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Reactions of Alkoxy and Peroxy Radicals with Carbon Monoxide

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Abstract—Experimental rate constants of the reactions $HO^{\bullet} + CO \longrightarrow H^{\bullet} + CO_2$, $RO^{\bullet} + CO \longrightarrow R^{\bullet} + CO_2$, $HO_2^{\bullet} + CO \longrightarrow HO^{\bullet} + CO_2$, and $RO_2^{\bullet} + CO \longrightarrow RO^{\bullet} + CO_2$ are analyzed in the framework of the intersecting-parabolas model. The transition states of the additions of the methoxy and methylperoxy radicals to carbon monoxide were calculated by quantum-chemical methods. The reactions occur in two consecutive steps: first the $HO^{\bullet}$ ($RO^{\bullet}$, $RO_2^{\bullet}$) radical adds to CO and then the resulting unstable intermediate radical decomposes to evolve CO_2. The kinetic parameters of these reactions are calculated by two methods (using the intersecting-parabolas model and the quantum-chemical method). The activation energies and rate constants of a series of $R_iO^{\bullet} + CO$ and $R_iO_2^{\bullet} + CO$ reactions are calculated. A comparison of the kinetic parameters suggests close similarity between the transition states in the additions of the O-centered radicals to CO and olefins.

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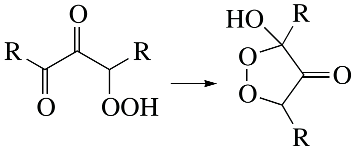
INTRODUCTION

The reactions of radicals with carbon monoxide play an important role in the modern combustion chemistry of hydrocarbons and other organic compounds [1–3], as well as their slow oxidation in the liquid phase [4]. The oxidation of CO occurs as a branched chain reaction [2]. The sources of CO are acyl radicals formed from aldehydes [1],

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

and ketohydroperoxides, for example [4],



$$\longrightarrow RCOOH + RCHO + CO.$$

The alkoxy and peroxy radicals involved in the chain oxidation of hydrocarbons react with CO, oxidizing it to CO_2:

$$RO^{\bullet} + CO \longrightarrow R^{\bullet} + CO_2,$$

$$RO_2^{\bullet} + CO \longrightarrow RO^{\bullet} + CO_2.$$

The experimental data concerning these reactions are scarce [1, 4, 5]. Only the reaction of the hydroxyl radical with CO has been studied in sufficient detail:

$$HO^{\bullet} + CO \longrightarrow H^{\bullet} + CO_2.$$

This reaction results in the oxidation of carbon monoxide via a branched chain mechanism [1, 2].

This work is aimed at analyzing the experimental data on the reaction of the oxygen-centered radicals with CO and at determining their mechanism. The intersecting parabolas model (IPM) [4, 6–8] and quantum-chemical calculations using the Gaussian 98 program package [9] were used in theoretical analysis. In the present study, we refined the mechanism of these reactions, compared them with other addition reactions involving the $RO^{\bullet}$ and $RO_2^{\bullet}$ radicals, determined the structure of the transition state (TS), and suggested an algorithm for the calculation of the activation energies and rate constants of the reactions of CO with various alkoxy and peroxy radicals.

COMPUTATIONAL PROCEDURE

Calculation of Reaction Enthalpies

The enthalpies (ΔH) of the reactions

$$RO^{\bullet} + CO \longrightarrow ROC^{\bullet}(O) \qquad \text{(I)}$$

and

$$ROC^{\bullet}(O) \longrightarrow R^{\bullet} + CO_2 \qquad \text{(II)}$$

were calculated using the formulas

$$\Delta H(\mathrm{I}) = \Delta H(ROC^{\bullet}(O)) - \Delta H(RO^{\bullet}) - \Delta H(CO) \qquad (1)$$

and

$$\Delta H(\mathrm{II}) = \Delta H(R^{\bullet}) + \Delta H(CO_2) - \Delta H(ROC^{\bullet}(O)). \qquad (2)$$

The enthalpies of the reactions

$$RO_2^{\bullet} + CO \longrightarrow ROOC^{\bullet}(O) \qquad \text{(III)}$$

and

$$\mathrm{ROOC^{\bullet}(O)} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{CO_2} \qquad \text{(IV)}$$

were calculated using the formulas

$$\Delta H(\mathrm{III}) = \Delta H(\mathrm{ROOC^{\bullet}(O)}) - \Delta H(\mathrm{RO_2^{\bullet}}) - \Delta H(\mathrm{CO}) \quad (3)$$

and

$$\Delta H(\mathrm{IV}) = \Delta H(\mathrm{RO^{\bullet}}) + \Delta H(\mathrm{CO_2}) - \Delta H(\mathrm{ROOC^{\bullet}(O)}). \quad (4)$$

