

(5) activation energy E from the Arrhenius equation, $E = RT(\ln nA/k)$, where A is the empirical preexponential factor, which is constant for reactions of a given class, k is the empirical rate constant, and n is the number of equireactive C–H bonds involved in the rearrangement.

These parameters are interrelated by the following expression [7, 8]:

$$br_{\mathrm{e}} = \alpha(E_{\mathrm{e}} - \Delta H_{\mathrm{e}})^{1/2} + E_{\mathrm{e}}^{1/2}. \qquad (1)$$

The parameter br_{e} characterizes the classical potential barrier of thermoneutral reaction ($E_{\mathrm{e,\,0}}$) for a class of reactions with $r_{\mathrm{e}} = \mathrm{const}$ and $b = \mathrm{const}$ [8]:

$$E_{\mathrm{e,\,0}} = (br_{\mathrm{e}})^2/(1 + \alpha)^2. \qquad (2)$$

Provided that α and br_{e} are known, the activation energy of each particular reaction of this class can be calculated using the following formula [9]:

$$E_{\mathrm{e}} = B^2\{1 - \alpha(1 - \Delta H_{\mathrm{e}}/Bbr_{\mathrm{e}})^{1/2}\}^2, \qquad (3)$$

where $B = br_{\mathrm{e}}(1 - \alpha^2)^{-1}$. This equation is valid when the following relationship is true for the reaction examined: $\Delta H_{\mathrm{e,\,min}} < \Delta H_{\mathrm{e}} < \Delta H_{\mathrm{e,\,max}}$. The $\Delta H_{\mathrm{e,\,max}}$ and $\Delta H_{\mathrm{e,\,min}}$ values are calculated using the formulas [9]

$$\begin{aligned}\Delta H_{\mathrm{e,\,max}} &= (br_{\mathrm{e}})^2 - 2\alpha br_{\mathrm{e}}(0.5hN_{\mathrm{A}}\nu_{\mathrm{O-H}})^{1/2} \\ &\quad + 0.5(\alpha^2 - 1)hN_{\mathrm{A}}\nu_{\mathrm{O-H}},\end{aligned} \qquad (4)$$

$$\begin{aligned}\Delta H_{\mathrm{e,\,min}} &= -(br_{\mathrm{e}}/\alpha)^2 + 2br_{\mathrm{e}}\alpha^{-2}(0.5hN_{\mathrm{A}}\nu_{\mathrm{C-H}})^{1/2} \\ &\quad - 0.5(1 - \alpha^2)hN_{\mathrm{A}}\nu_{\mathrm{C-H}}.\end{aligned} \qquad (5)$$

Ester decomposition is a reaction in which certain bonds break and others form in a concerted way. In such reactions, the preexponential factor A in the Arrhenius expression for the rate constant depends on the activation energy of decomposition and on the number of simultaneously breaking bonds (m). According to the oscillation model of concerted decomposition, this dependence is described by the following formula [11]:

$$A = A_0 \times (m/2^{(m-1)})(mRT/\pi E)^{(m-1)/2}. \qquad (6)$$

Table 2. Kinetic parameters (k_{exp}, E, br_e) and ΔH of the decomposition reactions of benzoic acid esters and chlorosubstituted esters ($\alpha = 0.815$, $\Delta\Delta H_e = -3.8$ kJ/mol, $\Delta E_e = 14.9$ kJ/mol, $A_1 = 3.2 \times 10^{12}$ s^{-1}, n is the number of equireactive bonds)

Reaction	T, K	n	k_{exp}(600 K), s^{-1}	E, kJ/mol	ΔH, kJ/mol	br_e^*	Reference
$PhCOOEt \longrightarrow CH_2{=}CH_2 + PhCOOH$	641–688	3	9.90×10^{-6}	206.6	80.5	24.69	[36]
	650–700	3	2.10×10^{-5}	202.3	80.5	24.40	[25]
						$br_e = 24.55 \pm 0.15$	
$PhCOOCHMe_2 \longrightarrow MeCH{=}CH_2 + PhCOOH$	633–689	6	7.49×10^{-4}	188.4	77.7	23.53	[37]
	592–650	6	7.49×10^{-4}	188.4	77.7	23.53	[36]
						$br_e = 23.53$	
$PhCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + PhCOOH$	544–600	9	9.73×10^{-2}	166.2	72.3	22.11	[25]
						$br_e = 22.11$	
$MeCOOCHMeCH_2Cl \longrightarrow ClCH{=}CHMe + MeCOOH$	600	2	2.23×10^{-5}	200.5	63.8	24.84	[2]
$MeCOOCHMeCH_2Cl \longrightarrow CH_2{=}CHCH_2Cl + MeCOOH$	650–710	3	4.52×10^{-5}	199.0	70.5	24.51	[18]
						$br_e = 24.67 \pm 0.17$	

* (kJ/mol)$^{1/2}$.

