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Kinetic Parameters and Geometry of the Transition State of Acyl Radical Decarbonylation

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Abstract—Experimental data on acyl radical decomposition reactions ($RC^{\bullet}O \rightarrow R^{\bullet} + CO$, where R = alkyl or aryl) are analyzed in terms of the intersecting parabolas method. Kinetic parameters characterizing these reactions are calculated. The transition state of methyl radical addition to CO at the C atoms is calculated using the DFT method. A semiempirical algorithm is constructed for calculating the transition state geometry for the decomposition of acyl radicals and for the reverse reactions of $R^{\bullet}$ addition to CO. Kinetic parameters (activation energy and rate constant) and geometry (interatomic distances in the transition state) are calculated for 18 decomposition reactions of structurally different acyl radicals. A linear correlation between the interatomic distance $r^{\#}$(C...C) (or $r^{\#}$(C...O)) in the transition state the enthalpy of the reaction (ΔH_e) is established for acyl decomposition reactions (at br_e = const). A comparative analysis of the enthalpies, activation energies, and interatomic distances in the transition state is carried out for the decomposition and formation of acyl, carboxyl, and formyl radicals.

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Acyl radicals result from a variety of chemical reactions, including ketone and diketone photolysis [1–3], the decarboxylation of α-ketocarboxyl radicals resulting from α-ketoacid decomposition [4], and the homolytic cleavage of the C–X bond in RC(O)X compounds (X is a halogen, hydrogen, or metal atom) [2]. The acyl radical decomposition kinetics has been investigated over a long time. The first kinetic data for acetyl radical decomposition were reported in 1939 [5]. As the chemistry of radicals makes progress, interest in the acyl radical kinetics is not eroded [6, 7].

Here, we analyze experimental data on the decarbonylation kinetics of acyl radicals in the framework of the intersecting parabolas (IP) model [8–11]. Parameters relating the activation energy of these reactions to their enthalpy are obtained and are used to calculate the activation energies and rate constants of the reverse reactions—alternative CO addition to various radicals with the formation of a C–C bond. The transition state (TS) geometry for these reactions has been determined by quantum chemical calculations, and an algorithm has been constructed for semiempirical calculation of TS parameters. Since acyl radical decomposition and the reverse reaction of $R^{\bullet}$ addition to CO (yielding a C–C bond) pass through the same transition state, this algorithm was used to calculate interatomic distances in the TS both for the addition reactions and for the decomposition reactions of various acyl radicals.

COMPUTATIONAL METHOD

IP Model Parameters for the Decomposition Reactions

In the IP model, the acyl decomposition reaction,

$$RC^{\bullet}O \longrightarrow R^{\bullet} + CO, \qquad (I)$$

where $R^{\bullet}$ is an alkyl or aryl radical, is characterized by the following parameters [8, 9]:

(1) classical enthalpy ΔH_e, which includes the difference between the zero point energies of the breaking C–C bond and the forming multiple bond C≡O,

$$\Delta H_e = \Delta H + 0.5hN_A(\nu_{C-C} - \nu_{C\equiv O}), \qquad (1)$$

where h is the Planck constant, N_A is Avogadro's number, and ν_{C-C} and $\nu_{C\equiv O}$ are the stretching frequencies of the breaking and forming bonds;

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

$$E_e = E + 0.5hN_A\nu_{C-C} - 0.5RT, \qquad (2)$$

where R is the gas constant and T is temperature (K);

(3) parameter r_e, which is the total extension of the breaking C–C bond and the forming C≡O bond in the TS;

(4) parameter b ($2b^2$ is the force constant of the breaking C–C bond), b_f ($2b_f^2$ is the force constant of the forming C≡O bond in the TS), and coefficient $\alpha = b/b_f$;

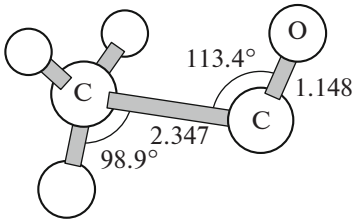


Fig. 1. TS geometry for acyl radical decomposition (quantum chemical calculations, Gaussian 98, DFT method).

(5) preexponential factor A.