The standard enthalpies of formation of the $R^{\bullet}$, $RO^{\bullet}$, and $RO_2^{\bullet}$ radicals were calculated by the equation

$$\Delta H(\mathrm{X^{\bullet}}) = \Delta H(\mathrm{XH}) + D(\mathrm{X{-}H}) - \Delta H(\mathrm{H^{\bullet}}), \qquad (5)$$

where $X^{\bullet} = R^{\bullet}$, $RO^{\bullet}$, or $RO_2^{\bullet}$, and D(X–H) is the dissociation energy of the corresponding bond. The numerical values of the enthalpies of formation of the molecules are given in [10], the dissociation energies of the C–H and O–H bonds are available from [11], the dissociation energy of the C–H bond in the carboxyl group of esters and peresters of formic acid was considered to be the same as that in formic acid (392.7 kJ/mol) [12]. The enthalpy of formation of a perester was calculated from the enthalpy of formation of the corresponding ester by adding the increment ΔH(O–(O)(C)) = –19.2 kJ/mol, which was determined by comparison of the enthalpies of formation of ethers and peroxides [10, 12]. The enthalpies of formation $\Delta H(\mathrm{CO}) = -110.5$ kJ/mol and $\Delta H(\mathrm{CO_2}) = -393.5$ kJ/mol are borrowed from [10].

Calculation of Kinetic Parameters of the Reactions of $RO^{\bullet}$ and $RO_2^{\bullet}$ with CO in the Framework of the IPM

In the framework of the IPM, the reaction of radical addition of the type

$$\mathrm{X^{\bullet}} + \mathrm{CO} \longrightarrow \mathrm{XC^{\bullet}O}$$

is characterized by the following parameters [6–8]:

(1) classical enthalpy ΔH_e, which includes the difference of the zero-point vibration energies of the attacked (C=O) and formed (C–X) bonds ($\Delta H_e = \Delta H + 0.5hN_A\nu_{C=O} - 0.5hN_A\nu_{C-X}$, where h is the Planck constant, N_A is Avogadro's number, and $\nu_{C=O}$ and ν_{C-X} are the stretching frequencies of the corresponding bonds);

(2) classical potential barrier E_e, which includes the zero-point vibration energy of the attacked bond and is related to the Arrhenius activation energy E by the equation

$$E_e = E + 0.5(hN_A\nu_{C=O} - RT); \qquad (6)$$

(3) parameter r_e, which is equal to the total extension of the attacked and formed bonds in the TS;

(4) parameters $b = 2\pi\nu_{C=O}\mu_{C=O}^{1/2}$ and $b_f = 2\pi\nu_{C-X}\mu_{C-X}^{1/2}$, where $\mu_{C=O}$ and μ_{C-X} are the reduced masses of the C=O and C–X groups, respectively; $b = 75.63 \times 10^{10}$ (kJ/mol)$^{1/2}$ m^{-1}, and the coefficient $\alpha = b/b_f$;

(5) preexponential factor A.

The reaction rate constant is related to the E activation energy and A value through the Arrhenius equation: $k = A\exp(-E/RT)$.

The kinetic and physical parameters of the considered reactions are given below.

Radical	b_f, (kJ/mol)$^{1/2}$ m^{-1}	α	$0.5hN_A\nu_{C=O}$, kJ/mol	$0.5hN_A(\nu_{C=O} - \nu_{C-X})$, kJ/mol	A, l mol^{-1} s^{-1} (gas phase)
$RO^{\bullet}$	39.21	1.929	13.0	6.3	2.0×10^8
$RO_2^{\bullet}$	37.01	2.044	13.0	6.7	2.0×10^8

These parameters are interrelated through the relationship [6–8]

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \qquad (7)$$

Knowing br_e, one can calculate the classical potential barrier of the thermally neutral reaction, $E_{e,0} = E_e$, at $\Delta H_e = 0$, br_e = const, and α = const, which is

$$E_{e,0} = \left\{\frac{br_e}{1+\alpha}\right\}^2, \qquad (8)$$

and the parameter $r_e = br_e/b$. Provided that the reactions of the class considered have been characterized by all parameters including br_e, the activation energy of an individual reaction can be calculated from its enthalpy

$$\begin{aligned} E_e &= B^2\{\alpha\sqrt{1 + \Delta H_e/br_eB} - 1\}^2, \\ E &= E_e - 0.5hN_A\nu + 0.5RT, \end{aligned} \qquad (9)$$

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

Quantum-Chemical Calculations

The coupled-cluster method was used for the theoretical analysis of the reactions of the $H_3CO^{\bullet}$ and $H_3COO^{\bullet}$ radicals with the CO molecule. The geometry of stationary points on the potential energy surface of the system was determined by the CCD optimization using the 6-31G* basis set. The geometric parameters obtained were used in the CCSD(T) calculation of the energy of the system using the 6-311++G** basis set taking into account the zero-point vibration energy in

