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Asymmetric $PhCH(CH_3)CH_2OOOOC(CH_3)_2Ph$ Tetroxide as an Intermediate in Chain-Termination Processes and Chemiluminescence Excitation in the Oxidation of Cumene

R. F. Vasil'ev and G. F. Fedorova

Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia

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Abstract—The process of chain termination in the oxidation of cumene was studied. With the use of the semiempirical PM3 method, the structures of primary and tertiary peroxide radicals ($PhCH(CH_3)CH_2OO^{\bullet}$ and $Ph(CH_3)_2COO^{\bullet}$), the $PhCH(CH_3)CH_2OOOOC(CH_3)_2Ph$ tetroxide (TO) (the product of the combination of the above radicals), and TO decomposition products were studied and their heats of formation (ΔH_f^0) were determined; the activation energy of TO decomposition was evaluated. Similar values of ΔH_f^0 were obtained by the thermochemical method of group additivity. The PM3 calculation demonstrated that the irreversible decomposition of the asymmetric TO in a six-membered transition complex into the $PhCH(CH_3)CHO$ aldehyde, the $Ph(CH_3)COH$ alcohol, and O_2 is a synchronous process: dramatic changes in the bond lengths and bond orders occurred simultaneously. In this case, ~100 kcal/mol was released, which is sufficient for the chemiexcitation of triplet $R_{-H}{=}O$ and singlet O_2. A conclusion was drawn that a small impurity of $PhCH(CH_3)CH_2OO^{\bullet}$ primary radicals plays an important role in chain termination and is the only reason for the excitation of chemiluminescence.

INTRODUCTION

The oxidation of cumene ($PhCH(CH_3)_2$) is accompanied by low-intensity chemiluminescence, and the reaction mixture is used as a chemiluminescent probe for the analysis of antioxidants. Because the rate constant of chain termination ($2k_6$) is low, the steady-state concentration of peroxide radicals is comparatively high. Therefore, they are effectively scavenged (with rate constant k_7) even by low-activity antioxidants; this is favorable for the determination of their concentrations as well as (if $2k_6 > 10k_7$) the rate constant k_7 [1] by chemiluminescence.

The mechanism of hydrocarbon (RH) oxidation is well understood [2, 3], except for the process of chain termination (which was considered in detail elsewhere [4, 5]). The primary step of chain termination can be the disproportionation of peroxide radicals (Benson mechanism)

$$ROO^{\bullet} + ROO^{\bullet} \longrightarrow ROOH + R_{-H}OO \text{ (zwitterion)}$$

or the reversible recombination of two $ROO^{\bullet}$ to form an intermediate tetroxide

$$ROO^{\bullet} + {}^{\bullet}OOR \longleftrightarrow ROOOOR.$$

The irreversible (synchronous or stepwise) decomposition of this tetroxide can give various product combinations:

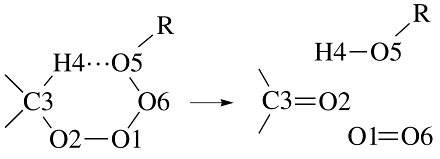
$$2RO^{\bullet} + O_2;$$

$$2R_{-H}{=}O + HOOH \text{ (Bennett–Summers mechanism)};$$

$$R_{-H}{=}O + ROH + O_2 \text{ (Russell mechanism)}.$$

Thus, the mechanism of chain termination is difficult to interpret because several reaction paths can occur and it is difficult to evaluate *a priori* their contributions.

Nevertheless, there is no question that the contribution of the Russell mechanism is crucial in the case of secondary and primary radicals. For example, in the case of R = $Ph\dot{C}HCH_3$ (oxidation of ethylbenzene ($PhCH_2CH_3$)), the corresponding $Ph(CH_3)CHOOOOCH(CH_3)Ph$ tetroxide decomposes through a six-membered complex into a ketone ($R_{-H}{=}O$), an alcohol (ROH), and dioxygen in accordance with the following reaction scheme:



Scheme. Rearrangement of a central tetroxide block according to Russell

Only in this process, which is sufficiently exothermic, does chemiluminescence occur; the products (trip-

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let ketone or singlet dioxygen) are chemiluminescence emitters.