The rate constant of the reaction, k, is related to the activation energy E and A by the Arrhenius equation:

$$k = A\exp(-E/RT). \quad (3)$$

The above parameters are interrelated as follows [11]:

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (4)$$

The parameter br_e makes it possible to calculate the classical barrier of thermoneutral reaction, an analogue of the reaction in question with $\Delta H_e = 0$, br_e = const, and α = const.

$$E_{e0} = \{b/(1 + \alpha)\}^2 r_e^2. \quad (5)$$

Provided that α and br_e are known for the class of reactions examined and the condition $\Delta H_{e,\,min} < \Delta H_e < \Delta H_{e,\,max}$ is satisfied, the activation energy of each particular reaction from this class can be calculated using the following relationship (here, $B = br_e(1 - \alpha^2)^{-1}$):

$$E_e = B^2\{1 - \alpha[1 - \Delta H_e/Bbr_e]^{1/2}\}^2. \quad (6)$$

The $\Delta H_{e,\,max}$ and $\Delta H_{e,\,min}$ values are calculated using the formulas [8, 9]

$$\Delta H_{e,\,max} = (br_e)^2 - 2\,br_e\alpha(0.5hN_A\nu_f)^{1/2} - 0.5(1 - \alpha^2)hN_A\nu_f, \quad (7)$$

$$\Delta H_{e,\,min} = -(br_e/\alpha)^2 + 2\,br_e\alpha^{-2}(0.5hN_A\nu_i)^{1/2} - 0.5(1 - \alpha^2)hN_A\nu_i. \quad (8)$$

The kinetic parameters for acyl radical decomposition were calculated in the following order. The enthalpy of decomposition of an acyl radical (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 radical:

$$\Delta H = \Delta H_f^0(R^\cdot) + \Delta H_f^0(CO) - \Delta H_f^0(RC^\cdot O). \quad (9)$$

The enthalpies of formation (ΔH_f^0) of acyl radicals were derived from C–H bond dissociation energies in aldehydes ($D_{(C-H)}$) [12] and ΔH_f^0 data for these aldehydes and the hydrogen atom [13]:

$$\Delta H_f^0 RC^\cdot O = \Delta H_f^0(RC(O)H) + D_{(C-H)} - \Delta H_f^0(H^\cdot). \quad (10)$$

For some aldehydes, ΔH_f^0 was calculated using increments evaluated by comparisons between compounds with a known enthalpy of formation and the –C(O)– increment, $\Delta H_f^0 = -111.8 \pm 3.8$ kJ/mol, also determined by comparisons between compounds with a known enthalpy [13].

For example,

$$\Delta H_f^0(HOC(O)C(O)H) = \Delta H_f^0(HOC(O)H) - 111.8\ \text{kJ/mol}. \quad (11)$$

The enthalpy of formation of glucose was calculated using Benson increments [14]:

$$\Delta H_f^0(HOCH_2(CH(OH))_4C(O)H) = \Sigma\Delta H_f^0(\text{increments}). \quad (12)$$

The enthalpies of formation of alkyl radicals were calculated as

$$\Delta H_f^0(R^\cdot) = (\Delta H_f^0 RH) + D_{(C-H)} - \Delta H_f^0(H^\cdot), \quad (13)$$

where $\Delta H_f^0(RH)$, $D_{(C-H)}$, and $\Delta H_f^0(H^\cdot)$ are taken from a handbook [13]. The resulting enthalpies of formation of compounds and radicals are listed in Table 1.

The activation energy E of the decomposition of radicals was calculated using formula (3) (where k is the experimental rate constant [15–25]) with the standard preexponential factor for the cleavage of the C–C bond in acyl radicals in the gas phase, $A = 1.57 \times 10^{13}$ s^{-1} (average of experimental data [15–25]). Next, we calculated E_e and br_e by formulas (2) and (4), respectively. The following parameters were used in these calculations:

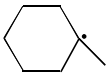
α	$b \times 10^{-10}$, kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}	$0.5hN_A\nu_{C-C}$, kJ/mol	$0.5hN_A(\nu_{C-C} - \nu_{C=O})$, kJ/mol
0.593	44.83	8.2	–4.8

The E_e and br_e values calculated from experimental data are presented in Table 2.