Three bonds are involved in the reactions considered here: two bonds (C–H and C–O) break and a new one (π–C–C) appears. The equation for the rate constant of ester decomposition (concerted reaction involving three bonds, $m = 3$) is written as

$$k = nA_0(9RT/4\pi E)\exp(-E/RT). \qquad (7)$$

The kinetic parameters for the decomposition of unsaturated acids of various structures were calculated in the following order. The enthalpy of decomposition of an acid (ΔH) was determined as the sum of the standard enthalpies of formation of the reaction products minus the standard enthalpy of formation of the initial ester. Enthalpy data were taken from [12]. For some compounds, ΔH_f^0 was calculated using enthalpy increments [12, 13]. Since the decomposition reactions were studied at $T = 600$ K, we applied a correction for the temperature variation of the enthalpy of reaction. For ethyl acetate decomposition, this correction was –1.1 kJ/mol.

$$\Delta H = \Delta H_f^0(R^1C1(O)OH) + \Delta H_f^0(R^2R^3C2 = C3R^4R^5) - \Delta H_f^0(R^1C1(O)OC2R^2R^3C3R^4R^5) - 1.1. \qquad (8)$$

Experimental activation energy (E) data for ester decomposition were acquired using the Arrhenius formula with the preexponential factor for gas-phase ester decomposition ($A = 3.2 \times 10^{12}$ s^{-1}, determined by averaging experimental A values) and experimental rate constant (k) values [14–37]. Next, the parameter br_e for ester decomposition was calculated using formula (1). In doing this, we used parameters derived from spectroscopic data: $\alpha = 0.815$; the values of b and $0.5hN_A\nu$ are given below.

Bond	$b \times 10^{-10}$, (kJ/mol)$^{1/2}$ m^{-1}	$0.5hN_A\nu$, kJ/mol
C–H	37.47	17.4
O–H (acid)	46.01	21.2

RESULTS AND DISCUSSION

Ester Decomposition

The calculated E, ΔH, and br_e data for the decomposition of carboxylic acid esters in the gas phase are listed in Table 1, and the same data for benzoic acid esters and chlorosubstituted esters are presented in Table 2.

As is clear from Tables 1 and 2, ester decomposition into an acid and olefin is an endothermic process ($\Delta H > 0$, ΔH range from 26 to 80 kJ/mol) and has a very high activation energy of 166 to 213 kJ/mol. The decomposition rate constants vary between 9.7×10^{-2} and 1.8×10^{-6} s^{-1} ($T = 600$ K). This wide variation of the kinetic parameters is due to the structural diversity of the decomposing esters. A comparison of br_e values (Tables 1, 2) suggests that the ester decomposition reactions can be divided into eight classes, each consisting of reactions of structurally similar esters with br_e = const. Each class of compounds is characterized by a certain value of the classical potential barrier of

Table 3. Kinetic parameters of ester decomposition via the reaction $R^1C1(O)OC2R^2R^3C3HR^4R^5 \longrightarrow R^1C1(O)OH + R^2R^3C2{=}C3R^4R^5$

Ester	br_e, $(kJ/mol)^{-1/2}$	$-\Delta H_{e,\,min}$,	$\Delta H_{e,\,max}$,	$E_{e,\,0}$,	$\Delta E_{e,\,0}$,	$r_e \times 10^{10}$, m
		kJ/mol				
R^1 = H, alkyl, $R^2 = R^3 = R^4$ = H, R^5 = H, alkyl, Ph	25.28 ± 0.14	650.5	442.1	194.0 ± 2.2	0.0	0.675
R^1 = H, alkyl, $R^2 = R^3$ = H; $R^4 = R^5$ = alkyl; or R^4 = H, R^5 = OR	26.05 ± 0.16	700.3	476.2	206.0 ± 2.5	12.0	0.696
R^1 = H, alkyl, R^2 = H, R^3 = alkyl, Ph, CH_2NMe_2, $CH_2CH{=}CH_2$ R^4 = H, R^5 = H, alkyl, Ph	23.93 ± 0.13	567.4	386.1	173.8 ± 1.9	−20.2	0.639
R^1 = H, alkyl; $R^2 = R^3$ = alkyl; $R^4 = R^5$ = H; or R^4 = H, R^5 = alkyl	22.54 ± 0.10	487.6	331.9	154.2 ± 1.4	−39.8	0.602
$MeCOOCHMeCH_2Cl$	24.67 ± 0.17	612.3	416.5	184.8 ± 2.5	−9.2	0.659
R^1 = Ph, $R^2 = R^3 = R^4$ = H, R^5 = H	24.55 ± 0.15	604.9	411.5	183.0 ± 2.2	−11.0	0.656
R^1 = Ph, R^2 = R, $R^3 = R^4 = R^5$ = H	23.53	543.9	370.1	168.1	−25.9	0.629
$PhCOOCMe_3$	22.11	464.1	315.9	148.4	−45.6	0.591

thermoneutral reaction, $E_{e,\,0}$, and a certain r_e value (Table 3).