However, this process is impossible in cumene oxidation, which occurs through $Ph(CH_3)_2COO^{\bullet}$ tertiary peroxide radicals, because the corresponding tetroxide lacks labile hydrogen. For this case, a complex scheme was proposed in the literature (see [4, 5]). This scheme includes the tetroxide decomposition into O_2 and oxy radicals

$$Ph(CH_3)_2COOOOC(CH_3)_2Ph \longrightarrow O_2 + 2Ph(CH_3)_2CO^{\bullet}$$

and the decomposition of the oxy radical into a ketone and a methyl (subsequently, methyl peroxide) radical

$$Ph(CH_3)_2CO^{\bullet} \longrightarrow PhCH_3C{=}O + CH_3^{\bullet} \xrightarrow{+O_2} CH_3OO^{\bullet}$$

Overall chain termination results from the reactions of all the above radicals (including cumyl) with each other.

However, this scheme cannot explain a decrease in $2k_6$ with increasing cumene concentration, and it does not include steps in which a chemiluminescence emitter could be excited. Earlier [6], we noted another possible direction of the process. In addition to tertiary radicals, primary radicals and, subsequently, primary peroxide radicals can appear in the reaction through hydrogen abstraction from one of the methyl groups:

$$PhCH(CH_3)_2 + \text{radical} \longrightarrow PhCH(CH_3)CH_2^{\bullet} \xrightarrow{+O_2} PhCH(CH_3)CH_2OO^{\bullet}$$

The steady-state concentration of primary radicals is low because primary hydrogen abstraction is less probable than tertiary hydrogen abstraction. However, chain termination by the reaction of primary radicals with tertiary radicals occurs rapidly because the asymmetric $PhCH(CH_3)CH_2OOOOC(CH_3)_2Ph$ tetroxide (TO) is formed in this case; this tetroxide has a labile hydrogen atom and can rapidly undergo irreversible decomposition, as in the case of ethylbenzene oxidation. The $PhCH(CH_3)CHO$ aldehyde is formed in the decomposition of TO; a fraction of molecules of this aldehyde can occur in an electronically excited state if sufficient energy is released in the process of decomposition.

In this work, the proposed mechanism was supported by thermodynamic and quantum-chemical calculations. The structure of TO and the heats of its reversible and irreversible decomposition reactions were calculated. The probable energy profile of irreversible decomposition and the energy and structure of a transition state were determined for the first time for a molecule from the class of tetroxides; a gain in the energy of the reaction was compared with the energy of the excited states of the products. Previously, the quantum-chemical calculations of equilibrium conformations were performed for several alkyl tetroxides; however, the possibility of studying reaction energy profiles and the structural evolution of complex molecules appeared only recently because of the accessibility of programs and fast computers.

CALCULATION PROCEDURE

The heats of formation ΔH_f^0 of the equilibrium structures of reactants and products were determined using the group additivity method (the additivity of thermochemical contributions or increments) according to Benson [7] or semiempirical (Dewar) quantum-chemical methods [8–10].

A study of the reaction path and the energies and structures of intermediate (including a transition state (TS)) and electronically excited states can be performed only with the use of quantum-chemical methods. The reaction is considered as the motion of an imaging point on a multidimensional potential-energy surface (PES) from the reactant valley through a saddle point (i.e., the TS) to the product valley. This is an idealized pattern because the concept of PES is rigorous only in the Born–Oppenheimer approximation (of fixed nuclei), which is hardly obeyed in the case of thermolysis. Indeed, the configuration of nuclei is rapidly changed in the process of instantaneous impact activation. Next, the activated molecule should undergo a rearrangement, that is, a horizontal transition (in particular acts, to the saddle region) before its deactivation, that is, in a very short time of about 10^{-14}–10^{-13} s. Many internal coordinates take part in energy redistribution, and the transition to the saddle region can occur via various routes rather than only along the minimum-energy reaction path. Nevertheless, important data on reaction mechanisms can often be obtained from the calculation of an idealized reaction path (by a slow change in the internal coordinates of a reactant following the minimum-energy reaction path).

