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The DDCI Method Applied to Reactivity: Chemiluminescent Decomposition of Dioxetane

E. Rodríguez and M. Reguero*

Departament de Química Física i Inorgànica i Institut d'Estudis Avançats,
Universitat Rovira i Virgili, Pl. Imperial Tarraco 1, 43005-Tarragona, Spain

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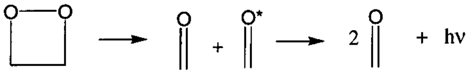
This paper describes how the DDCI method can be applied to study the reactivity of dioxetane, a molecule that decomposes thermally into 2 formaldehyde molecules. One of these molecules is in an excited state that decays radiatively. Previous experimental and theoretical studies proposed that this decomposition takes place through a stepwise mechanism, but the relative energies of the two transition states involved in the reaction have been a source of controversy. While experimental evidence shows that the first transition state is higher in energy, one of the latest and most accurate theoretical studies does not produce the same results. In this paper the projection of the reaction path over the ground-state potential energy surface (PES) is calculated with a conventional method. We calculate the energies of the species on the excited states involved in the reaction by adding the energy of the vertical transition to the ground-state energies. To do so we use the DDCI method, which was specifically designed to calculate energy differences. The first transition state, located in the ground-state PES, is found to be higher in energy than the second one, located in the T_1 PES. This result agreed with the experimental result.

Introduction

The theoretical elucidation of reaction mechanisms is, in general, a difficult task. One of the difficulties arises from the need to compare the energies of species at points that are sometimes far apart on the potential energy surface (PES). When excited states are involved in the reaction mechanism, the difficulty increases, as the energies of different states must also be compared. Moreover, if a mechanism is to be quantitatively described, the data must be obtained with the same level of accuracy. This requirement sometimes makes the theoretical calculations much more expensive, as the study of excited states requires greater computational effort.

The aim of this paper is to show how the difference dedicated configuration interaction method (DDCI),[1] an economical method that is usually used to calculate energies of excited states in static problems, performs well in the qualitative and possibly quantitative study of chemiluminescent decomposition of dioxetane. This method, described in more detail in Section II, has been specifically designed to calculate vertical energy differences, and has already proved to give excellent results even in the more severe benchmarks when it is applied to calculate optical, magnetic, and spectroscopic energy differences.[2−4] It has also been applied to locate avoided crossing by means of adiabatic potential energy curves[5] and to compute potential energy surfaces of excited states when the surface of the ground state is known by independent theoretical calculations or experimental data.[6,7] This kind of application is extended here: the potential energy surface of a chosen reference state is computed with a conventional method and then the energy difference between the reference state and the other states involved in the reaction is calculated with the DDCI method at the crucial points of the reaction path (minima, transition states, intersections, etc.). From these data the PES of the other states can be built. The challenge this time is to apply the method to a nonacademic problem and to compare the DDCI results with experimental data. The overall cost of the whole set of calculations is expected to be low. First, the cost of the conventional calculations can be kept to a minimum by making an appropriate choice of reference state (one whose electronic distribution can be easily described). Second, the other states involved in the reaction are generally excited states that often require expensive conventional calculations because of their complex electronic configuration. In our proposal, however, these energies are obtained with the cheaper DDCI method, which means a non-negligible saving in the computational effort but which still ensures the accuracy of the results.

SCHEME 1



The case under study is the chemiluminescent decomposition of dioxetane. This compound decomposes with low activation energy into two formaldehyde molecules, one in the ground state and the other mostly in a triplet state (Scheme 1) but occasionally in a singlet excited state. The radiative decay of the excited molecule gives rise to the luminiscence, mainly phosphorescence with a small portion of fluorescence.[8−13]

This reaction has been thoroughly studied several times from the theoretical point of view,[14−21] but we have decided to study it again because, although most previous studies propose the broadly accepted stepwise reaction mechanism,[14,15,18−21] the relative energies of the two transition states (TS) (of the two steps of the reaction) depend to a considerable extent on the theoretical method used. In fact, most theoretical results disagree with the hypotheses about the rate-determinant step that are based on experimental data. Our main aim was not to search for a reaction mechanism, but to determine whether the DDCI method is suitable for studying reactivity problems The results

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* Corresponding author. Fax: +34−977 559563. E-mail: reguero@quimica.urv.es.