It is clear from Table 3 that, even under thermoneutral conditions ($\Delta H_e = 0$), ester decomposition is characterized by a very high classical potential barrier ($E_{e,\,0}$ = 148–206 kJ/mol). The variation of the barrier is likely due to the presence of substituents at the C2 and C3 atoms in the six-membered transition state and their mutual influence.

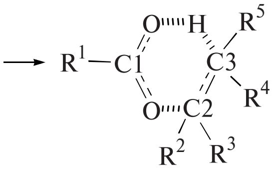
Comparison with Experimental Data

The br_e values derived from experimental data for the decomposition of four classes of esters were used to calculate the activation energies E (Eq. (3)) and rate constants k (Eq. (7)) for the reactions of particular esters from these classes. The preexponential factor A_0 was calculated using Eq. (6) with E = 187 kJ/mol (average activation energy of ester decomposition) and $A = 3.2 \times 10^{12}$ s^{-1}. From Eq. (6), we obtained $A_0 = 1.67 \times 10^{14}$ s^{-1} (Table 4). Kinetic parameters were calculated for ester decomposition reactions described in the literature and for those which were not studied before. The calculated E and k data are listed in Table 4. Comparison with experimental data demonstrated that the mean value of $\Delta E = |E_{calc} - E_{exp}| = 1.5 \pm 1.1$ kJ/mol (Table 4); that is, the calculated and experimental data are in good agreement.

Acid Addition to Alkenes

The reverse of ester decomposition (I) is acid addition to an alkene (II). The latter proceeds via the same six-membered transition state as ester decomposition.

$$R^1C1(O)OH + R^2R^3C2{=}C3R^4R^5$$



$$\longrightarrow R^1C1(O)OC2R^2R^3C3R^4R^5. \qquad \text{(II)}$$

There are no kinetic data for these reactions in the literature. We used kinetic parameters obtained for ester decomposition (I) by the IP method (Table 4) to calculate kinetic parameters for a number of reactions of ester formation through acid addition to an alkene (reaction (II)). The ester decomposition reactions are endothermic (see above); therefore, the reverse reactions—ester formation—are exothermic, so $\Delta H_{II} = -\Delta H_I$ and $E_{II} = E_I - \Delta H_I$. The addition of olefins to acids is characterized in the IP method by the parameters $\alpha = 1.227$, $b = 46.01$ (kJ/mol)$^{1/2}$ m^{-1}, and $0.5hN_A\nu_{O-H} = 21.2$ kJ/mol. To calculate the standard preexponential factor for acid addition to an alkene (A_{II}), we used the equilibrium constant equation from [38], from which we obtained $A_{0,\,II} = A_{0,\,I}/e^{\Delta S_I/R}$. The value of $\Delta S = 139.6$ J mol^{-1} K^{-1} was calculated for the reaction $CH_3C(O)OC_2H_5 \rightleftharpoons CH_2{=}CH_2 + CH_3COOH$ using the equation

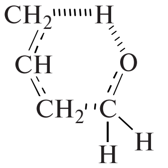
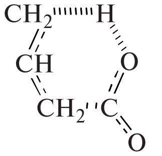
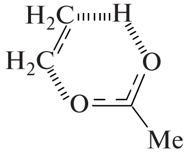
Table 4. ΔH and kinetic parameters (k, E, $|\Delta E|$) of the decomposition reactions of the esters of various acids, calculated by the IP method ($\alpha = 0.815$, $\Delta\Delta H_e = -3.8$ kJ/mol, $\Delta E_e = 14.9$ kJ/mol, $A_0 = 1.67 \times 10^{14}$ s^{-1})