Quantum Chemical Calculations for the Decomposition of the $CH_3C^\cdot O$ Radical

In the theoretical study of the addition of the $CH_3^\cdot$ radical to CO, we employed B3LYP hybrid density functional theory (DFT). The calculations were carried out using the Gaussian 98 program [26]. Stationary-point geometries were determined by optimiza-

Table 1. Enthalpies of formation (ΔH_f^0, kJ/mol) of aldehydes (RC(O)H) and $RC^{\bullet}O$ and $R^{\bullet}$ radicals and the RC(O)–H bond dissociation energies (D, kJ/mol)

R	ΔH_f^0 RC(O)H	D (RC(O)–H)	ΔH_f^0 ($RC^{\bullet}O$)	ΔH_f^0 ($R^{\bullet}$)
$Me^{\bullet}$	–165.7	373.8	–9.9	147.5
$Et^{\bullet}$	–187.4	371.2	–34.2	119.9
$Pr^{\bullet}$	–207.5	371.2	–54.3	99.4
$Bu^{\bullet}$	–230.5	372.0	–76.5	77.6
$Me_2CH^{\bullet}$	–215.5	364.5	–69.0	89.4
$Me_3C^{\bullet}$	–242.7	375.1	–85.6	47.7
$MeCH_2C^{\bullet}HMe$	–234.3	360.8	–91.5	68.6
$PhCH_2^{\bullet}$	–318.9	362.0	89.6	207.2
$PhCMeH^{\bullet}$	–82.1	362.0	61.9	175.4
$PhMe_2C^{\bullet}$	–109.8	362.9	35.1	140.9
	–264.5	375.1	–107.4	22.7
	–228.0	364.5	–81.5	67.4
	–181.3	364.5	–34.8	112.2
$HOC^{\bullet}(O)$	–494.6	375.3	–337.3	–204.0
$HOCH_2(CHOH)_3C^{\bullet}HOH$	–1058.3	371.4	–904.9	757.1

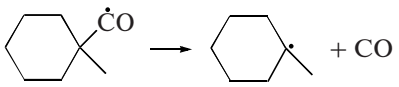
tion with the 6-31G* basis set. Geometry data obtained by the B3LYP/6-31G* method were used to calculate the energy of the system including the zero point energy with the 6-311++G(d,p) basis set in the B3LYP/6-31G* approximation. When comparing theoretical and experimental data, the heat and activation energy of the reaction at 298 K were derived from statistical sums for the harmonic oscillator–rigid rotor model. The calculated TS geometry is shown in Fig. 1.

Below, we compare the calculated enthalpy $-\Delta H(298)$ and activation energy $E(298)$ of the addition reaction with experimental data.

Reaction	$\Delta H(298)$, kJ/mol			$E(298)$, kJ/mol		
	theory B3LYP	theory CCSD(T)	experiment	theory B3LYP	theory CCSD(T)	experiment
$C^{\bullet}H_3 + CO \longrightarrow MeC^{\bullet}O$	–56.7	–18.7	–46.9	15.5	37.0	25.4

Refined calculation of the activation energy by the CCSD(T) method with the 6-311++G(d,p) basis set for the B3LYP/6-31G* geometry demonstrates that the maximum discrepancy between the experimental and theoretical data is on the level of 10 kJ/mol. The discrepancy between the enthalpies is –9.8 and –28.2 kJ/mol for the above two computational methods. The TS in $CH_3C^{\bullet}O$ decomposition can be qualified as late. The C–O distance in the TS, which is 1.148×10^{-10} m, differs only slightly from the same distance in the CO molecule (1.138×10^{-10} m) and is 0.041×10^{-10} m shorter than the C–O bond length in

Table 2. Kinetic (k_{exp}, E, br_e) and thermodynamic (T, ΔH) parameters of the TS for acyl radical decomposition reactions with C–C bond breaking ($\alpha = 0.593$, $\Delta\Delta H_e = -4.8$ kJ/mol, $\Delta E_e = 7.0$ kJ/mol, $A = 1.57 \times 10^{13}$ s^{-1})