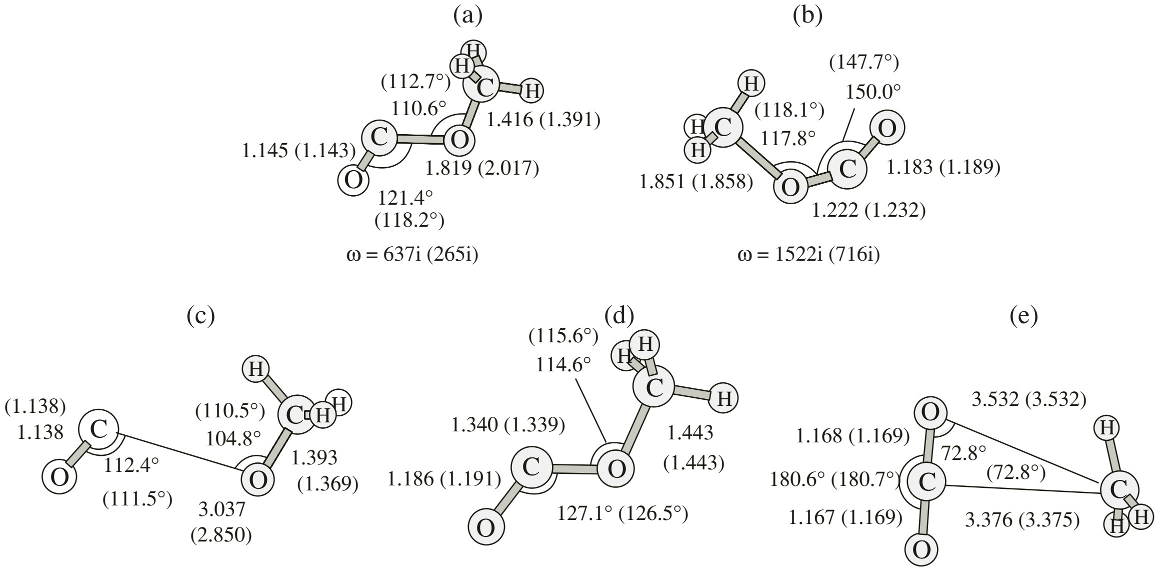


Fig. 1. Structures of (c) the prereaction complex and (a) the TS in the addition of $H_3CO^\bullet$ to CO, (d) the $H_3COC^\bullet O$ intermediate product and (b) the TS in the reaction of its decomposition to $H_3C^\bullet$ and CO_2, and (e) the postreaction complex as determined by the CCD/6-31G* and B3LYP/6-31G* methods (in parentheses). The distances are in Å, the angles are in deg, and the imaginary frequencies are in cm^{-1}.

the harmonic approximation at the CCD/6-31G* level. An alternative approach based on the B3LYP density functional hybrid method and the 6-31G* basis set was used, for comparison, to optimize the geometry followed by the calculation of the energy of the system by the B3LYP or CCSD(T) method in the 6-311++G** basis set. When the molecular system had open shells, the UCCD, UB3LYP, and UCCSD(T) unrestricted methods were applied in all cases. The intrinsic reaction coordinate was analyzed to determine the true nature of all TS found. The enthalpy and activation energy of the reaction at 298 K were determined from the statistical sums in the harmonic oscillator–rigid rotator model.

RESULTS AND DISCUSSION

Reaction of $RO^\bullet$ with CO

In principle, this reaction can occur via two channels. The first is a two-step channel consisting of an addition reaction and subsequent decomposition of the resulting alkoxyformyl radical (reactions (I) and (II)). The second channel is single-step oxygen atom transfer from $RO^\bullet$ to CO:

$$RO^\bullet + CO \longrightarrow R^\bullet + CO_2. \qquad \text{(V)}$$

The $ROC^\bullet(O)$ radical is unstable and decomposes rather rapidly to $R^\bullet$ and CO_2. If the decomposition occurs more rapidly than the formation of $ROC^\bullet(O)$ in reaction (I), then, evidently, the reaction of $RO^\bullet$ with CO includes the fast sequence of steps (I) and (II). The methoxy radical reacts with CO, and the rate constant of this process is $k = 35$ l mol^{-1} s^{-1} (298 K, gas phase) [13]. Under a CO pressure of $p_{CO} = 1$ atm, the specific rate of the reaction of $CH_3O^\bullet$ with CO is $k[CO] = 35(4 \times 10^{-2}) = 1.4$ s^{-1}. The rate constant of $MeOC^\bullet(O)$ decomposition is $k_d = 10^{13}\exp(-42.7/RT) = 3.3 \times 10^5$ s^{-1} [12]; i.e., this reaction is faster by five orders of magnitude. Therefore, there is every reason to believe that the reactions of the alkoxy radicals with CO occur in two consecutive steps and addition step (I) is rapidly followed by step (II). It is likely that the fast interaction of the hydroxyl radical with CO occurs similarly.

This conclusion is consistent with the results of the quantum-chemical calculation of the TS for the reaction of the methoxy radical with CO. The TS structures in the addition of $MeO^\bullet$ to CO and in the decomposition of $MeOC^\bullet(O)$ are shown in Fig. 1.

The TS in the addition of $MeO^\bullet$ to CO is characterized by the distances $r^\#(Me–O) = 1.416 \times 10^{-10}$ m and $r^\#(OC–O) = 1.819 \times 10^{-10}$ m and the angle $\varphi(COC) = 110.6°$. When studying the forward reaction of $MeO^\bullet$ with CO via O atom transfer from $MeO^\bullet$ to CO, it was found that this route does not occur in fact, because this is possible only when the dissociation of $MeO^\bullet$ to $Me^\bullet$ and O is coupled with the subsequent recombination of O and CO. This agrees with the theoretical analysis results [14] indicating the absence of the forward reaction of O atom transfer from the $HOO^\bullet$ radical to CO.