Reaction	ΔH,	E,	$\lvert\Delta E\rvert$,	k(600 K), s^{-1}	$\Delta E_e/\Delta H_e$
	kJ/mol				
$br_e = 25.28$ (kJ/mol)$^{1/2}$					
$MeCOOEt \longrightarrow CH_2{=}CH_2 + MeCOOH$	62.7	206.7	0.1	8.75×10^{-6}	0.47
$MeCOOPr \longrightarrow MeCH{=}CH_2 + MeCOOH$	51.1	201.1	3.1	1.84×10^{-5}	0.46
$MeCOOBu^n \longrightarrow EtCH{=}CH_2 + MeCOOH$	52.1	201.5	1.1	1.70×10^{-5}	0.46
$MeCOOCH_2Bu^n \longrightarrow PrCH{=}CH_2 + MeCOOH$	51.7	201.3	1.8	1.77×10^{-5}	0.47
$MeCOO(CH_2)_2CHMe_2 \longrightarrow CH_2{=}CHCHMe_2 + MeCOOH$	50.2	200.6	2.9	2.04×10^{-5}	0.46
$MeCOO(CH_2)_2Ph \longrightarrow CH_2{=}CHPh + MeCOOH$	44.6	197.9	2.4	3.56×10^{-5}	0.46
$EtCOOEt \longrightarrow CH_2{=}CH_2 + EtCOOH$	60.1	205.4	0.6	1.14×10^{-5}	0.47
$PrCOOEt \longrightarrow CH_2{=}CH_2 + PrCOOH$	65.0	207.8	2.5	6.98×10^{-6}	0.47
$PhCH_2COOEt \longrightarrow CH_2{=}CH_2 + PhCH_2COOH$	63.2	206.9	2.1	8.40×10^{-6}	0.47
$HCOOEt \longrightarrow CH_2{=}CH_2 + HCOOH$	58.6	204.7	1.0	1.32×10^{-5}	0.47
$br_e = 26.05$ (kJ/mol)$^{1/2}$					
$MeCOOCH_2CHMe_2 \longrightarrow CH_2{=}CMe_2 + MeCOOH$	42.4	208.9	4.4	1.86×10^{-6}	0.46
$MeCOOCH_2CHMeEt \longrightarrow CH_2{=}CMeEt + MeCOOH$	42.5	208.9	1.6	1.86×10^{-6}	0.46
$MeCOO(CH_2)_2OMe \longrightarrow CH_2{=}CHOMe + MeCOOH$	46.2	210.7	1.8	2.57×10^{-6}	0.46
$MeCOO(CH_2)_2OEt \longrightarrow CH_2{=}CHOEt + MeCOOH$	46.3	210.7	1.4	2.57×10^{-6}	0.46
$br_e = 23.93$ (kJ/mol)$^{1/2}$					
$MeCOOCHMe_2 \longrightarrow CH_2{=}CHMe + MeCOOH$	68.3	189.4	2.8	6.13×10^{-4}	0.47
$MeCOOCHMeEt \longrightarrow CH_2{=}CHEt + MeCOOH$	68.9	189.7	3.5	2.88×10^{-4}	0.47
$MeCOOCHMePr \longrightarrow CH_2{=}CHPr + MeCOOH$	68.3	189.7	4.2	3.06×10^{-4}	0.47
$MeCOOCHMeCHMeEt \longrightarrow CH_2{=}CHCHMeEt + MeCOOH$	63.9	187.2	1.0	4.82×10^{-4}	0.47
$MeCOOCHMeCH_2Bu \longrightarrow MeCH{=}CHBu + MeCOOH$	68.3	189.4	1.5	2.04×10^{-4}	0.47
$MeCOOCHEtBu \longrightarrow EtCH{=}CHPr + MeCOOH$	56.9	183.8	1.2	6.46×10^{-4}	0.46
$MeCOOCHEtBu \longrightarrow MeCH{=}CHBu + MeCOOH$	56.7	183.7	0.7	6.60×10^{-4}	0.46
$MeCOOCHPr_2 \longrightarrow EtCH{=}CHPr + MeCOOH$	57.0	183.8		1.29×10^{-4}	0.46
$MeCOOCHMeCH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH_2CH{=}CH_2 + MeCOOH$	70.0	190.2	0.2	2.60×10^{-4}	0.47
$MeCOO\text{-}(\textit{cyclo}\text{-}C_6H_{11}) \longrightarrow \textit{cyclo}\text{-}C_6H_{10} + MeCOOH$	56.8	183.7	0.8	6.49×10^{-4}	0.47
$MeCOOCHMeCH_2NMe_2 \longrightarrow CH_2{=}CHCH_2NMe_2 + MeCOOH$	67.1	188.8	0.4	3.47×10^{-4}	0.47
$MeCOOCHMePh \longrightarrow CH_2{=}CHPh + MeCOOH$	71.8	191.1	1.6	2.16×10^{-4}	0.47
$MeCOOCHPhCH_2Ph \longrightarrow PhCH{=}CHPh + MeCOOH$	46.2	178.6	0.2	1.89×10^{-3}	0.46
$EtCOOCHMe_2 \longrightarrow MeCH{=}CH_2 + EtCOOH$	69.4	189.9	2.6	5.52×10^{-4}	0.47
$PrCOOCHMe_2 \longrightarrow MeCH{=}CH_2 + PrCOOH$	68.4	189.5		6.00×10^{-4}	0.47
$HCOOCHMe_2 \longrightarrow MeCH{=}CH_2 + HCOOH$	68.5	189.5		6.00×10^{-4}	0.46
$br_e = 22.54$ (kJ/mol)$^{1/2}$					
$MeCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + MeCOOH$	71.2	171.5	0.6	3.07×10^{-2}	0.46
$MeCOOCMe_2Et \longrightarrow CH_2{=}CMeEt + MeCOOH$	59.2	165.5	3.2	8.44×10^{-2}	0.46
$MeCOOCMe_2Et \longrightarrow MeCH{=}CMe_2 + MeCOOH$	67.0	169.3	0.9	1.28×10^{-2}	0.46
$MeCOOCMeEt_2 \longrightarrow MeCH{=}CMeEt + MeCOOH$	67.4	169.5		2.47×10^{-2}	0.46
$MeCOOCMeEt_2 \longrightarrow CH_2{=}CEt_2 + MeCOOH$	77.0	174.4		6.73×10^{-3}	0.46
$EtCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + EtCOOH$	72.3	172.0	0.9	3.31×10^{-2}	0.46
$PrCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + PrCOOH$	72.3	172.0	0.2	3.31×10^{-2}	0.46
$HCOOCMe_3 \longrightarrow CH_2{=}CMe_2 + HCOOH$	72.3	172.0	0.1	3.31×10^{-2}	0.46
$\lvert\Delta E\rvert = 1.5 \pm 1.1$					