Reaction	T, K	Medium	k_{exp} (298 K), s^{-1}	E, kJ/mol	ΔH, kJ/mol	br_e^*	Reference
$MeC^{\cdot}O \longrightarrow C^{\cdot}H_3 + CO$	332–391	Gas	2.83	72.7	46.9	12.56	[15]
$MeC^{\cdot}O \longrightarrow C^{\cdot}H_3 + CO$	333–413	Gas	3.79	72.0	46.9	12.56	[16]
						$br_e^* = 12.52 \pm 0.05$	
$EtC^{\cdot}O \longrightarrow CH_3C^{\cdot}H_2 + CO$	303–353	Gas	3.5×10^2	60.8	43.6	11.42	[17]
$EtC^{\cdot}O \longrightarrow CH_3C^{\cdot}H_2 + CO$	238–278	Gas	1.6×10^2	62.7	43.6	11.65	[18]
$PrC^{\cdot}O \longrightarrow EtC^{\cdot}H_2 + CO$	273–426	Gas	6.8×10^2	59.1	43.2	11.25	[19]
						$br_e^* = 11.44 \pm 0.2$	
$Me_2CHC^{\cdot}O \longrightarrow Me_2C^{\cdot}H + CO$	313–353	Gas	2.8×10^4	49.9	47.9	9.75	[20]
$Me_3CC^{\cdot}O \longrightarrow Me_3C^{\cdot} + CO$	296	Hexane	8.3×10^5	41.5	22.8	10.23	[21, 22]
	296	Hexane	5.9×10^5	42.3	19.6	10.50	[23]
$PhCH_2C^{\cdot}O \longrightarrow PhC^{\cdot}H_2 + CO$	245–331	Isooctane	8.1×10^6	35.9	7.1	10.32	[24]
$PhCH_2C^{\cdot}O \longrightarrow PhC^{\cdot}H_2 + CO$	298	Propan-2-ol	3.1×10^6	38.2	7.1	10.61	[21]
$PhCH_2C^{\cdot}O \longrightarrow PhC^{\cdot}H_2 + CO$	298	Acetonitrile	1.7×10^6	39.7	7.1	10.78	[21]
$PhCHMeC^{\cdot}O \longrightarrow PhC^{\cdot}HMe + CO$	223–251	Isooctane	4.6×10^7	31.6	3.0	9.98	[25]
$PhCMe_2C^{\cdot}O \longrightarrow PhC^{\cdot}Me_2 + CO$	178–203	Isooctane	1.6×10^8	28.5	−4.7	9.93	[25]
						For nonpolar media $br_e^* = 10.12 \pm 0.29$	

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

the acyl radical. In the TS, about 90% of the spin density is transferred to the methyl radical. This is further evidence that the TS is late.

Semiempirical Calculation of the Geometry of Decomposition Reactions

Combining the results of semiempirical (IP model) calculations with the results of quantum chemical (Gaussian 98, DFT) calculations of TS geometry enabled us to construct a fairly simple semiempirical algorithm for calculating interatomic distances in the TS of decomposition reactions from experimental data [27]. In order to reconcile the TS interatomic distances obtained by the IP method with those resulting from quantum chemical calculations, we introduce the correlation parameter $b_m = E_e^{1/2}/\Delta r^{\#}(\mathrm{DFT})$, where $\Delta r^{\#}(\mathrm{DFT})$ is the bond extension in the TS according to DFT calculations. With this correlation parameter taken into account, the interatomic distance $r^{\#}(\mathrm{C...X})$ is calculated as

$$r^{\#}(\mathrm{C...X}) = r(\mathrm{C–X}) + E_e^{1/2}/b_m, \qquad (14)$$

where r(C–X) is the length of the bond in the initial radical. To calculate the $r^{\#}$(C...X) distances in the TS, we used the lengths of molecular C–X bonds available from the literature [28] (listed below) and the b_m values obtained for these bonds in this work.