The enthalpies of formation of the $R^\bullet$ and $RO^\bullet$ radicals and the enthalpies of addition (I) and decomposition (II) are listed in Table 1. As can be seen, both steps are exothermic and ΔH(I) ranges from –75 to –95 kJ/mol and ΔH(II) varies from –53 to –126 kJ/mol. The addition of the hydroxyl radical to CO is a very exothermic reaction (ΔH(I) = –132.5 kJ/mol), but the decomposition of

Table 1. Enthalpies of formation of the $R^{\bullet}$, $RO^{\bullet}$, and $ROC^{\bullet}O$ radicals and the enthalpies of reactions (I) and (II) (kJ/mol)

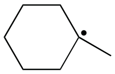
$R^{\bullet}$	$\Delta H(R^{\bullet})$	$\Delta H(RO^{\bullet})$	$-\Delta H(ROC^{\bullet}O)$	$-\Delta H$(I)	$-\Delta H$(II)
$H^{\bullet}$	218.0	39.0	204.0	132.5	–28.5
$C^{\bullet}H_3$	147.5	12.7	180.9	83.1	65.1
$CH_3C^{\bullet}H_2$	119.9	–20.4	210.2	79.3	63.4
$Me_2C^{\bullet}H$	89.4	–58.7	251.1	81.9	53.0
$Me_3C^{\bullet}$	47.7	–91.1	283.1	81.5	62.7
$EtMe_2C^{\bullet}$	27.1	–107.6	299.6	81.5	66.8
cyclo-$C_6H_{11}^{\bullet}$	67.4	–65.7	268.7	92.5	57.4
	22.8	–96.1	301.1	94.6	65.8
$CH_2{=}CHC^{\bullet}HMe$	130.4	55.0	137.4	81.9	125.7
$PhC^{\bullet}H_2$	207.0	113.6	71.6	74.7	114.9
$PhC^{\bullet}Me_2$	140.9	42.1	145.3	76.9	107.3

Table 2. Experimental rate constants of the reactions of various radicals with CO and the br_e parameters calculated using formula (7)

Radical	T, K	k, l mol^{-1} s^{-1}	E, kJ/mol	$-\Delta H$, kJ/mol	br_e, (kJ/mol)$^{1/2}$	References
$HO^{\bullet}$	298	$(8.52 \pm 0.75) \times 10^7$	2.1	132.5	26.55 ± 0.04	[15–17]
$DO^{\bullet}$	298	6.62×10^7	2.7	132.5	26.70	[18]
$CH_3O^{\bullet}$	298	34.5	38.5	83.1	28.84	[13]
$Me_3CO^{\bullet}$	298	0.236	50.9	81.5	30.57	[19]
$HO_2^{\bullet}$	298	$(7.66 \pm 0.74) \times 10^7$	82.2	18.1	30.68 ± 0.04	[20, 21]
$PhMe_2CO_2^{\bullet}$	393	1.81	65.8	30.7	29.33	[22]
$PhMe_2CO_2^{\bullet}$	403	2.81	66.0	30.7	29.36	[22]
$PhMe_2CO_2^{\bullet}$	413	3.11	67.3	30.7	29.51	[22]
					Average 29.40 ± 0.08	

the $HOC^{\bullet}(O)$ radical is endothermic (ΔH(II) = 28.5 kJ/mol). These values are close to the results of the theoretical calculation performed in this work.

The parameter br_e was calculated by formula (7) using experimental data obtained for the reactions of $HO^{\bullet}$, $DO^{\bullet}$, and $MeO^{\bullet}$ with CO in the gas phase. The initial data and calculation results are presented in Table 2. Knowing br_e, we found, by formula (8), the following values of the classical potential of the thermally neutral reaction ($E_{e,0}$) and the parameter r_e for these reactions:

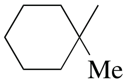
Parameter	$HO^{\bullet}$	$DO^{\bullet}$	$CH_3O^{\bullet}$	$Me_3CO^{\bullet}$
br_e, (kJ/mol)$^{1/2}$	26.55	26.70	28.84	30.57
$E_{e,0}$, kJ/mol	82.2	83.1	97.0	108.9
$r_e \times 10^{10}$, m	0.351	0.353	0.381	0.404

The $E_{e,0}$ values for the reactions of $HO^{\bullet}$ and $DO^{\bullet}$ with CO are nearly the same (the estimation error for $E_{e,0}$ is ±1.5 kJ/mol [7]); $E_{e,0}$ for $CH_3O^{\bullet}$ addition to CO is 14 kJ/mol higher than $E_{e,0}$ for the addition of $HO^{\bullet}$, and for $Me_3CO^{\bullet}$ $E_{e,0}$ is 12 kJ/mol higher than that for $CH_3O^{\bullet}$. The difference in reactivity between the methoxy and *tert*-butoxy radicals is likely due to the steric effect, and the difference between the hydroxyl and methoxy radicals is due to their different electron affinities. The results of the quantum-chemical calculation of ΔH(298 K) and E for reactions (I) and (V) are presented in Table 3. They

Table 3. Results of the quantum-chemical calculation of the enthalpy and activation energy for the reactions of the methoxy and methylperoxy radicals with CO