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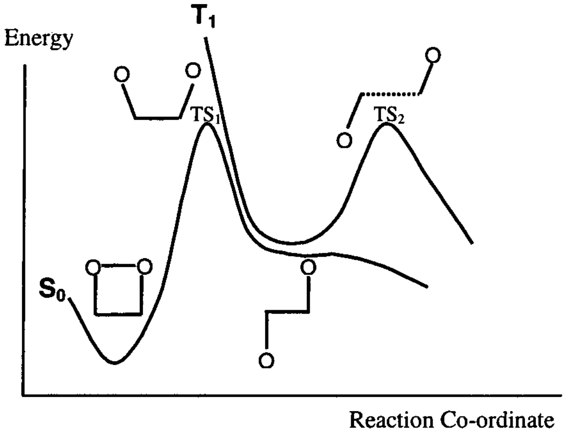


Figure 1. Schematic representation of the reaction mechanism proposed by Rob et al. in ref 19b.

show that the performance of our method is quite satisfactory, as they are in better agreement with experimental data than those obtained with well-established but more expensive methods. The level of accuracy in the quantitative description is more difficult to establish, as the experimental data are not precise enough, but it seems that further work is required to determine critical point geometries and energies for the reference state.

The Mechanism of the Decomposition of Dioxetane. A very sound mechanism for the thermal decomposition of the dioxetane was proposed not long ago.[19b] It uses data obtained from the CASSCF (Complete Active Space Self-Consistent Field) and multireference MP2 (Møller–Plesset) methods to compute the potential energy surfaces (PES) of the states involved in the reaction. This mechanism was confirmed by density functional theory (DFT) calculations (uB3LYP and uB3P86 functionals).[21] The states of interest are classified according to the number of electrons on the oxygen p orbitals of π symmetry perpendicular to the molecular plane (4π, 3π, and 2π). The reactant and product ground states correspond to a singlet 4π state ($^1(4\pi)$). The 3π and 2π states are created by promoting 1 or 2 electrons from the π symmetry orbitals. A summary of the mechanism proposed in ref 19b can be seen in Figure 1. The reactant is a nonplanar structure from which the reaction begins at the ground state (S_0, $^1(4\pi)$) with a ring opening produced by rotation about the C–C bond (that is, enlarging the O–C–C–O dihedral angle) and enlargement of the O–C–C angle. The transition state of this step (called TS_1 all throughout this paper) was found to be 16.3 kcal mol^{-1} high. After the ring opening, a biradical structure is obtained in which the 4π, 3π, and 2π singlet and triplet states are almost degenerate because of the distance between the oxygen atoms where the unpaired electrons are located. In the biradical region, minima have been localized at gauche and anti geometries (with a 70° and 180° O–C–C–O dihedral angle, respectively) for most of these states. This was not the case for the ground state, where no minimum was found although the PES is very flat in this region. Neither could the transition state for the C–C bond breaking, which leads to products be located. This means that throughout the ground-state surface the second step of the decomposition reaction occurs with no activation energy. But this channel does not seem to be open, because the state distribution of the products indicates that the reaction finishes mainly on the $^3(3\pi)$ (T_1) surface, and to a lesser extent on the $^1(3\pi)$ surface. This is because there is a T_1/S_0 intersystem crossing (ISC) seam (n-1-dimensional) parallel to the S_0 reaction channel between the reactant and the biradical intermediate which is reached with a small motion orthogonal to the reaction coordinate. Given that the spin–orbit coupling (SOC) is quite large in this region, the ISC provides an efficient channel for populating the $^3(3\pi)$. On this excited-state surface a transition state corresponding to the C–C cleavage (TS_2) was located 16.5 kcal mol^{-1} above the reactant energy. In a previous study by the same group,[19a] the TS_2 was also located on the $^1(3\pi)$ state surface with an energy 3.2 kcal mol^{-1} higher than that on the $^3(3\pi)$ state surface, in good agreement with the experimental $^3(3\pi)/^1(3\pi)$ product rate.

The mechanism reported in ref 21 is similar to the one described above although it has certain unsteadiness along the proposed reaction paths, which cannot easily be explained. The main difference with the previous results is between the energy of the two transition states: TS_1 is 8.93 kcal mol^{-1} higher than TS_2 (17.89 and 9.40 kcal mol^{-1}, respectively, for the trans route, zero-point energy (ZPE) corrections included).