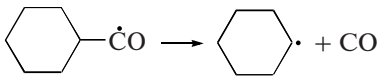
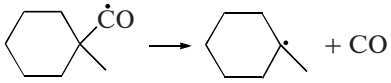
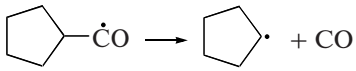
Bond	$r \times 10^{10}$, m	$b_m \times 10^{10}$, kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}
C–C	1.513	10.68
C–O	1.138	–

RESULTS AND DISCUSSION

Activation Energy of Acyl Radical Decomposition

The decomposition of acyl radicals at the C–C bond with CO formation is an endothermic process ($\Delta H > 0$, ΔH range of 3.0–53.1 kJ/mol). The only exception is the $PhCMe_2C^{\cdot}O$ radical, for which $\Delta H =$

Table 3. Kinetic (E, k), thermodynamic (ΔH), and geometric ($r^{\#}$(C–C)) parameters of the TS for acyl radical decomposition reactions with C–C bond breaking ($\alpha = 0.593$, $\Delta\Delta H_e = -4.8$ kJ/mol, $\Delta E_e = 7.0$ kJ/mol, $A = 1.57 \times 10^{13}$ s^{-1})

Reaction	ΔH, kJ/mol	E, kJ/mol	ΔE, kJ/mol	k (298 K), s^{-1}	$r^{\#}$(C–C) × 10^{10}, m
$br_e = 12.52$ (kJ/mol)$^{1/2}$					
$MeC^{\cdot}O \longrightarrow C^{\cdot}H_3 + CO$	46.9	72.3	−0.4	3.33	2.347
$br_e = 11.44$ (kJ/mol)$^{1/2}$					
$EtC^{\cdot}O \longrightarrow CH_3C^{\cdot}H_2 + CO$	43.6	60.9	−1.8	3.3×10^2	2.284
$PrC^{\cdot}O \longrightarrow EtC^{\cdot}H_2 + CO$	43.2	60.7	1.6	3.6×10^2	2.285
$BuC^{\cdot}O \longrightarrow PrC^{\cdot}H_2 + CO$	43.6	60.9	–	3.3×10^2	2.285
iso-$BuC^{\cdot}O \longrightarrow$ *iso*-$PrC^{\cdot}H_2 + CO$	53.1	65.5	–	51.8	2.310
$br_e = 10.12$ (kJ/mol)$^{1/2}$					
$Me_2CHC^{\cdot}O \longrightarrow Me_2C^{\cdot}H + CO$	47.9	52.5	2.6	9.8×10^3	2.235
$MeCH_2CHMeC^{\cdot}(O) \longrightarrow MeCH_2C^{\cdot}HMe + CO$	49.6	53.4	–	6.9×10^3	2.241
$Me_3CC^{\cdot}O \longrightarrow Me_3C^{\cdot} + CO$	22.8	40.6	−0.9	1.2×10^6	2.159
$HOC(O)C^{\cdot}O \longrightarrow HOC^{\cdot}(O) + CO$	22.8	40.6	–	1.2×10^6	2.159
$HOCH_2(CHOH)_4C^{\cdot}O \longrightarrow HOCH_2(CHOH)_3C^{\cdot}HOH + CO$	37.3	47.2	–	8.4×10^4	2.202
	38.4	51.3	–	6.8×10^4	2.206
	19.6	39.2	−3.1	2.1×10^6	2.149
	36.5	46.8	–	9.8×10^4	2.200
$PhCH_2C^{\cdot}O \longrightarrow PhC^{\cdot}H_2 + CO$	7.1	34.2	−1.7	1.6×10^7	2.114
$PhCHMeC^{\cdot}O \longrightarrow PhC^{\cdot}HMe + CO$	3.0	32.7	1.1	2.9×10^7	2.103
$PhCMe_2C^{\cdot}O \longrightarrow PhC^{\cdot}Me_2 + CO$	−4.7	30.0	1.5	8.7×10^7	2.083

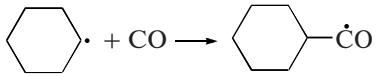
−4.7 kJ/mol. The activation energy of the decomposition reactions varies between 28.5 and 72.7 kJ/mol.

An analysis of the br_e data (Table 2) suggests that the acyl radical decomposition reactions can be divided into three classes, each made up of decomposition reactions of structurally similar radicals. These classes are characterized by similar values br_e and the classical potential barrier of thermoneutral reaction ($E_{e,0}$).