Parameter, kJ/mol	IPM	CCSD(T)/6-311++ G**//CCD/6-31G*	CCSD(T)/6-311++ G**//B3LYP/6-31G*	B3LYP/6-311++G** //B3LYP/6-31G*
$MeO^\bullet + CO \longrightarrow MeOC^\bullet O$ (I)				
ΔH	–83.1	–44.0 (–59.4)	–43.7 (–58.7)	–65.6 (–98.1)
E	38.5	31.2	28.9	16.7
$MeOC^\bullet O \longrightarrow Me^\bullet + CO_2$ (II)				
ΔH	–65.1	–96.7	–96.1	–94.0
E	42.7	60.1	60.9	38.1
$MeO_2^\bullet + CO \longrightarrow MeOOC^\bullet O$ (III)				
ΔH	–12.3	45.5 (19.4)	44.4 (19.4)	22.7 (–19.5)
E	77.5	82.0	81.3	58.3
$MeOOC^\bullet O \longrightarrow MeO^\bullet + CO_2$ (IV)				
ΔH	–273.3	–312.1	–312.1	–316.5
E		21.5	17.8	1.4

Table 4. Activation energies and rate constants of the $RO^\bullet + CO \longrightarrow ROC^\bullet O$ reaction in the gas and liquid phases

R	$-\Delta H$, kJ/mol	E, kJ/mol	k (300), l mol^{-1} s^{-1}	
			gas phase	liquid phase
Me	83.1	38.5	39.5	1.97×10^2
Et	79.3	40.6	17.0	85.1
Me_2CH	81.9	39.2	30.3	1.51×10^2
Me_3C	81.5	50.9	0.27	1.37
$EtMe_2C$	81.5	50.9	0.27	1.37
cyclo-C_6H_{11}	92.5	33.4	3.02×10^2	1.51×10^3
	94.6	43.6	5.07	25.4
CH_2=CHCHMe	81.9	39.2	30.3	1.51×10^2
$PhCH_2$	74.7	43.2	6.07	30.4
$PhMe_2C$	76.9	53.5	9.61×10^{-2}	0.48

will be considered further along with the data concerning the addition of $CH_3OO^\bullet$ to CO.

The numerical values of br_e in combination with other kinetic parameters (see above) were used to calculate the activation energies and rate constants of the reactions of the alkoxy radicals of different structures with CO. The activation energies were calculated by Eq. (9), and the rate constants were calculated by the Arrhenius equation using the preexponential factor $A = 2.0 \times 10^8$ l mol^{-1} s^{-1} for the reactions in the gas phase and $A = 1.0 \times 10^9$ l mol^{-1} s^{-1} for the same reactions in the liquid phase. These A values are typical of radical addition to multiple bonds [8] (the difference is due to the higher collision frequency in the liquid [23]). The results of these calculations are given in Table 4. As can be seen from the calculated data, the activation energies of addition of various alkoxy radicals to CO range from 33 to 53 kJ/mol, and the rate constants in the gas phase at 300 K vary between 0.1 and 300 l mol^{-1} s^{-1}.

Reactions of $RO_2^\bullet$ with CO

The enthalpies of formation of the $RO^\bullet$ and $RO_2^\bullet$ radicals and the enthalpies of reactions (III) and (IV) are listed in Table 5. Both steps are exothermic; ΔH(III) ranges between –8 and –35 kJ/mol, and ΔH(IV) ranges between –236 and –278 kJ/mol. The high exothermicity of $ROOC^\bullet O$ radical decomposition is due to the low strength of the O–O bond being cleaved.

Table 5. Enthalpies of formation of the $RO^•$, $RO_2^•$, and $ROOC^•O$ radicals and the enthalpies of reactions (III) and (IV) (kJ/mol)

$R^•$	$\Delta H(RO^•)$	$\Delta H(RO_2^•)$	$-\Delta H(ROOC^•O)$	$-\Delta H$(III)	$-\Delta H$(IV)
$H^•$	39.0	10.5	118.1	18.1	236.4
$C^•H_3$	12.7	15.3	107.5	12.3	273.3
$CH_3C^•H_2$	–20.4	–17.8	136.8	8.5	277.1
$Me_2C^•H$	–58.7	–50.8	177.7	16.4	274.5
$Me_3C^•$	–91.1	–101.4	220.9	9.0	263.7
$EtMe_2C^•$	–107.6	–122.0	241.5	9.0	259.6
cyclo-$C_6H_{11}^•$	–65.7	–67.4	195.3	17.4	263.9
	–96.1	–99.8	227.7	17.4	261.9
$CH_2{=}CHC^•HMe$	55.0	81.3	64.0	34.8	274.5
$PhC^•H_2$	113.6	139.9	–1.8	27.6	278.1
$PhC^•Me_2$	42.1	55.3	85.9	30.7	265.5

The br_e parameter was calculated by formula (7) using experimental data available for the reactions of CO with $HO_2^•$ in the gas phase and with $Me_2PhCO_2^•$ in the liquid phase [20–22]. The initial data and calculation results are presented in Table 2. Using Eq. (8), we found the following classical barriers of the thermally neutral reaction ($E_{e,\,0}$) and r_e parameters for these reactions:

Parameter	$HO_2^•$	$Me_2PhCO_2^•$
br_e, (kJ/mol)$^{1/2}$	30.68	29.40
$E_{e,\,0}$, kJ mol^{-1}	101.6	93.3
$r_e \times 10^{10}$, m	0.406	0.389

As can be seen, the $E_{e,\,0}$ value for $HO_2^•$ addition is 8 kJ/mol higher than that for the addition of $Me_2PhCO_2^•$; i.e., these values differ substantially. The different reactivities of the $HO_2^•$ and $RO_2^•$ radicals are likely due to the polar effect, which differs from that of the radicals having O–H and R–O groups.