All the quantum-chemical methods are approximate and complicated by random and systematic errors. They cannot be evaluated *a priori.* Vasil'ev [11] proposed and implemented the following procedures for increasing the signal-to-noise ratio: (a) multiple calculation or, equivalently, a great number of points (small steps of increasing the argument); (b) the rejection of improbably high values; and (c) an analysis of an iteration protocol for revealing "poor" points. As a result, for example, semiempirical calculations reproduced experimental activation energies E_a for the decomposition of dioxetanes to an accuracy of ~2 kcal/mol (which is better than that in *ab initio* calculations) and explained the effect of photon energy on photolysis and the reason for the high efficiency of spin-forbidden chemical generation of a triplet product. This approach was also used in this work.

The activation energy is calculated as the difference between the heats of formation of the transition state and the reagent: $\Delta H_f^0(TS) - \Delta H_f^0(TO)$. Semiempirical

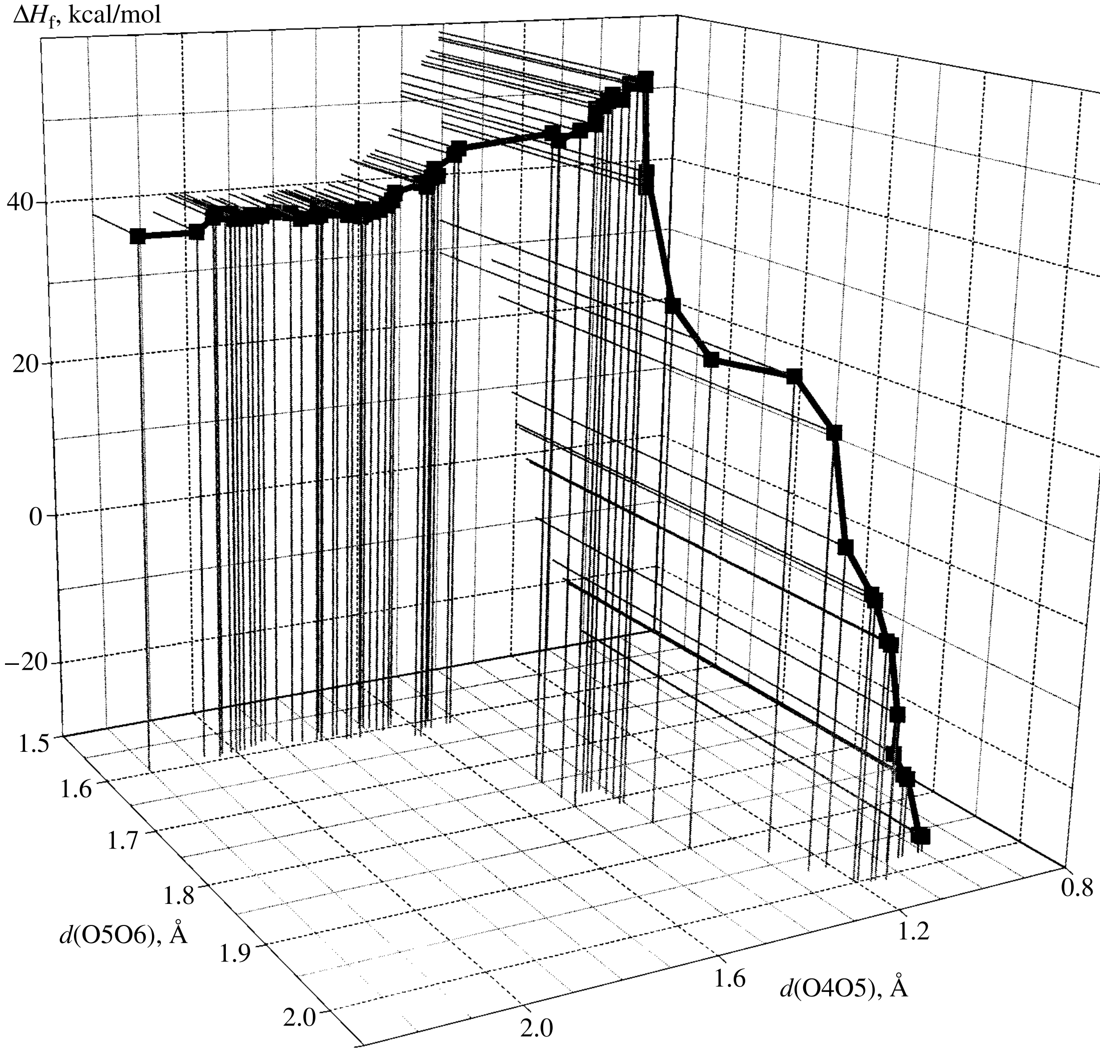

Fig. 1. Three-dimensional energy profile along the reaction path of tetroxide decomposition according to the Russell mechanism. Calculated by the semiempirical PM3 method with CI = 3HOMO + 3LUMO with full geometry optimization on varying O–O and C–C bond lengths.