Experimental data are in general in good agreement with the mechanism proposed in the above references, but some evidence suggests that the TS_1 barrier must be higher than the TS_2 barrier. First, it has been found that the activation energy for the decomposition of tetramethyldioxetane (TMD)[22] and *cis*-diethoxy-1,2-dioxetane (DED)[23] is the same for the ground and excited-state reactions, which means that the rate-determinant step must be the same for both reactions. Second, the lack of trapping of the triplet biradical intermediate[8d] indicates that the lifetime of this intermediate is too short to be compatible with a TS_2 barrier higher than TS_1.

It seems that, while theoretical calculations are precise enough to give a correct quantitative description of a reaction mechanism, there are still serious difficulties when quantitative results are looked for. The sounds calculations of ref 19b yield the TS_2 0.2 kcal mol^{-1} higher than TS_1, in disagreement with the experimental evidence. The analysis of the results shows that as the basis set is enlarged and the computations refined (better methods, larger active space, corrections added, etc.), the quantitative description of the mechanism hardly changes, but the energy difference between TS_1 and TS_2 decreases continuously. This indicates that the problem here comes from the low precision of the energetics, and not from the description of the mechanism. On the other hand, the DFT results of ref 21 are in good agreement with the experimental hypotheses in this particular case, despite the unsteadiness of the reaction path obtained.

With this background, the problem of the luminiscent decomposition of dioxetane seems to be a suitable benchmark for checking the reliability of our novel DDCI method in the qualitative and quantitative study of reactivity problems.

The DDCI Method and Its Application to Reactivity Problems. The DDCI was designed specifically to calculate energy differences. It is a variational method in which the CI space is chosen on the grounds of the second-order perturbation criteria. It was first developed to calculate S–T energy gaps,[24,25] but it has been applied very successfully in many type of vertical transitions.[1,4,6,7]

In the DDCI method the transition of interest is described at the zero-order level by a complete active space, formed with a minimal number of active orbitals. An effective Hamiltonian is formally built on it at the second order of the quasi-degenerated perturbation, but only the configurations contributing to the transition energy are included. These configurations are the double excitations that involve at least one active orbital, because the purely inactive double excitations (which create two holes in the doubly occupied inactive orbitals and two particles in the inactive virtual orbitals) only contribute as a constant shift to the diagonal elements of the effective Hamiltonian. The CI obtained is a subspace of the space created with all single and double excitations over the CAS (CAS*SDCI), and it is then treated variationally, so higher orders of perturbation are included and the problem of the intruded states, frequent in multireference perturbative calculations, avoided. The dimension of the DDCI space grows proportionally to the third power of the basis set dimension, while for the dimension of the SDCI it grows proportionally to the fourth power.

The main characteristics of the method are that (i) it is variational; (ii) because it is variational, it is uncontracted (i.e., the external correlation affects and modifies the coefficients of the CAS; (iii) the DDCI matrix is invariant under rotations of the molecular orbitals in the active, doubly occupied, and virtual subsets; (iv) the dimension of the DDCI space is proportional to the third power of the basis set dimension; and (v) DDCI is not strictly size-consistent, but the size-consistency error is quite small.

In principle, the results depend on the MO used, but the method can be extended to avoid this dependency and improve the results: in the iterative DDCI (IDDCI)[26] the active orbitals are adapted to better describe the transition being iteratively modified. They are obtained in each cycle from a one-particle density matrix, which in turn is obtained as the average of the density matrixes of the states that describe the transition. With such active orbitals, the zero-order description improves. The occupancy of these orbitals also provides a criterion for checking if the active space can be reduced: those orbitals with occupations not significantly different from 2 or 0 can be considered inactive, i.e., included in the CI but not in the CAS calculation.

Because the selected DDCI space does not include purely inactive double excitations which do not contribute to energy differences but play a large role in the correlation energy of each state, the energy difference calculations are only strictly correct when vertical transitions are calculated, and with a common set of molecular orbitals for all the states. This means that this method is is suitable neither for computing PES, nor for optimizing geometries. However, it can be applied to calculate excited PES if the ground-state potential energy surface is known from experimental results or other independent calculations.[5−7] When comparison with Full-CI results was possible[5,7] the performance of the DDCI method proved to be excellent.

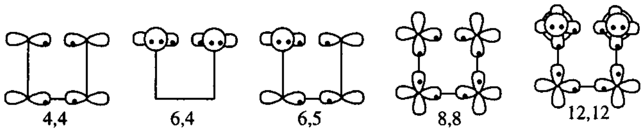
The challenge now is to apply the DDCI method to a reactivity study in which the results are compared with experimental data. It should be taken into account that many other factors other than the method (basis set, thermal factors, enviromental influence, experimental uncertainty, etc.) can influence the degree of agreement.