The TS structure determined by the quantum-chemical calculation for $MeO_2^•$ addition to CO is shown in Fig. 2. It is characterized by a rather long distance $r^{\#}(OC\ldots O) = 1.727 \times 10^{-10}$ m; i.e., this reaction is characterized by an early TS, like the reaction of $MeO^•$ with CO (Fig. 1). The enthalpy and activation energy values for reactions (III) and (IV) obtained by the quantum-chemical method are listed in Table 3.

As can be seen from the data in Table 3, the alternative DFT calculation at the B3LYP/6-311++G**//B3LYP/6-31G* level gives somewhat different results. However, if the coupled-cluster CCSD(T)/6-311++G** method using the B3LYP/6-31G* geometry is used in the calculation of the energy of the system, the differences in energy profiles of the reactions are negligible. This indicates that geometry optimizations by the CCD/6-31G* and B3LYP/6-31G* methods, which require essentially different amounts of computation, give very similar results. The most serious discrepancies are observed in the TS geometry for the addition of $MeO^•$ to CO and in the geometry of the weakly bonded prereaction and postreaction complexes. These complexes are of the van der Waals nature and are characterized by low bond energies (several kilocalories per mole).

A comparison of the theoretical and direct experimental data on the overall heats of reactions (I)–(IV) indicates that the discrepancies do not exceed 25 kJ/mol. However, the enthalpies of particular reactions (I)–(IV) calculated by the quantum-chemical methods differ considerably from their thermochemical estimates. The discrepancies are as large as 40 kJ/mol for the addition of the methoxy radical to CO and 58 kJ/mol for the addition of the methylperoxy radical. A qualitative distinction is also observed in the latter case: according to the quantum-chemical calculations, the enthalpy of formation of the intermediate compound $MeOOC^•(O)$ is positive, whereas the thermochemical calculation gives a negative value. Earlier quantum-chemical calculations [14] also gave a positive value of the enthalpy of the reaction $HO_2^• + CO \longrightarrow HOOC^•(O)$ (ΔH = 48.5 kJ/mol). A similar value of ΔH = 43.7 kJ/mol is also obtained by the CCSD(T)/6-311++G**//CCD/6-31G* method. The O–O, O–C, and C=O distances in the $HOOC^•(O)$ and $MeOOC^•(O)$ rad-

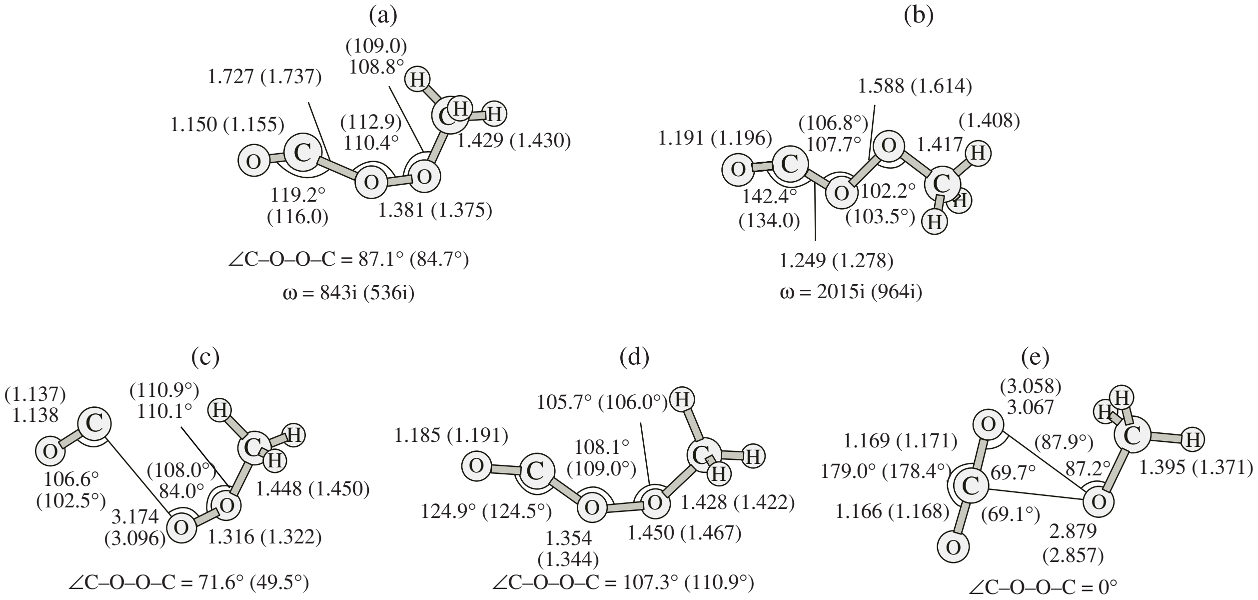


Fig. 2. Structures of (c) the prereaction complex and (a) the TS in the addition reaction of $H_3COO^\bullet$ to CO, (d) the $H_3COOC^\bullet O$ intermediate product and (b) the TS in the reaction of its decomposition to $H_3CO^\bullet$ and CO_2 and (e) the postreaction complex as determined by the CCD/6-31G* and B3LYP/6-31G* methods (in parentheses). The distances are in Å, the angles are in deg, and the imaginary frequencies are in cm^{-1}.