methods are calibrated with the use of experimental data for the ground state of molecules, and configuration interaction (CI) should not be taken into account in the calculation of ΔH_f^0(TO). On the contrary, to determine ΔH_f^0(TS), the energy profile (the dependence of ΔH_f^0 on the reaction coordinate) should be calculated and its highest point should be taken. In this case, not only highest occupied molecular orbitals (HOMOs) but also lowest unoccupied molecular orbitals (LUMOs) should be considered; consequently, CI should be taken into account. We included CI = 3HOMO + 3LUMO. Configuration interaction always decreases energy; therefore, if this decrease is significant, the first points of the energy profile can be lower than the true values. Consequently, the initial points of the profile are determined with a systematic error, which cannot be estimated. Fortunately, the true shape of an initial portion is of no particular interest in contrast to a region near the activation barrier, where antibonding molecular orbitals (MOs) and repulsion states manifest themselves in full measure (the first points of the profiles in Figs. 1 and 2 are omitted).

RESULTS AND DISCUSSION

Let us consider the results of calculations summarized in Tables 1 and 2.

Heats of formation of the equilibrium conformations of stable molecules. The values of ΔH_f^0 of products (an alcohol and an aldehyde) calculated by the group additivity method and the semiempirical PM3 method are in good agreement, probably because both of the methods are based on the experimental heats of

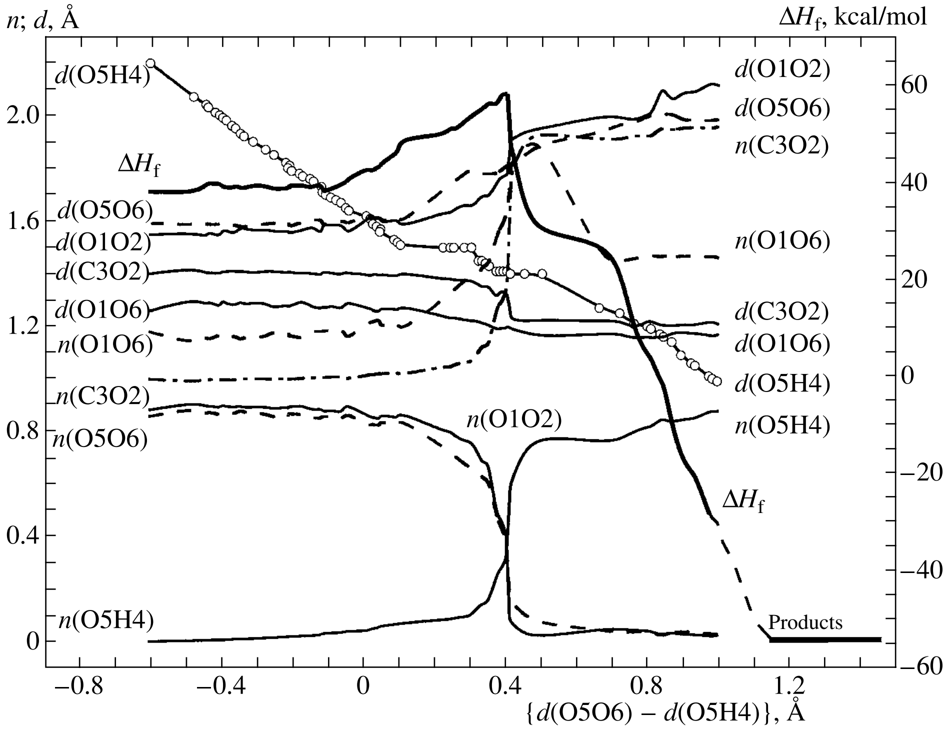

Fig. 2. Dependence of bond energies, bond lengths, and bond orders of the six-membered tetroxide center on the reaction coordinate of Russell decomposition, which is the difference between O5O6 and O5H4 bond lengths. Calculated by the PM3 method with CI = 3HOMO + 3LUMO. Points in the *d*(O5H4) curve illustrate the increment of bond lengths taken in the calculations.

formation of many compounds. However, the agreement was much worse in the calculations of ΔH_f^0 by the MNDO and AM1 methods.

