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Mechanism and Energetics of 1,2-Addition of Dioxygen $^1O_2(^1\Delta g)$ to Ethylene

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Abstract—The optimal geometry and energy parameters for five electronic states of the $\{^1O_2\ (^1\Delta g) + C_2H_4\}$ system that characterize the elementary reactions of two-step 1,2-addition giving the dioxetane molecule were calculated using various quantum chemical methods (RHF, B3LYP, MPn, n = 2−4, QCISD, and CCSD) and basis sets (from 6-31+G(d,p) to 6-311+G(3df,2p) and pVTZ). The first step of the reaction was found to pass through the ethylene perepoxide intermediate. Considering experimental and published calculated data, the dependence of the results on the calculation procedure was exampled. The higher-level methods (QCISD, CCSD, CASSCF) and the standard methods (DFT, MPn) were found to reliably lead to virtually the same description of the energetics of this two-step reaction corresponding to experimental estimates.

The interest in oxidation reactions of various inorganic and organic substrates with singlet dioxygen $^1O_2(^1\Delta g)$ is dictated by a number of factors, as these reactions determine the processes important for catalysis, environmental issues, medicine, and some other areas [1−8]. Studies of the mechanisms of these reactions have a rather long history and comprise not only experimental works but also theoretical, in particular, quantum chemical modeling [9−18]. Among these systems, the system that plays the role of "prototype" due to its small size has been most theoretically studied to date.

Out of the attempted adequate microscopic descriptions of the mechanisms of possible reactions in this prototype system, we would like to note the series of studies [15−18] (see also the references therein) in which the system was considered resorting to different quantum chemical approaches including high-level numerical methods (CASSCF, CCSD, and so on). The key outcome of these works was the conclusion about the two-step mechanism of 1,2-addition to give 1,2-dioxetane (DO), which passes through an intermediate, as can be seen in Scheme 1. It can also be seen that the energy profile of this 1,2-addition is determined by four parameters: ΔE_{Int}, ΔE_{Pr}, E_1^*, and E_2^*. These are differences between the energies of particular electronic states and, except for the last one, the sum of the energies of the reactants or the energy of the weakly bonded intermolecular complex of the reactants (RgC). The first two parameters characterize the relative stability of the system in its minima, thus determining the endo- or exothermic nature of each step, while the other two values correspond to the saddle points and describe the activation barriers of each step.

The nature and stability of all stationary points of the reaction were analyzed in [15−18] using the approximate spin projection method based on the Heisenberg model of ferromagnetism with modified determination of the energy gradient and the Hessian matrix (AP method). It should be emphasized that this method is specially directed toward the search for the optimal structure of singlet biradical systems and can partly eliminate the errors related to spin mixing in finding the local minima. The results of calculations of the energetics, geometry, and some other parameters of these points (TS1, Int, TS2) demonstrated the biradical (BR) nature of these species (but not the DO molecule). This conclusion was drawn using various density functional theory (DFT) schemes and validated at a higher level of theory (see below).

However, a number of issues remained unexplored. First of all, this is the chemically important problem of how the reaction kinetics is affected by replacement of H atoms by electron-donating or -withdrawing substituents. The effect of molecules of the medium on the elementary reaction has not been investigated either. No optimal calculation protocol for extended systems (in connection with medical applications) was proposed. The triplet configurations of various states were considered too briefly, in particular, triplets were not obtained for the TS2 states and 1,2-dioxetane. Our interest in oxidation reactions involving dioxygen

Table 1. Ranges of the energy parameters for Scheme 1 (kcal/mol) according to calculations by various DFT schemes

| Parameter	A	B	C	D
E_1^*	8.5–10.4	14.0–18.0	17.1–37.0	16.7–18.7
ΔE_{PE}	2.7–4.3	1.8–9.8	16.1–20.6	4.0–9.2
E_2^*	19.1–20.8	6.8–10.6	22.4–31.7	9.9–12.0
$-\Delta E_{DO}$	37.3–39.3	19.8–30.8	19.8–26.8	24.6–33.1

A. Results of (U)B3LYP calculations with four basis sets with full geometry optimization for the critical points.
B. Data of four DFT schemes with the 6-31+G(d) basis set in terms of the spin-projected AP procedure for the BR pathway of both reaction steps [16].
C. Data of three DFT schemes with the 6-31+G(d) basis set for fully PE pathway of both reaction steps [16].
D. Refined data of six DFT schemes with the 6-311 + G(d,p) basis set in terms of spin-projected AP procedure for the BR pathway of both reaction steps [17, 18].