Reaction	br_e, (kJ/mol)$^{1/2}$	$\Delta H_{e,min}$	$\Delta H_{e,max}$ kJ/mol	$E_{e,0}$
$MeC^{\cdot}O \longrightarrow C^{\cdot}H_3 + CO$	12.52	–247.2	94.8	61.8
$RR^1R^2CCH_2C^{\cdot}O \longrightarrow RR^1R^2H_2C^{\cdot} + CO$ (R, R^1, R^2 = H, alkyl)	11.44	–191.2	73.5	51.6
$RR^1R^2CC^{\cdot}O \longrightarrow RR^1R^2C^{\cdot} + CO$ (R, R^1, R^2 = H, alkyl, Ph)	10.12	–131.7	50.7	40.4

Evidently, the classical potential barrier of thermoneutral reaction for CH_3CO decomposition is much higher than that for the decomposition of the other acyl radicals (61.8 against 51.6 and 40.4 kJ/mol). Sub-

Table 4. Kinetic (k_{exp}, E) and thermodynamic (ΔH) parameters of the TS for acyl radical formation reactions

Reaction	T, K	Medium	k_{exp} (298 K), l mol^{-1} s^{-1}	E_{exp}, kJ/mol	Reference
$C^{\bullet}H_3 + CO \longrightarrow MeC^{\bullet}O$	260–296	Gas	6.55×10^3	25.0	[17]
"	300–500	Gas	4.66×10^3	28.7	[30]
"	303–343	Gas	8.02×10^3	27.4	[31]
"	298	Gas	3.61×10^3		[32]
"	298	H_2O	2.0×10^6		[33]
"	298	H_2O	2.3×10^6		[34]
$CH_3C^{\bullet}H_2 + CO \longrightarrow EtC^{\bullet}O$	238–378	Gas	4.68×10^4	20.1	[35]
$CH_2{=}CH(CH_2)_2CH(C^{\bullet}H_2)CH_2CH{=}CHPh + CO \longrightarrow CH_2{=}CH(CH_2)_2CH(CH_2C^{\bullet}O)CH_2CH{=}CHPh$	353	Benzene	6.3×10^5		[36]
	323	Cyclohexane	1.2×10^5		[37]

stituents at the carbon atom at which the acyl radical decomposes reduce $E_{e,0}$ by 11.2 kJ/mol.

In the case of $PhCH_2C^{\bullet}O$ decomposition, the effect of solvent polarity on the rate constant and activation energy E is noticeable. The contribution to activation energy from the interaction between the radical and the polar solvent is given by the formula

$$\Delta E_\mu = E_2 - E_1 = RT\ln(k_1/k_2), \quad (15)$$

where k_1 and E_1 refer to decomposition in a nonpolar solvent and k_2 and E_2 refer to decomposition in the polar solvent (Table 2). Below, we list the calculated

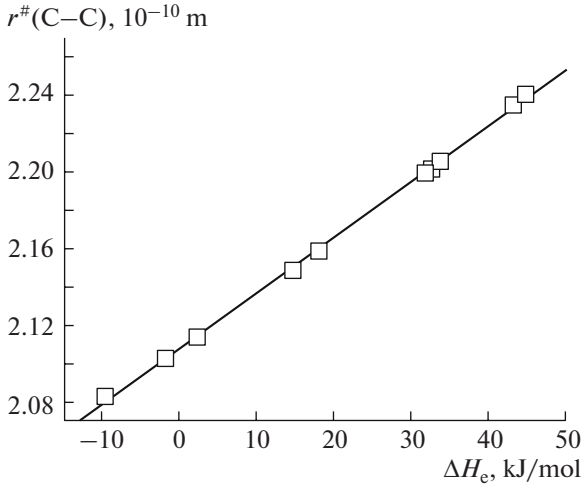


Fig. 2. $r^{\#}$(C...C) versus ΔH_e for acyl radical decomposition reactions.

ΔE_μ values and the dipole moments (μ) [29] and dielectric constants (ε) [29] of some solvents.