Table 5. Kinetic parameters (k, E) and ΔH of acid addition to olefins ($\alpha = 1.227$, $\Delta\Delta H_e = 3.8$ kJ/mol, $\Delta E_e = 18.7$ kJ/mol, $A_0 = 8.5 \times 10^6$ $\mathrm{l\ mol^{-1}\ s^{-1}}$)

Reaction	$-\Delta H$, kJ/mol	E, kJ/mol	k(600 K), $\mathrm{l\ mol^{-1}\ s^{-1}}$
$br_e = 31.02\ (\mathrm{kJ/mol})^{1/2}$			
$\mathrm{CH_2{=}CH_2 + MeCOOH \longrightarrow MeCOOEt}$	62.7	144.0	6.13×10^{-8}
$\mathrm{MeCH{=}CH_2 + MeCOOH \longrightarrow MeCOOPr}$	51.1	150.0	1.77×10^{-8}
$\mathrm{EtCH{=}CH_2 + MeCOOH \longrightarrow MeCOOBu^{\mathit{n}}}$	52.1	149.4	2.00×10^{-8}
$\mathrm{PrCH{=}CH_2 + MeCOOH \longrightarrow MeCOOCH_2Bu^{\mathit{n}}}$	51.7	149.6	1.92×10^{-8}
$\mathrm{CH_2{=}CHCHMe_2 + MeCOOH \longrightarrow MeCOO(CH_2)_2CHMe_2}$	50.2	150.4	1.63×10^{-8}
$\mathrm{CH_2{=}CHPh + MeCOOH \longrightarrow MeCOO(CH_2)_2Ph}$	44.6	153.3	8.93×10^{-9}
$\mathrm{CH_2{=}CH_2 + EtCOOH \longrightarrow EtCOOEt}$	60.1	145.3	4.74×10^{-8}
$\mathrm{CH_2{=}CH_2 + PrCOOH \longrightarrow PrCOOEt}$	65.0	142.8	7.86×10^{-8}
$\mathrm{CH_2{=}CH_2 + PhCH_2COOH \longrightarrow PhCH_2COOEt}$	63.2	143.7	6.52×10^{-8}
$\mathrm{CH_2{=}CH_2 + HCOOH \longrightarrow HCOOEt}$	58.6	146.1	3.97×10^{-8}
$br_e = 31.96\ (\mathrm{kJ/mol})^{1/2}$			
$\mathrm{CH_2{=}CMe_2 + MeCOOH \longrightarrow MeCOOCH_2CHMe_2}$	42.4	166.5	5.83×10^{-10}
$\mathrm{CH_2{=}CMeEt + MeCOOH \longrightarrow MeCOOCH_2CHMeEt}$	42.5	166.4	5.95×10^{-10}
$\mathrm{CH_2{=}CHOMe + MeCOOH \longrightarrow MeCOO(CH_2)_2OMe}$	46.2	164.5	8.81×10^{-10}
$\mathrm{CH_2{=}CHOEt + MeCOOH \longrightarrow MeCOO(CH_2)_2OEt}$	46.3	164.4	8.99×10^{-10}
$br_e = 29.36\ (\mathrm{kJ/mol})^{1/2}$			
$\mathrm{CH_2{=}CHMe + MeCOOH \longrightarrow MeCOOCHMe_2}$	68.3	121.1	7.18×10^{-6}
$\mathrm{CH_2{=}CHEt + MeCOOH \longrightarrow MeCOOCHMeEt}$	68.9	120.8	7.65×10^{-6}
$\mathrm{CH_2{=}CHPr + MeCOOH \longrightarrow MeCOOCHMePr}$	68.3	121.1	7.18×10^{-6}
$\mathrm{CH_2{=}CHCHMeEt + MeCOOH \longrightarrow MeCOOCHMeCHMeEt}$	63.9	123.3	4.54×10^{-6}
$\mathrm{MeCH{=}CHBu + MeCOOH \longrightarrow MeCOOCHMeCH_2Bu}$	68.3	121.1	7.18×10^{-6}
$\mathrm{EtCH{=}CHPr + MeCOOH \longrightarrow MeCOOCHEtBu}$	56.9	126.9	2.14×10^{-6}
$\mathrm{MeCH{=}CHBu + MeCOOH \longrightarrow MeCOOCHEtBu}$	56.7	127.0	2.00×10^{-6}
$\mathrm{MeCH{=}CHPr + MeCOOH \longrightarrow MeCOOCHEtPr}$	57.0	126.8	2.19×10^{-6}
$\mathrm{CH_2{=}CHCH_2CH{=}CH_2 + MeCOOH \longrightarrow MeCOOCHMeCH_2CH{=}CH_2}$	70.0	120.2	8.67×10^{-6}
cyclo-$\mathrm{C_6H_{10} + MeCOOH \longrightarrow MeCOO\text{-}(}$*cyclo*-$\mathrm{C_6H_{11})}$	56.8	126.9	2.14×10^{-6}
$\mathrm{CH_2{=}CHCH_2NMe_2 + MeCOOH \longrightarrow MeCOOCHMeCH_2NMe_2}$	67.1	121.7	6.34×10^{-6}
$\mathrm{CH_2{=}CHPh + MeCOOH \longrightarrow MeCOOCHMePh}$	71.8	119.3	1.05×10^{-5}
$\mathrm{PhCH{=}CHPh + MeCOOH \longrightarrow MeCOOCHPhCH_2Ph}$	46.2	132.4	6.82×10^{-7}
$\mathrm{MeCH{=}CH_2 + EtCOOH \longrightarrow EtCOOCHMe_2}$	69.4	120.5	8.14×10^{-6}
$\mathrm{MeCH{=}CH_2 + PrCOOH \longrightarrow PrCOOCHMe_2}$	68.4	121.1	7.18×10^{-6}
$\mathrm{MeCH{=}CH_2 + HCOOH \longrightarrow HCOOCHMe_2}$	68.5	121.0	7.34×10^{-6}
$br_e = 27.66\ (\mathrm{kJ/mol})^{1/2}$			
$\mathrm{CH_2{=}CMe_2 + MeCOOH \longrightarrow MeCOOCMe_3}$	71.2	100.3	5.61×10^{-4}
$\mathrm{CH_2{=}CMeEt + MeCOOH \longrightarrow MeCOOCMe_2Et}$	59.2	106.3	1.59×10^{-4}
$\mathrm{MeCH{=}CMe_2 + MeCOOH \longrightarrow MeCOOCMe_2Et}$	67.0	102.3	3.68×10^{-4}
$\mathrm{MeCH{=}CMeEt + MeCOOH \longrightarrow MeCOOCMeEt_2}$	67.4	102.1	3.84×10^{-4}
$\mathrm{CH_2{=}CEt_2 + MeCOOH \longrightarrow MeCOOCMeEt_2}$	77.0	97.4	1.03×10^{-3}
$\mathrm{CH_2{=}CMe_2 + EtCOOH \longrightarrow EtCOOCMe_3}$	72.3	99.7	6.37×10^{-4}
$\mathrm{CH_2{=}CMe_2 + PrCOOH \longrightarrow PrCOOCMe_3}$	72.3	99.7	6.37×10^{-4}
$\mathrm{CH_2{=}CMe_2 + HCOOH \longrightarrow HCOOCMe_3}$	72.3	99.7	6.37×10^{-4}