$O_2(^1\Delta g)$ is directly related to the above issues and involves reactions with more complex and extended substrates (styrenes, anthracene, etc.) [19–22]. Nevertheless, we still started the modeling of elementary steps of these reactions from the same prototype system $\{^1O_2 + C_2H_4\}$ to pursue two key goals. The first one was to acquire the experience of modeling such systems and the second was to attempt to find an efficient but rather economical calculation method for extended systems and to answer the question of how necessary it is to use the AP procedure proposed in [15–18] in all cases of determining the geometrical and energy characteristics of electronic states.
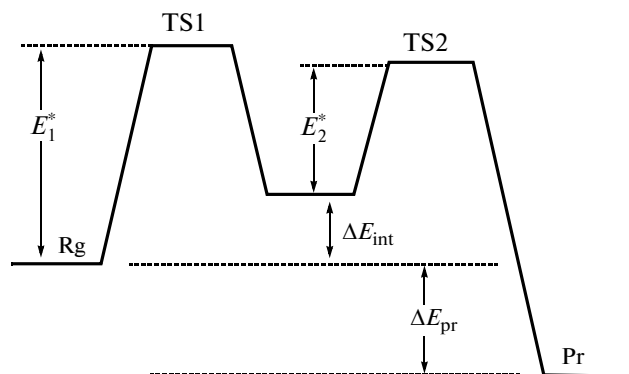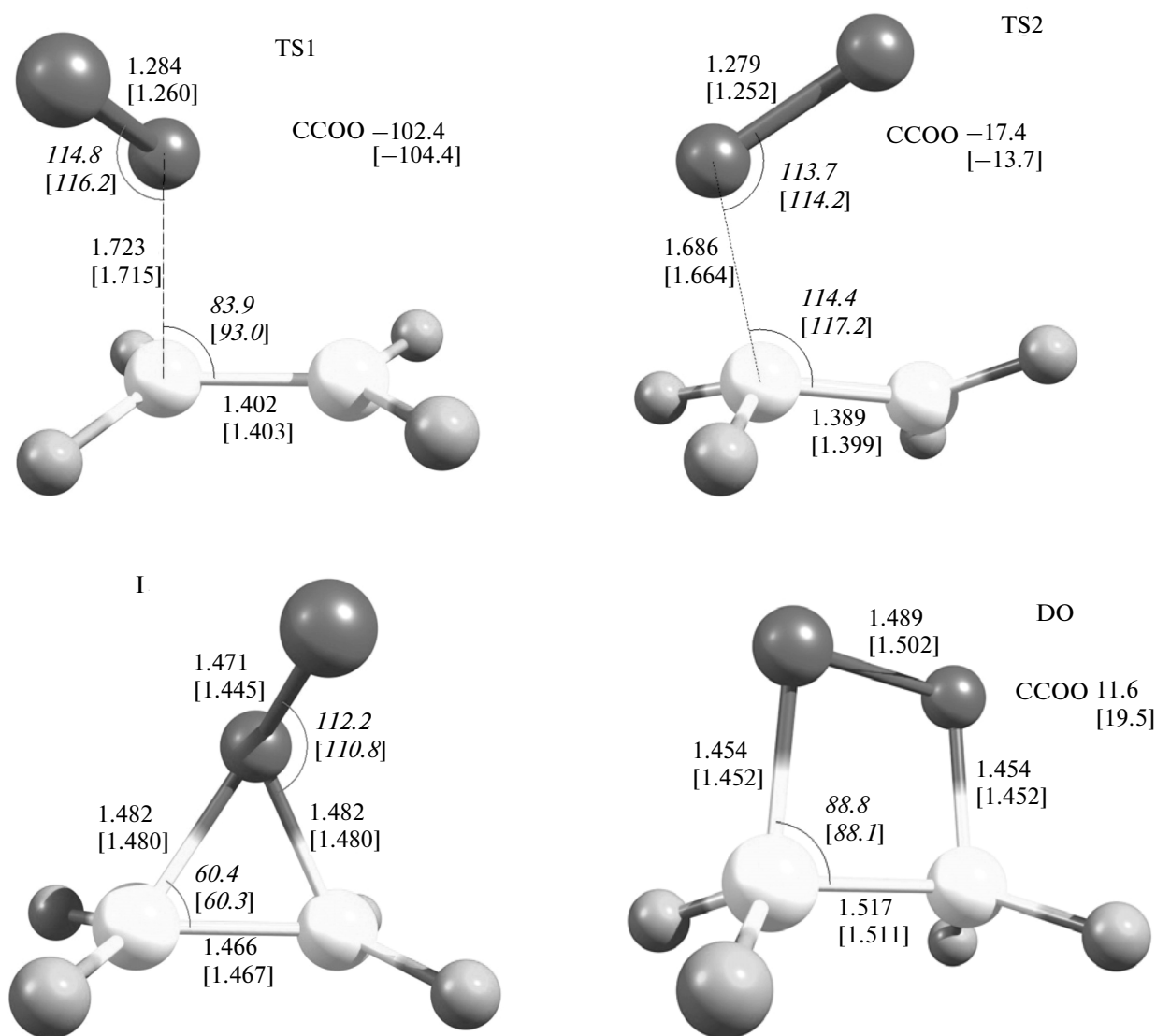