Heat of formation of an equilibrium conformation of the tetroxide. We did not expect a high accuracy in the thermochemical calculations of ΔH_f^0 (ROOOOR). The point is that tetroxides were not isolated and studied experimentally, and their occurrence was supported experimentally only with the use of indirect methods. Six compounds were studied; the strength of the ROO–OOR bond (*D*) was estimated at 7.5–11 kcal/mol with an error of 5–20%. For the symmetrical dicumyl tetroxide ($Ph(CH_3)_2COO–OOC(CH_3)_2Ph$), *D* = 9–11 kcal/mol was obtained (see [12] and references therein). Various procedures for the evaluation of the group contribution ΔH_f^0 [O–(O)$_2$], which is required for the calculation of ΔH_f^0 (TO) by the Benson method, resulted in values within the range 11–17 kcal/mol [13, 14]. This is the main reason for the scatter of ΔH_f^0 (TO) (Table 1).

Note that only the PM3 method resulted in the exothermic formation of R^1OOOOR^3 from the primary and tertiary radicals $R^1OO^{\bullet}$ and $R^3OO^{\bullet}$. The MNDO and AM1 methods gave negative (!) values of the strength of the central O–O bond. For this reason, the PM3 method was used in this work.

Structure of tetroxides. The thermochemical calculation procedure according to Benson ignores the interaction of remote bulky substituents ("nongroup interaction"); however, this interaction can increase ΔH_f^0 by a few (up to ten) kcal/mol [7, p. 43]. This effect will result in several different values of ΔH_f^0 for different conformations.

A quantum-chemical method is free of this disadvantage. Six "quantum-chemical" values of ΔH_f^0 (TO) in Table 2 correspond to six of a great number of possible TO conformations. They primarily differ in torsion angles and, as a consequence, the distance between H4 and O5 atoms; this distance should shorten in the course of reaction to the standard length of the OH bond in alcohols. Of course, this distance is shortest in the least stable TO structure. It is most likely that various conformations result from different mutual orientations of $R^1OO^{\bullet}$ and $R^3OO^{\bullet}$ at the instant they combine. The PM3 method does not support a widespread notion that the central O–O bond is the weakest: the bond order is greater than unity and it is shorter than lateral O–O bonds. The problem invites further investigation.

Table 1. Parameters of the $PhCH(CH_3)CH_2OOOOC(CH_2)Ph$ (R^1OOOOR^3) and reactions with its participation

Reagents, intermediates, products, and parameters		ΔH^0_f, kcal/mol			
		thermochemical calculations	quantum-chemical calculations		
			semiempirical methods		
			PM3	MNDO	AM1
Tetroxide	R^1OOOOR^3	16–28	31, 33, 34, 33, 36, 38	55, 57, 57, 58	43, 43, 44, 46, 50
Primary and tertiary peroxide radical	$R^1OO^{\bullet}$	20	23	19	9
	$R^3OO^{\bullet}$	18	23	26	14
Strength of the $R^1OO–OOR^3$ bond (D)	$D = \Delta H^0_f(R^1OO^{\bullet} + R^3OO^{\bullet}) - \Delta H^0_f(R^1OOOOR^3)$	10–22	8–15	(–10…–13)	(–20…–27)
Transition state (TS = TO$^{\#}$)	TS = $(R^1OOOOR^3)^{\#}$	40	58	(150)	(113)
Activation energy of chain termination $E_{a,6}$	$E_{a,6} = \Delta H^0_f(TS) - \Delta H^0_f(R^1OO^{\bullet} + R^3OO^{\bullet})$	2**	12	(105)	(90)
Products of irreversible tetroxide decomposition	Alcohol R^3OH	–37	–35	–26	–36
	Aldehyde $R^1_{-H}{=}O$ (S_0)	–19	–19	–14	–17
	$O_2(^3\Sigma)$, $O_2(^1\Delta)$	0***, 22***	–4, 18	–15, 12	–27, 1
Sum of the products without dioxygen (Σ)	$R^3OH + R^1_{-H}{=}O$ (S_0)	–56	–54	–40	–53
Sum of the products including dioxygen ($^3\Sigma$)	$R^3OH + R^1_{-H}{=}O$ (S_0) + O_2	–56	–58	–55	–80
Chemiexcitation energy of products	$E = \Delta H^0_f(TS) - \Delta H^0_f(\Sigma)$	96	112	(190)	(166)
Excited states of $R^1_{-H}{=}O$	$R^1_{-H}{=}O(T_1)$, $R^1_{-H}{=}O(S_1)$	74**, 84***	61, 93	–	–