Table 6. Classical potential barrier $E_{e,0}$ for various classes of decomposition reactions of molecules and radicals

Reaction	Transition state	$E_{e,0}$, kJ/mol	Reference
$CH_2{=}CHCH_2CH_2OH \longrightarrow CH_3CH{=}CH_2 + CH_2(O)$		152	[5]
$CH_2{=}CHCH_2C(O)OH \longrightarrow CH_3CH{=}CH_2 + CO_2$		173	[6]
$CH_3C(O)OCH_2CH_3 \longrightarrow CH_2{=}CH_2 + CH_3COOH$		194	This work
$CH_3CH_2O^{\bullet} \longrightarrow C^{\bullet}H_3 + CH_2(O)$	$\mathrm{C{-}\,{-}C\overset{---}{=}O}$	65	[4]
$CH_3C^{\bullet}(O) \longrightarrow C^{\bullet}H_3 + C{\equiv}O$	$\mathrm{C{-}\,{-}C\overset{---}{=}O}$	62	[39]
$CH_3OC^{\bullet}(O) \longrightarrow C^{\bullet}H_3 + CO_2$	$\mathrm{C{-}\,{-}O\overset{---}{=}\dot{C}\overset{---}{=}O}$	68	[40]
$RCO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2$	$\mathrm{C{-}\,{-}O\overset{---}{=}\dot{C}\overset{---}{=}O}$	45	[40]
$ROCH_2CH_2^{\bullet} \longrightarrow RO^{\bullet} + CH_2{=}CH_2$	O...C–C	88	[42]
$Me_2C(O^{\bullet})(CH_2)_3R \longrightarrow Me_2C(OH)(CH_2)_2C^{\bullet}HR$	O...H...C	53	[43]
$CH_3O^{\bullet} + CH_3CH_3 \longrightarrow CH_3OH + CH_3C^{\bullet}H_2$	O...H...C	55	[8]

ΔS(reaction) = S^0(products) – S^0(ester). The resulting value of $A_{II,0} = 8.5 \times 10^6$ l mol^{-1} s^{-1} was used to calculate the rate constants of ester formation reactions (k; see Eq. (7)). The calculated enthalpies (ΔH), activation energies (E), and rate constants (k, 600 K) are listed in Table 5.