Scheme 1.

CALCULATION PROCEDURE

The calculations were carried out using various quantum chemical procedures, including those that have not been used previously. Several versions of DFT/B3LYP with different parametrizations (Gaussian-03/09 and Gamess) and several functionals in the M11 and CAMB3LYP schemes were used. Also, we utilized methods of the perturbation theory MPn

($n = 2$–4) and one version of the configurational interaction method (QCISD method), which is the quadratic modification of the coupled cluster singlets and doublets (CCSD) technique. A number of basis sets from 6-31+G(d,p) to 6-311+G(3df,2p) and the pVDZ and pVTZ basis sets extended by diffuse functions were employed. Most of calculations of the optimal geometric parameters for all states were performed with the 6-311+G(d,p) and 6-311+G(2d,2p) basis sets. The critical points (minima and saddle points) were found by two methods: with inclusion of the normal-mode analysis in terms of the TS procedure (Gamess) and the QST2(3) procedure (Gaussian-03/09). A special series of calculations was carried out to verify the equivalence of both methods for determination of these points. For all methods (DFT, MPn and so on), both restrained and unrestrained protocols were used.

RESULTS AND DISCUSSION

The prototype system was investigated in three stages. In the first stage, the possibility of formation of the DO product in one step was analyzed. Our attempts to model the process as a one-step reaction using various calculation methods, mainly B3LYP and MP2 with the 6-311+G(d,p) basis set, were unsuccessful. The transition structures obtained in some cases proved to be saddle points with several (most often, two) imaginary frequencies and, moreover, they failed to pass the intrinsic coordinate (IRC) determination test.

Subsequently, we considered the two-step oxidation of ethylene to the DO molecule, which may possibly involve an intermediate according to Scheme 1. The optimal geometry and the energies for the five critical points arising along this reaction pathway were calculated using various DFT protocols and by MP2 with the above-indicated basis sets according to the above-described procedure. Irrespective of the calculation procedure used (method, parametrization, basis set, search for the points), the results provided three key conclusions. First of all, this confirmed Scheme 1 proposed previously [15–18]. To a reasonable accuracy, the optimal geometry of the critical points depends little (figure) on the particular calculation method used. However, the estimates of all indicated energy parameters substantially depend on the calculation procedure (and to a much lesser extent on the basis set), providing different conclusions concerning the rate-limiting step of the whole reaction. According to DFT calculations, this is the second step, Int → TS2 → DO ($E_1^* < E_2^*$), whereas according to the MP2 calculations, $E_1^* \approx E_2^*$ (Tables 1 and 2). Note that these conclusions are fully retained if the zero-point vibration energies of all critical points are taken into account.

Optimal geometrical parameters of the electronic states of the $\{^1O_2(^1\Delta g) + C_2H_4\}$ system in the critical points (Scheme 1) according to B3LYP and MP2 (in brackets) calculations with the 6-311+G(d,p) basis set.

It is pertinent to compare the obtained DFT and MP2 calculation results concerning the energies and geometries of critical points with experimental results and with relevant published theoretical data. Unfortunately, only the activation energy of the whole reaction ($E^* \approx 21$ kcal/mol) and the energy of formation of DO from the reactants ($-\Delta E_{DO} \approx 35.5$ kcal/mol) are known from experiments with molecular beams in the gas and thermochemical measurements [23−25]. If we take that activation of the whole reaction is determined by $E^* = \max(E_1^*, E_2^*)$, our estimates obtained by both methods can be considered to be in a reasonable agreement with the experimental data. However, it is necessary to note that the data of Table 1, which briefly presents for comparison the results of DFT cal-

culations taken from the literature, in particular, obtained by the AP method [3, 4], clearly show differences in the values of virtually all of the energy parameters, which attests to the dependence of the results on the calculation procedure.