icals almost coincide and differ slightly from the published values [24]

Bond	$r \times 10^{10}$, m		
	HOOC$^\bullet$(O)	MeOOC$^\bullet$(O)	HOOC$^\bullet$(O) [24]
O–O	1.450	1.450	1.393
O–C	1.356	1.354	1.330
C=O	1.184	1.185	1.160

The increment method using experimental dissociation energies of the Me–OMe (344.3 kJ/mol) and Me–OOMe (288.7 kJ/mol) bonds is applied to the thermochemical estimation of the enthalpy of formation of the ROC$^\bullet$(O) and ROOC$^\bullet$(O) intermediates. To rule out any possible influence of the errors arising from the choice of the calculation method, the dissociation energies of these bonds were also calculated by the quantum-chemical method using three approaches: CCSD(T)6-311++G**//CCD/6-31G*, CCSD(T)6-311++G**//B3LYP/6-31G*, and B3LYP/6-311++G**//B3LYP/6-31G*. As a result, the following values were obtained:

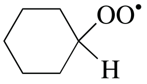
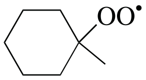
Method	$D_{\text{Me–OMe}}$, kJ/mol	$D_{\text{Me–OOMe}}$, kJ/mol
CCSD(T)/6-311++G**//CCD/6-31G*	329.9	262.8
CCSD(T)/6-311++G**//B3LYP/6-31G*	329.3	263.7
B3LYP/6-311++G**//B3LYP/6-31G*	311.8	246.5
Thermochemical	344.3	288.7

Estimating the discrepancy between these values and experimental data, one can determine the empirical corrections to the enthalpies of reactions (I) and (III). The thus-corrected ΔH values are given in Table 3 (in parentheses). When the B3LYP method is used for reaction (III), the signs of the values determined by the quantum-chemical and thermochemical methods are consistent. However, the error of the determination of the overall enthalpy of reactions (III) and (IV) becomes very high (~50 kJ/mol), whereas the error is reduced to 6 kJ/mol when the CCSD(T) coupled-cluster method is used. Thus, the calculation using empirical corrections is unlikely to lead to a very large error in the enthalpy of reaction (III). Therefore, the totality of quantum-chemical and thermochemical data suggests that the most probable ΔH(III) value is close to zero.

The formation of a complex between HOO$^\bullet$ and CO in low-temperature matrices was observed [24]. However, the spectrum of this weakly bonded, van der Waals complex exhibits a 22-cm^{-1} blue shift of the vibrational frequency of the carbonyl group, whereas the chemically bonded HOOC$^\bullet$(O) complex must be characterized by a red shift. According to CCD/6-31G* calculations, this shift is 235 cm^{-1}. At the same time, the calculations using both approaches (CCD and B3LYP) indicate a 5-cm^{-1} blue shift of this frequency in the spectrum of the van der Waals complex between MeOO$^\bullet$ and CO.

The activation energies calculated by the B3LYP/6-311++G**//B3LYP/6-31G* method are systematically underestimated by 15–20 kJ/mol as compared to the values determined using the more rigorous approaches CCSD(T)6-311++G**//CCD/6-31G* and CCSD(T)6-

Table 6. Activation energies and rate constants of the $RO_2^\bullet$ + CO $\longrightarrow$ $ROOC^\bullet O$ reaction in the gas and liquid phases

$RO_2^\bullet$	$-\Delta H$, kJ/mol	E, kJ/mol	k (300), l mol^{-1} s^{-1}	
			gas phase	liquid phase
$MeO_2^\bullet$	12.3	77.5	5.77×10^{-6}	2.88×10^{-5}
$EtO_2^\bullet$	4.4	80.3	2.09×10^{-6}	1.04×10^{-5}
$Me_2CHO_2^\bullet$	16.4	75.1	1.69×10^{-5}	8.44×10^{-5}
$Me_3CO_2^\bullet$	9.0	79.9	2.40×10^{-6}	1.20×10^{-5}
$EtMe_2CO_2^\bullet$	9.0	79.9	2.40×10^{-6}	1.20×10^{-5}
	17.4	74.4	2.19×10^{-5}	1.09×10^{-4}
	17.4	74.4	2.19×10^{-5}	1.09×10^{-4}
$CH_2{=}CHCH(O_2^\bullet)Me$	34.8	63.6	1.71×10^{-3}	8.54×10^{-3}
$PhCH_2O_2^\bullet$	27.6	68.0	2.91×10^{-4}	1.46×10^{-3}
$PhMe_2CO_2^\bullet$	30.7	66.1	6.28×10^{-4}	3.14×10^{-3}

311++G**//B3LYP/6-31G*. The imaginary frequencies of vibrations in the TS calculated using the B3LYP/6-31G* approach are also approximately two times lower than those calculated by the CCD/6-31G* method.