As is clear from Table 5, acid additions to alkenes are characterized by a high activation energy (E_{II} = 97–166 kJ/mol). The rate constants of these reactions vary between 5.8×10^{-10} and 1.0×10^{-3} l mol^{-1} s^{-1}. The $E_{e,0}$ values determined by the IP method for ester decomposition (Table 3) characterize the corresponding reverse reactions of ester formation under thermoneutral conditions as well (Table 5).

Factors in the Activation Barrier of Ester Decomposition

Enthalpy of reaction. Within each particular class of ester decomposition reactions, the higher the enthalpy of reaction the higher the activation energy (Tables 1–3). The following inequality is true for these reactions: $\Delta H_e \ll (br_e)^2/(1 - \alpha^2) \approx 2000$ kJ/mol. This makes it possible to represent E_e as a function of ΔH_e (Eq. (3)) as follows:

$$E_e = E_{e,0} + \{\alpha/(1+\alpha)\}\Delta H_e + \{\alpha/2(br_e)\}^2\Delta H_e^2. \quad (9)$$

Hence, we obtain the following formula for the $\Delta E_e/\Delta H_e$ ratio:

$$\begin{aligned}\Delta E_e/\Delta H_e &= (E_e - E_{e,0})/\Delta H_e \\ &= \alpha/(1+\alpha) + \{\alpha/2(br_e)\}^2\Delta H_e.\end{aligned} \quad (10)$$

The $E_e/\Delta H_e$ values calculated with this formula are listed in Table 4. They characterize the dependence of the activation energy on the enthalpy of decomposition.

Ester decomposition as a concerted two-center reaction. Earlier, we carried out an IP analysis of the decomposition of alcohols and acids [5, 6] versus the decomposition of various radicals [3, 4, 39, 40]. Table 6 presents the $E_{e,0}$ values for these reactions.

The classical potential barriers of thermoneutral reaction for the decomposition of molecules is much higher than the $E_{e,0}$ values (kJ/mol) for the decomposition of structurally similar radicals: $E_{e,0}(ROH) = 152 \gg E_{e,0}(RO^{\bullet}) = 65$, $E_{e,0}(RCOOH) = 173 \gg E_{e,0}(RCO_2^{\bullet}) = 45$, and $E_{e,0}(RC(O)OR^1) = 194 \gg E_{e,0}(ROC^{\bullet}(O)) = 45$. For ester decomposition, the difference $\Delta E_{e,0} = E_{e,0}(\text{ester}) - E_{e,0}(\text{carboxyl radical})$ is 149 kJ/mol. What is the cause of this great difference between the activation energies of decomposition of molecules and structurally similar radicals? In the decomposition of radicals, such as $RO^{\bullet}$, $RCO_2^{\bullet}$, $ROC^{\bullet}(O)$, and $RC^{\bullet}(O)$, the *breaking of only one bond* (C–C or C–O) takes place, so the transition state has a single reaction center accumulating all the energy necessary for the activation of decomposition. The decomposition of a molecule into two molecules proceeds in a quite different way. The transition state of ester decomposition is like a biradical having *two reaction centers*: one is C...H...O, in which the H atom is abstracted from the C atom and adds to the O atom, and the other is C...O, in which the C–O bond breaks. The molecule is activated and passes into a near-biradical state, in which the H atom is abstracted in one center and, simultaneously, the C–O bond breaks in the other. Obviously, the total activation barrier is equal to the sum of the activation energies for the two centers: $E_{e,0} = E_{e,0}(\text{H abstraction}) + E_{e,0}(\text{C–O bond breaking})$. Therefore, $E_{e,0}(RC(O)OR^1 \text{ decomposition}) \approx E_{e,0}(\text{H abstraction}) + E_{e,0}(\text{C–O bond breaking})$. The abstraction of H from the C–H bond by alkoxyl radicals is characterized by $E_{e,0} = 55$ kJ/mol (Table 6). The barrier $E_{e,0}(\text{C–O bond breaking})$ is equal to $E_{e,0}(RO^{\bullet} + C{=}C \text{ addition}) = 88$ kJ/mol (Table 6). The total activation barrier is $E_{e,0}(\text{H abstraction}) + E_{e,0}(\text{C–O bond breaking}) = 143$ kJ/mol, which is well below $E_{e,0} = 194$ kJ/mol for ester decomposition. In turn, the $E_{e,0}$ values for both H atom abstraction and the addition reaction include the contributions from triplet repulsion, the electronegativities of the atoms of the reaction center, and the radii of these atoms [8, 9].