No experimental data on the geometry of the critical points TS1, Int, and TS2 are available; therefore, the obtained results can be compared only with the available published data [5−8]. This demonstrated the considerable differences in the Int geometry and, as a consequence, the TS2 geometry, although to a much lower extent. According to our data obtained at this calculation level, Int has the structure of the ethylene perepoxide (PE) rather than BR, as has been indicated by most of calculations [5−8] in which the relative stability of these isomers was discussed in considerable

Table 2. Ranges of the energy parameters for Scheme 1 (kcal/mol) according to calculations by perturbation theory methods MPn, n = 2–4

Parameter	A'	B'	C'
E_1^*	16.9–21.6	25.4–29.6	23.5–27.7
ΔE_{PE}	8.4–14.7	6.4–9.9	5.7–10.5
E_2^*	21.1–24.3	33.6–36.1	32.7–35.8
$-\Delta E_{DO}$	30.9–37.6	37.4–39.9	34.6–38.8

A'. Data of (U)MP2 calculations with four basis sets with full geometry optimization for the critical points and using the B3LYP geometry of these points.
B'. Data of the MP3 calculations with three basis sets for the optimized geometry of critical points found by MP2 and B3LYP calculations.
C'. Data of the MP4(SDQ) calculations with three basis sets for the optimized geometry of critical points found by MP2 and B3LYP calculations.

detail. We attempted to analyze this situation in a separate series of calculations using various methods (DFT and MPn, n = 2–4, QCISD) and various basis sets (from 6-31+G* to 6-311+G(3df,2p) and cc-pVTZ). The calculations were done using the optimal geometry of the PE structure we found and the geometry of the BR structures from [18]. It follows from the performed analysis that the relative stability of the isomers is markedly affected by the calculation procedure; however, in most cases, in particular, when extended basis sets are used, for example, 6-311+G(2d,2p), these differences are moderate (≤5 kcal/mol) but in favor of the PE structure. An additional series of B3LYP/6-311+(2d,2p) and CCSD/aug-cc-pVDZ calculations with direct optimization of a number of TS1-like structures with different starting geometry also support the conclusion that the PE structure is preferred. All series of calculations also prompt the conclusion about a "non-rigid" character of the intermediate structure.

The next stage of calculations of the energy parameters of the reaction made use of the perturbation theory methods MPn (n = 3, 4) and a higher-level method QCISD. For a number of reasons, in particular, for time saving, in this series of calculations carried out with five basis sets (from 6-31+G** to 6-311+G(3df,2p) and cc-pVTZ), we used the geometries of all critical points that we found at the DFT and MP2 levels with the same basis sets. The results of this series of calculations are fully consistent with Scheme 1; in all cases, the advantage of the PE structure for Int and the non-rigid character of Int were confirmed. However, it should be emphasized that irrespective of the basis set used, MPn methods (n = 3, 4) markedly (≈10 kcal/mol and more) increase the values for both barriers E_1^* and E_2^* (especially the latter) with respect to the MP2 and DFT methods and simultaneously noticeably deteriorate the agreement with the experimental data.

A different situation is predicted by the QCISD calculations with the five indicated basis sets using the critical point geometry found in the B3LYP and MP2 calculations with the same basis sets. The results of these calculations are presented in Table 3 (columns A'' and B'') together with published data (columns C'' and D'') and experimental estimates. It follows from the Table that irrespective of the geometry of the points, the QCISD calculations are in reasonable quantitative agreement with experimental data and provide the same conclusions concerning the rate-limiting step of the reaction in question. In both cases, this is the first endothermic step RgC → TS1 → Int (PE), although when the MP2 geometry is used, the

Table 3. Ranges of the energy parameters for Scheme 1 (kcal/mol) according to higher-level calculations

Parameter	A''	B''	C''	D''	Experiment [23–25]
E_1^*	17.6–19.1	16.7–19.8	17.5–25.8	21.6–28.2	≈21
ΔE_{PE}	8.7–9.1	8.8–9.5	7.0–12.1	17.2–20.0	
E_2^*	6.3–11.3	14.9–16.5	7.8–9.5	23.0–27.3	
$-\Delta E_{DO}$	35.0–37.0	34.8–36.9	29.2–31.7	24.2–31.8	≈35.5