Parameter	Cyclohexane	Propan-2-ol	Acetonitrile
μ, D	0	1.68	3.92
ε (298 K)	2.02	20.1	36.2
ΔE_μ, kJ/mol	0	2.4	3.8

Clearly, as the solvent polarity increases, the activation energy of the reaction increases by 2.4 kJ/mol for propan-2-ol and by 3.8 kJ/mol for acetonitrile.

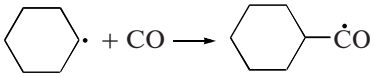
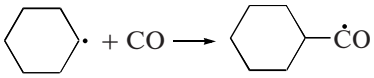
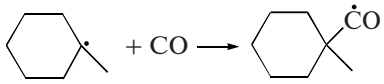
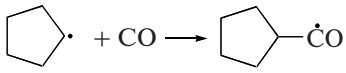
The br_e values derived from experimental data for the three classes of radical decomposition reactions were used to calculate the activation energy E (Eq. (6)) and rate constant (Eq. (3)) for particular reactions from these classes. Calculations were carried out both for reactions described in the literature and for radical decomposition reactions modeled by us. The calculated E and k values are presented in Table 3 (the condition $\Delta H_{e,min} < \Delta H_e < \Delta H_{e,max}$ is satisfied in all cases).

As is clear from Tables 2 and 3, the calculated activation energies of acyl radical decomposition are in good agreement with experimental data: ΔE ranges between 3.1 and 2.6 kJ/mol.

TS Geometry

According to the quantum chemical calculations, the TS configuration in CH_3CO decomposition at the C–C bond is nonlinear (Fig. 1). Calculated $r^{\#}$(C...C) data (Eq. (14)) for various acyl radicals are listed in Table 3. In all cases, there is a significant extension of the C–C bond in the TS, so the TS can be qualified as

Table 5. Kinetic (k, E) and thermodynamic (ΔH) parameters of the TS for carbonylation

Reaction	$-\Delta H$, kJ/mol	E, kJ/mol	k (298 K), l mol^{-1} s^{-1}
$C^{\cdot}H_3 + CO \longrightarrow MeC^{\cdot}O$	46.9	25.4	6.3×10^3
$C^{\cdot}H_3 + CO \longrightarrow MeC^{\cdot}O$ (liquid phase)	46.9	25.4	3.2×10^4
$CH_3C^{\cdot}H_2 + CO \longrightarrow EtC^{\cdot}O$	43.6	17.3	1.6×10^5
$EtC^{\cdot}H_2 + CO \longrightarrow PrC^{\cdot}O$	43.2	17.5	1.5×10^5
$PrC^{\cdot}H_2 + CO \longrightarrow BuC^{\cdot}O$	43.6	17.3	1.6×10^5
$Me_2CHC^{\cdot}H_2 + CO \longrightarrow$ *iso*-$BuC^{\cdot}O$	53.1	12.4	1.2×10^6
$Me_2C^{\cdot}H + CO \longrightarrow Me_2CHC^{\cdot}O$	47.9	8.0	7.1×10^6
$MeCH_2C^{\cdot}HMe + CO \longrightarrow MeCH_2CHMeC^{\cdot}(O)$	49.6	7.3	9.5×10^6
$Me_3C^{\cdot} + CO \longrightarrow Me_3CC^{\cdot}O$	22.8	21.5	3.1×10^4
$HOC^{\cdot}(O) + CO \longrightarrow HOC(O)C^{\cdot}O$	22.8	21.5	3.1×10^4
$HOCH_2(CHOH)_3C^{\cdot}HOH + CO \longrightarrow HOCH_2(CHOH)_4C^{\cdot}O$	37.3	13.5	7.7×10^5
	38.4	12.9	9.8×10^5
 (liquid phase, 323 K)	38.4	12.9	7.4×10^6
	19.6	23.3	1.4×10^4
	36.5	13.9	6.6×10^5
$PhC^{\cdot}H_2 + CO \longrightarrow PhCH_2C^{\cdot}O$	7.1	30.9	689
$PhC^{\cdot}HMe + CO \longrightarrow PhCHMeC^{\cdot}O$	3.0	33.4	251
$PhC^{\cdot}Me_2 + CO \longrightarrow PhCMe_2C^{\cdot}O$	−4.7	38.4	33.4