* Improbable data are given in parentheses.

** Experimental data for the secondary peroxide radicals of ethylbenzene [15].

*** Experimental data [16].

Energy profile of tetroxide decomposition. It is believed that, in accordance with the scheme, the process could begin with the transfer of the H4 atom to O5, that is, the cleavage of C3H4 and O5O6 bonds and the formation of the O5H4 bond. Figure 1 demonstrates the profile along a minimum-energy reaction path on gradually shortening d(H4O5) and lengthening d(O5O6) through a maximum in the transition state region. In this case, other internal coordinates were also changed, and the program generated a set of these coordinates at which the energy had a minimum value at each step of calculation. Even though we restrict our consideration to the six-membered ($N = 6$) tetroxide center, the rearrangement occurs in 12-dimensional ($3N–6 = 12$) space and the question arises of the pictorial representation of the results. The image of a three-dimensional plot is the feasible upper limit on a two-dimensional carrier (a sheet of paper) (Fig. 1).

Mechanism of processes in a transition state region. Figure 2 shows how the lengths and orders of other bonds are changed. Here, the difference between the lengths of the O5–O6 and O5–H4 bonds was taken as a reaction coordinate (points in the d(O5H4) curve illustrate an increment in the bond length taken in the calculation). The PM3 calculation demonstrated that irreversible decomposition in the six-membered transition complex is a synchronous process: abrupt changes in bond lengths and bond orders occurred simultaneously. In principle, another mechanism is also possible: the initial elimination of an alcohol and the subsequent reactions in the $–R_{-H}OOO–$ biradical. However, an attempt to optimize the biradical structure was unsuccessful.

Table 2. Heats of formation (ΔH_f^0, kcal/mol), bond lengths (d, Å), bond orders (n), and bond and torsion angles (ω and φ, respectively, deg) calculated by the PM3 method for five equilibrium TO conformations (TO_1, TO_2, TO_3, TO_4, and TO; without considering configuration interaction (CI = 0)) and for the transition state ($TO^{\#}$; CI = 3HOMO + 3LUMO) of the $PhCH(CH_3)C3(H)H4O2O1O6O5C7H(CH_3)_2Ph$ tetroxide

Parameter	TO_1	TO_2	TO_3	TO_4	TO	$TO^{\#}$
ΔH_f^0	31	34	33	33	38	58
d(O5H4)	4.16	3.11	3.62	3.62	2.59	1.40
d(O5O6)	1.58	1.58	1.60	1.60	1.57	1.81
d(O1O6)	1.27	1.28	1.27	1.27	1.30	1.20
d(O1O2)	1.60	1.59	1.58	1.58	1.53	1.78
d(C3O2)	1.39	1.39	1.38	1.38	1.39	1.32
d(C3H4)	1.11	1.11	1.11	1.11	1.12	1.31
n(O5H4)	0.00	0.00	0.00	0.00	0.00	0.33
n(O5O6)	0.87	0.87	0.87	0.87	0.89	0.38
n(O1O6)	1.19	1.17	1.18	1.19	1.14	1.64
n(O1O2)	0.85	0.86	0.85	0.85	0.90	0.40
n(C3O2)	1.03	1.02	1.03	1.03	1.00	1.36
n(C3H4)	0.96	0.96	0.96	0.96	0.96	0.47
ω(C3O2O1)	109	110	110	110	112	107
ω(O2O1O6)	101	104	100	100	105	130
ω(O1O6O5)	99	99	99	99	105	90
ω(O2C3H4)	111	112	111	111	108	109
φ(O2O1O6O5)	102	–91	–94	–94	96	82
φ(C3O2O1O6)	–164	–104	169	167	–116	–68
φ(O1O6O5C7)	–151	–175	–152	–156	151	165
φ(H4C3O2O1)	–21	–7	–40	–40	35	7