A''. Data of the QCISD calculations with four basis sets for the optimized geometry according to B3LYP calculations.
B''. Data of QCISD calculations with four basis sets for the optimized geometry according to MP2 calculations.
C''. Data of CASSCF and CASPT2 calculations with the 6-31+G(d) basis sets for the AP/B3LYP geometry with the same basis set and CCSD(T) calculations with the 6-311+G(d,p) basis set for the AP/B3LYP geometry together with the refined data of CASPT2 (10e, 10o) and CCSD (2e, 2o) calculations with the 6-311+G(d,p) basis set for CASSCF(10e, 8o) geometry with the same basis set for the BR reaction pathway [16–18].
D''. Data of CASSCF and CASPT2 calculations with the 6-31+G(d) basis set for the AP/B3LYP geometry with the same basis set for the fully PE reaction pathway [16].

two steps become more equivalent but the inequality $E_1^* > E_2^*$ still holds.

For additional verification, the energies of all critical points of Scheme 1 were estimated at the CCSD level with the aug-cc-pVDZ basis set. In these calculations, the optimal geometries used for the minima were those obtained at the same level, while for saddle points, the geometries found at the B3LYP level with 6-311+G(2d,2p) were used for time saving. The results obtained at these levels, $E = 6.7$, $E = 37.7$; $E_1^* = 22.0$ and $E_2^* = 13.1$ kcal/mol, fully correspond to the QCISD data and actually do not go beyond the ranges presented in Table 3 (A″, B″). This confirms the statement about the stability of numerical energy estimates made by high-level methods. In this case, inclusion of the zero-point vibrations energies does not change the essence of the conclusions.

This conclusion is supported by comparison of the data of our QCISD and CCSD calculations with the results from publications [15−18], which were also obtained by higher-level CCSD and CASSCF methods but using other basis sets and a different geometry of critical points. It can also be seen from this comparison that numerical estimates of all energy parameters in the "mixed" mechanism with the PE intermediate we obtained are much closer to those for a biradical rather than for fully perepoxide mechanism. As a result, the application of higher-level methods largely mitigates the problem of dependence of the results of calculations of energy parameters on the calculation procedure, in particular, on the details of the geometrical structure of critical points.

Giving obvious preference to the results obtained in terms of QCISD and CCSD over DFT and MP2, we arrive at the key structural and chemical result of this study. This is the conclusion about the two-step mechanism of the 1,2-addition $^1O_2 + C_2H_4 \rightarrow OD$ involving the formation of intermediate with non-rigid PE structure. Both TS1 and TS2 retain the biradical geometry, although for the latter species, a certain conformational non-rigidity can also be noted.

The performed analysis also provides a methodical conclusion related to the possibility of calculations of extended systems where the use of high-level methods to the full extent is problematic. A reasonable approach in this case is apparently to find the geometry of critical points by the DFT and/or MP2 calculations and then to refine the energy parameters by probably any higher-level method.

The results obtained in this study allow one more interpretation of the mechanism of the addition in the $\{^1O_2 + C_2H_4\}$ system if the two steps are considered as separate reactions giving perepoxide and dioxetane molecules, respectively. For complete consideration, it is reasonable to analyze the subsequent decomposition of the dioxetane molecule to give two aldehyde molecules [26]. Then the first step involves the asymmetric attack of the multiple C=C bond by the $^1O_2$ molecule followed by either symmetrical (PE) or asymmetrical (BR) addition to the substrate. In this case, the non-rigid structure of the intermediate can be interpreted as interconversion of isomers PE ↔ BR. A similar possibility of symmetrical and/or asymmetrical attack of the multiple C=C bond was encountered in our earlier study of oxidation of ethylene and some other substrates with peroxycarboxylic acids [27, 28], where the subsequent similar dual addition of a reactive oxygen atom gave different products, for example, oxide and/or ester in the case of ethylene. Our calculations also imply the possibility of considering the second step as a separate reaction, which is in any case highly exothermic. The occurrence of this reaction from the BR form has a lower activation energy, as it does not require cleavage of the PE C−O bond. Undoubtedly, of interest is also decomposition of the dioxetane molecule to give two aldehyde molecules from the ground (singlet) and triplet states. The results of this consideration will be published elsewhere.

In conclusion, note that, in our opinion, owing to the non-rigid structure of the intermediate found in the calculations, the 1,2-addition of singlet oxygen to ethylene should better be considered as a two-step reaction.

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