To carry out reactivity studies, a more complex strategy must be used and it is our aim here to propose a strategy and check its applicability. The steps proposed are summarized below:

1. The critical points of interest (on both the ground-state surface and the excited states) are localized in the corresponding PES with a conventional method.

2. A reference state must be chosen. To obtain good results with the minimum computational effort, it is best to choose the state that is most accurately described by conventional methods. In most cases this will be the ground state, but any other PES could also be chosen as reference. Accurate energies of the critical points in step one are calculated on the PES of the reference state with a conventional high-level method. In this way, an accurate profile of the projection of the reaction path over the reference PES is obtained.

SCHEME 2



3. For all the critical points the energy difference between the reference state and the other states of interest are calculated using the DDCI method.

4. The reference state energies of step 2 are added to the energy differences obtained in step 3 to build the potential energy surface of the other states.

This methodology provides reliable PES at low cost for two reasons:

1. High-quality conventional methods, which are usually expensive, are only needed for the reference state. The freedom to choose the reference state makes it possible to choose one with an electronic distribution reliable to be described accurately at low computational cost (no need for a large active space, no appearance of intruder states, etc.).

2. The DDCI was designed to get good results with small active spaces, so the calculation of reliable energies of excited states is not expensive in any case.

It is evident that the bottleneck in this strategy is the location of the critical points, but this is a problem that all methods must face. The computational saving in our proposal comes in the calculation of more accurate energies for the stationary points located in states other than the reference one. In a more conventional method, the complex electronic distribution of these states would need more sophisticated and expensive computations. In our method, however, the calculations are cheaper but still reliable.

Results and Discussion

All the calculations in this study were carried out with the MOLCAS package (4.1 version)[27] and the DDCI-SCIEL program[28] linked to it. A standard MOLCAS basis set of Atomic Natural Orbitals (ANOs) was used (Pierloot: C: 4s3p1d, O: 4s3p1d, H: 2s1p).

The main point of disagreement between the experimental evidence and the theoretical results is the relative energies of the first and second transition states of the reaction mechanism, so we focused on calculating the energy of these two crucial structures.

Using the strategy described in the section above, the first step is to locate the reaction mechanism's critical points on the ground state as well as on the excited-state potential energy surfaces. For this task, the CASSCF method was used. To keep the active spaces of a moderate size, they are not the same for all structures. Table 1 shows the size of the active spaces used for each structure and the geometrical parameters, and Scheme 2 shows the active orbitals. Figure 2 shows the geometries obtained for the nonplanar reactant (S_0 state), the intermediate (S_0 state), and the transition states (S_0 state for TS_1 and $^3(3\pi)$ state for TS_2). A planar transition state connecting the two possible nonplanar reactant structures was also located (TS_0), although this structure is not involved in the reaction mechanism. Its geometry only differs from the reactant in the value of the dihedral OCCO angle, 0×b0° in the TS_0, and 7.8°×b0 in the reactant. All these structures were characterized by frequency calculations carried out with (4,4) active spaces and with the frequencies the ZPE correction was estimated.

TABLE 1: Size of the Active Spaces Used for the CASSCF Geometry Optimizations and Geometrical Parameters Obtained[a,b,c]

structure	d_{C-C}	$d_{C-O}*$	$d_{C-O}\dagger$	d_{O-O}	$\hat{a}_{C-C-O}*$	$\hat{a}_{C-C-O}\dagger$	$\theta_{O-C-C-O}$
Reac, CAS(4,4)	1.540	1.423	1.423	1.542	90.0	90.0	7.8
	1.538	*1.423*	*1.423*	*1.554*	*90.0*	*90.0*	*9.0*
AADO[d]	**1.549**	**1.476**	**1.474**	**1.491**	**86.9**	**86.8**	**21.3**
DMTOH[e]b	**1.584**	**1.485**	**1.459**	**1.497**	**87.1**	**89.0**	**7.7**
TS_1, CAS(6,4)	1.507	1.412	1.412	2.105	99.1	99.1	32.4
	1.533	*1.410*	*1.410*	*2.118*	*99.0*	*99.0*	*33.0*
Intermed, CAS(6,4)	1.565	1.368	1.368		105.5	105.5	180.0
	1.560	*1.366*	*1.366*		*106.0*	*106.0*	*180.0*
TS_2, CAS(6,5)	2.021	1.341	1.249		109.8	104.3	180.0
	2.043	*1.343*	*1.250*		*110.0*	*104.0*	*180.0*

[a] Numbers in italics correspond to results reported in ref 19b; numbers in bold correspond to experimental data of two dioxetane derivatives. [b] "*" and "†" superscripts correspond to the two different product formaldehyde molecules. [c] Distances in angstroms, angles in degrees. [d] AADO: adamantylideneadamantane-1,2-dioxetane. [e] DMTOH:1-aryl-5-(9-methylfluorene-9-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3,2,0]heptane.