The activation energies of $MeO^\bullet$ addition to CO calculated by the CCSD(T)6-311++G**//CCD/6-31G* (31.2 kJ/mol) and CCSD(T)6-311++G**//B3LYP/6-31G* (28.9 kJ/mol) methods are rather close to the value determined using the IPM (38.5 kJ/mol). For the activation energy of $MeOC^\bullet O$ decomposition, the B3LYP/6-311++G**//B3LYP/6-31G* and IPM methods also give very close values (39.7 and 42.7 kJ/mol, respectively). The difference between the theoretical and IPM activation energies of the $MeO^\bullet$ + CO reaction generally does not exceed 20 kJ/mol.

The activation energy of $MeOO^\bullet$ addition to CO determined by the CCSD(T)6-311++G**//CCD/6-31G* (82.0 kJ/mol) and CCSD(T)6-311++G**//B3LYP/6-31G* (81.3 kJ/mol) methods agrees well with the value calculated using the IPM (77.5 kJ/mol). The B3LYP approach gives an underestimated value. In the very exothermic reaction of $MeOOC^\bullet O$ decomposition, the transition state is very early and the O–O bond extension is as small as 0.15 Å and is characterized by a very low activation barrier. For the calculations using the CCSD/6-311++G**//CCD/6-31G* and CCSD(T)6-311++G**//B3LYP/6-31G* approaches, this value is 21.5 and 117.8 kJ/mol, respectively. The B3LYP approach gives a much underestimated value. The empirical estimation of this barrier using the IPM is impossible because the necessary experimental data are lacking.

The br_e parameter in combination with other kinetic parameters (see above) was used to calculate the activation energies and rate constants of the reactions of various peroxy radicals with CO. The activation energy was calculated using Eq. (9), and the rate constants were calculated using the Arrhenius equation with the preexponential factors $A = 2.0 \times 10^8$ l mol^{-1} s^{-1} for the gas phase and $A = 1.0 \times 10^9$ l mol^{-1} s^{-1} for the liquid phase. The enthalpies of addition reactions (III) are listed in Table 4, and the results of calculation are given in Table 6. As can be seen from these data, the activation energy of the addition of various peroxy radicals to CO ranges from 64 to 80 kJ/mol and the rate constant of the reaction in the gas phase at 300 K varies from 2.1×10^{-6} to 1.7×10^{-3} l mol^{-1} s^{-1}.

Comparison of Addition Reactions

The data obtained in this work make it possible to compare the addition reactions to CO of the hydroxyl, alkoxy, and peroxy radicals with other addition reactions. Table 7 lists the enthalpies, activation energies, $E_{e,0}$ values, and r_e parameters for these reactions and for the additions of the methyl and methoxy radicals to multiple bonds. As can be seen from these data, the

Table 7. Enthalpies, activation energies, and $E_{e,0}$ and r_e values for the addition reactions of $RO^•$ and $RO_2^•$ to CO and other addition reactions of the $CH_3^•$ and $CH_3O^•$ radicals

Reaction	$-\Delta H$, kJ/mol	E, kJ/mol	$E_{e,0}$, kJ/mol	$r_e \times 10^{10}$, m
$HO^• + CO$	132.5	2.1	82.2	0.35
$CH_3O^• + CO$	83.1	38.5	97.0	0.38
$HO_2^• + CO$	18.1	82.2	101.6	0.41
$CH_3O_2^• + CO$	12.3	77.5	93.3	0.39
$CH_3^• + CH_2{=}CH_2$	98.5	30.3 [8]	82.6	0.37
$CH_3O^• + CH_2{=}CH_2$	89.1	13.7 [8]	65.2	0.36
$CH_3^• + O{=}CMe_2$	20.7	51.5 [8]	72.9	0.37
$CH_3^• + CH{\equiv}CH$	108.9	29.0 [8]	97.7	0.36

reactions of addition of the $HO^•$, $RO^•$, and $RO_2^•$ radicals (R = Me) to CO are exothermic, their enthalpies vary in a wide range (from –12 to –132 kJ/mol), and the activation energies range from 2 to 77 kJ/mol. The low activation energy of the reaction of the hydroxyl radical with CO (2 kJ/mol) is due to its high exothermicity ($\Delta H = -132.5$ kJ/mol). The $E_{e,0}$ values for the addition of oxygen-centered radicals to CO are rather similar (82–102 kJ/mol), and the r_e parameters for the additions of $HO^•$, $MeO^•$, and $MeO_2^•$ to CO almost coincide, being $(0.38 \pm 0.2) \times 10^{-10}$ m. The additions of the methoxy radical to ethylene and of the methyl radical to ethylene, acetone, and acetylene, for which $r_e = (0.365 \pm 0.005) \times 10^{-10}$ m, are also similar to the additions of the oxygen-centered radicals to CO. This additionally confirms the fact that the addition of the oxygen-centered radicals to CO is the first rate-determining step of the overall process. The quantum-chemical calculation showed that the activation energy of the forward reaction of O atom abstraction by the CO molecule from $MeO^•$ is very high (above 300 kJ/mol). A similar result was obtained for the reaction of $HO_2^•$ with CO [14]. Thus, the results of this work indicate unambiguously that the $HO^•$, $RO^•$, and $RO_2^•$ radicals first add to CO and then the resulting unstable radical decomposes to yield CO_2. This sequence of transformations is fully consistent with Hammond's postulate [25]. The kinetic parameters determined in the framework of the IPM make it possible to calculate the activation energies and rate constants of the reactions under study (Tables 4, 6).

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