Delocalization of π-electrons. Another factor in $E_{e,0}$ for the abstraction and addition reactions is the participation of π-electrons adjacent to the reaction center in the formation of the transition state [8, 9]. When the abstraction reaction takes place and there are π-electrons near the reaction center, they interact with electrons of the reaction center, increase the electron density on it, and thus raise the activation barrier [41]. The same is observed in radical addition to multiple bonds [9]. For H abstraction from the X–H bond by $RO^{\bullet}$ radicals, the contribution from the π-electrons of the adjacent C=C bond to the activation energy is $\Delta E_{\pi} = 9$ kJ/mol [8]. For $RO^{\bullet}$ addition to the C=C bond, the contribution from π-interaction with the adjacent aromatic ring is $\Delta E_{\pi} = 29$ kJ/mol [42]. In view of this, the following approximate formula is valid for ester decomposition: $E_{e,0}(\text{decomposition}) \approx E_{e,0}(\text{H abstraction}) + \Delta E_{\pi}(\text{H abstraction}) + E_{\pi}(ROC{-}C^{\bullet} \text{ decomposition}) + \Delta E_{\pi}(ROC{-}C^{\bullet} \text{ decomposition}) = 55 + 9 + 88 + 29 = 181$ kJ/mol, which is close to $E_{e,0} = 194$ kJ/mol (Table 3). Thus, there are two factors in $E_{e,0}$ for ester decomposition, namely, the synchronous activation of two reaction centers in the transition state and the participation of the π-electrons of the C=C and C=O bonds in the activation process.

Substituent effect. The transition state of ester decomposition is like two reacting biradicals (Table 3), namely the alkyl radical $C^{\bullet}2R^2R^3{-}C^{\bullet}3R^4R^5$ and the carbonyl radical $R^1C(O^{\bullet})O^{\bullet}$. Therefore, the stabilization of the radical state must reduce $E_{e,0}$. The substituents (fragments) of the ester contribute to this effect. The stabilization of the carboxyl radical can be judged from the O–H bond dissociation energy in the corresponding acid. All fatty acids have nearly the same O–H bond strength [44]. The strength of this bond in benzoic acid is lower (238 kJ/mol against 446 kJ/mol for acetic acid). Accordingly, the decomposition of $PhC(O)OCH_2CH_2R^5$ esters is characterized by $E_{e,0} = 183$ kJ/mol, while the decomposition of $RC(O)OCH_2CH_2R^5$ esters is characterized by $E_{e,0} = 194$ kJ/mol, an 11 kJ/mol larger value. Clearly, there is symbasis between the stabilization energy of the carboxyl radical of benzoic acid (8 kJ/mol) and the decrease in $E_{e,0}$ for benzoic acid esters as compared to fatty acid esters owing to the interaction of electrons of the reaction center with the π-electrons of the benzene ring.

The energy $E_{e,0}$ is also influenced by the substituents at the C2 atom: the appearance of one alkyl substituent reduces the barrier by 20.2 kJ/mol, and two ones reduce the barrier by 39.8 kJ/mol. This effect is again due to the stabilizing action of the substituents R^2 and R^3 on the biradical transition state $C^{\bullet}2R^2R^3{-}C^{\bullet}3R^4R^5$. This is indicated by the symbasis between $E_{e,0}$ and the D_{C-H} values for the corresponding hydrocarbon fragments.

The substituents Ph–, $CH_2{=}CHCH_2{-}$, and $Me_2NCH_2{-}$ also stabilize the biradical transition state, and this reduces $E_{e,0}$. A similar effect is exerted by the Cl atom in the decomposition of the $MeCOOCHMeCH_2Cl$ ester ($E_{e,0} = 181.8$ kJ/mol against 174 kJ/mol for $MeCOOCHMeCH_2R$). The Cl atom stabilizes the transition state through its inductive effect.

Alkyl or alkoxyl substituents at the C3 atom of the alcohol residue (R^4 and R^5) increase the classical barrier energy from 194 to 206 kJ/mol (here, the substituents at the C2 atom are hydrogen atoms). this is likely due to the steric effect of these substituents.

CONCLUSIONS

Thus, the major factor in ester decomposition is the enthalpy of the reaction: the higher the enthalpy, the higher the activation energy. The proportionality coefficient between ΔE_e and $\Delta\Delta H_e$ is 0.46–0.47 (see Eq. (10)). A significant feature of ester decomposition is the synchronous concentration of energy on two reaction centers. This markedly raises $E_{e,\,0}$ over the activation energy of radical abstraction and addition reactions, which take place on a single reaction center. The additional increase in $E_{e,\,0}$ in ester decomposition is due to π-electron delocalization and the increase in electron density on the two reaction centers of the transition state. Along with the enthalpy, another factor in the activation energy is the substituents at the C2 and C3 atoms of the alcohol residue. Alkyl groups at the C2 atom reduce the classical potential barrier $E_{e,\,0}$, and so do the Ph–, CH_2=$CHCH_2$–, and Me_2NCH_2– substituents. This is due to the stabilization of the biradical transition state. Conversely, alkyl substituents at the C3 atom increase $E_{e,\,0}$ likely through their steric effect. The kinetic parameters calculated by the IP method make it possible to calculate the activation energies and rate constants for various ester decomposition reactions and for the reverse reactions of olefin addition to acids.

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