late. An analysis of the $r^{\#}$(C...C) data and the enthalpies of reaction (ΔH_e) in the TS suggests that these quantities are correlated for structurally similar radicals (br_e = const). Figure 2 plots $r^{\#}$(C...C) versus ΔH_e for the decomposition of the acyl radicals $RR^1R^2CC(O)$ (R, R^1, R^2 = H, alkyl, Ph) with br_e = 10.12 (kJ/mol)$^{1/2}$. The plot is linear, and the larger the ΔH_e value the longer the $r^{\#}$(C...C) distance:

$$r^{\#}(\text{C...C}) \times 10^{10}\ \text{m} = 2.10 + 2.92 \times 10^{-3}\,\Delta H_e\ \text{kJ/mol}. \quad (16)$$

A linear dependence of the $r^{\#}$(C...C) distance in the RS on ΔH_e is also observed for the decomposition of the $RR^1R^2CCH_2C(O)$ radicals (br_e = 11.44 (kJ/mol)$^{1/2}$):

$$r^{\#}(\text{C...C}) \times 10^{10}\ \text{m} = 2.15 + (3.85\times 10^{-3} \pm 1.46 \times 10^{-3})\Delta H_e\ \text{kJ/mol}. \quad (17)$$

CO Addition to R$^{\cdot}$ Radicals

The reverse reaction to acyl radical decomposition (reaction (I)) is CO addition to the alkyl radical (carbonylation):

$$R^{\cdot} + CO \longrightarrow RC^{\cdot}O. \quad \text{(II)}$$

Kinetic studies of the carbonylation of alkyl radicals are rare. The most significant kinetic parameters reported for this reaction [30–36] are presented in Table 4.

The acyl radical decomposition reactions are endothermic (see above); therefore, the formation of these radicals is exothermic: $\Delta H_2 = -\Delta H_1$ and $E_2 = E_1 - \Delta H_1$. We used the E_1 and ΔH_1 values obtained for the decomposition reactions (I) to calculate the activation energy for a number of new, hitherto unreported carbonylation reactions (II). The calculated E_2 values are listed in Table 5. Furthermore, this approach allowed the preexponential factor A_2 to be correctly estimated for carbonylation reactions. For methyl radical carbonylation, $E_2 = 72.3 - 46.9 = 25.4$ kJ/mol. Next, using experimental carbonylation rate constants [17, 30, 31], we derive, from Eq. (3), the average value of $A = 1.8 \times 10^8$ l mol^{-1} s^{-1} for gas-phase carbonylation. The standard preexponential factor A for bimolecular reactions in a nonpolar liquid medium is, on the average, five times larger than the A value for the gas phase [11]; hence, for liquid-phase carbonylation, $A = 9.0 \times 10^8$ l mol^{-1} s^{-1}. The standard preexponential factors thus obtained were used in the calculation of the rate constants of CO addition to various radicals in gas and liquid media. The calculated carbonylation rate constants are given in Table 5. For the methyl radical, the calculated and experimental data are in good agreement. For the ethyl and cyclohexyl radicals, there is some discrepancy between the calculated and experimental values (Tables 4, 5).

In the carbonylation of the methyl radical, there is an appreciable effect of the polar solvent (H_2O) on the rate constant and activation energy E (Table 4). The contribution from TS hydration to the activation energy was calculated using formula (15), where k_1 and k_2 are the rate constants of methyl radical carbonylation in a nonpolar medium and water, respectively.

Below, we present the calculated ΔE_μ values, the dipole moments (μ) of the reactants and TS [29], and the dielectric constant (ε) of water [29]. The dipole moments of the acyl radical and TS were calculated by quantum chemical means.

Parameter	μ(CO), D	$\mu(CH_3C^{\cdot}O)$, D (calculated)	μ(TS), D (calculated)	ε (298 K)	ΔE_μ, kJ/mol
Value	0.11	2.43	1.025	78.5	−10.2

Clearly, TS solvation in the aqueous medium reduces the activation energy by 10 kJ/mol. This correlates well with the fact that the dipole moment of the initial reactant (CO) is as small as 0.11 D, while that of the TS is μ(TS) = 1.025 D. Thus, the higher polarity of the TS in water reduces the activation energy.

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