Chemiexcitation. When the tetroxide irreversibly decomposes to a carbonyl compound (R_{-H}=O), an alcohol (ROH), and O_2, ~100 kcal/mol is released, which is sufficient for the excitation of the electron levels of R_{-H}=O and O_2 (Table 1).

The singlet ground state S_0 of the tetroxide correlates with the first excited singlet state of products: the set R_{-H}=O(S_0) + ROH(S_0) + $O_2(^1\Delta)$; 22 kcal/mol. The following state that includes the $^1\Delta'$ state, which is degenerate with the $^1\Delta$ state, is energy degenerate with it. Next is the set R_{-H}=O(S_0) + ROH(S_0) + $O_2(^1\Sigma)$; 37 kcal/mol. The fourth excited singlet state corresponds to the set R_{-H}=O(T_1) (chemiluminescence emitter) + ROH(S_0) + $O_2(^3\Sigma)$. Therefore, in accordance with experimental data, high (0.03–0.14; measured for several secondary $ROO^{\bullet}$ [17]) yields of $O_2(^1\Delta)$ and low (of the order of 0.001 [6]) yields of the R_{-H}=O(T_1) triplet ketone would be expected.

The behavior of the O1O6 bond order of the future molecule of O_2 is of interest. At the beginning of a final stage, its value tends to 2; this corresponds to the double bond of singlet O_2: the system moves along a singlet PES. However, the end point—triplet dioxygen—is a biradical with a bond order of 1.5, and radiationless intersystem crossing to the lowest triplet PES is inevitable: the set R_{-H}=O(S_0) + ROH(S_0) + $O_2(^3\Sigma)$.

Kinetic consequences. As the concentration of cumene was increased, the rate and efficiency of replacement of $Ph(CH_3)_2CO^{\bullet}$, $CH_3^{\bullet}$, and $CH_3OO^{\bullet}$ radicals by $R^1OO^{\bullet}$ and $R^3OO^{\bullet}$ cumyl radicals, their steady-state concentrations, and the contribution of processes whose mechanism was discussed above to the rate of termination increased. This resulted in a decrease in the rate constant of termination $2k_6$ [6]. According to our data, $2k_6 = (2.0 \pm 0.2) \times 10^5$ l mol^{-1} s^{-1} at 333 K and a cumene concentration of 5 vol % in chlorobenzene. The value of $2k_6$ decreased with concentration and became constant and equal to (3.9 ± 0.2) × 10^4 l mol^{-1} s^{-1} at 50%.

CONCLUSIONS

A quantum-chemical study of the irreversible decomposition of a tetroxide (an intermediate in the termination of hydrocarbon oxidation chains) was performed for the first time. The parameters of the R^1OOOOR^3 tetroxide (a product of the combination of tertiary ($R^3OO^{\bullet}$) and primary ($R^1OO^{\bullet}$) cumyl peroxide radicals) were determined. Attention was focused on an analysis of bond orders because they reflect changes in the molecular structure (an electron-density flow from one bond to another) better than bond lengths. It was found that, in accordance with published data [18], the semiempirical PM3 method gave the best agreement with experimental data and thermochemical calculations. A conclusion was drawn that irreversible decomposition to a carbonyl product (R_{-H}=O), an alcohol (ROH), and dioxygen is a concerted process and an elementary act in which chemiluminescence is excited. An "impurity" of the $R^1OO^{\bullet}$ radical, which is the product of less probable hydrogen atom abstraction from the methyl group of cumene by radicals, plays an important kinetic role because the reaction $R^1OO^{\bullet}$ + $R^3OO^{\bullet}$ strongly contributes to the termination of cumene oxidation chains.

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