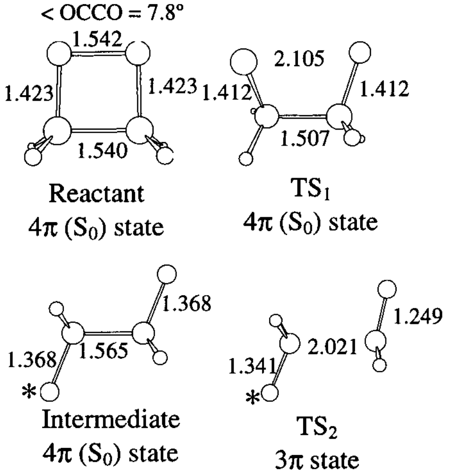


Figure 2. Geometries obtained in this work by optimization at the CASSCF level.

Given the small size of the active spaces in these geometry optimizations, we decided to check the accuracy of our first results. For this reason, Table 1 compares our geometries with those reported in ref 19b, in which larger active spaces were used (CAS(12,10)/6-31+G* and GVBCAS(12,12)/6-31G) to include a part of the dynamic correlation in the geometry optimizations. The small differences observed (less than 1.8% in the worst case) indicate that the geometries obtained here were good enough to be used even for a quantitative analysis. There was, nevertheless, a surprising but not significant difference between our results and those in ref 19b: the minimum of the S_0 state in the intermediate region was not located in the latest, so a restricted geometry optimization with a fixed C−C distance was carried out instead. In our case, though, the S_0 intermediate minimum was located with no geometrical restriction.

Table 1 also includes the geometrical parameters of two dioxetane derivatives obtained by X-ray crystal structure analysis.[29,30] Comparison of the theoretical and experimental data shows discrepancies in the bond distances of between 1.6 and 4.0%. In the experimental description the C−C distance is larger than the O−O distance, while in the theoretical results they are practically the same. It must not be forgotten that in the dioxetane derivatives studied experimentally the C−C distance is larger than in the parent system due to the effect of the bulky substituent groups.

To carry out the next step of our computational strategy a reference state had to be established. For all the stages in the evolution of this system the $^1(4\pi)$ state is well described in first approximation by a single determinant, so S_0 (understood as the closed shell configuration state) proved to be the most suitable reference state. The energy of this state at the relevant structures had to be computed (even if the corresponding critical point was located on another surface) with a standard high-level method to obtain the profile of the reaction path projection over the ground-state surface. We used two methods to do this. The first of them, a multireference single double configuration interaction, SDCI (with the average coupled-pair functional (ACPF) size-consistency correction added) was performed over a (4,4) active space, that properly describes the $^1(4\pi)$ electronic distribution along the whole length of the reaction path. The energies obtained are collected in Table 2.

The second method used was a second-order perturbational method over a complete active space, CASPT2. In this case it is more difficult to decide what size the active space should be for the method to perform well at a moderate cost. For this reason, three different active spaces, (4,4), (8,8), and (12,12), were used to calculate the energies of the TS_1 and TS_2 structures on the ground-state surface. The results (Table 3) show that the oscillating convergence within the chemical precision limits, typical of this method, is reached. Enlarging the active space beyond (12,12) will not ensure a more precise result and, given that we were looking for a cheap method, we chose the (4,4) active space to carry out the CASPT2 calculations. Unfortunately, given the small magnitude of the energy difference that is to be calculated, the low convergence introduces a nonnegligible uncertainty in the quantitative results. To ensure that this active space described all the structures during the reaction with the same quality, (i.e., that the energies of the different species were comparable) an additional requirement had to be fulfilled: the weight in the perturbative expansion of the reference wave function should not change by more than 10%. The extreme values of the weights in this set of calculations were 0.838 and 0.872, which is 4%, below the established threshold.

Once the energies of the reference state surface had been calculated, the energy differences between the S_0 and the $^3(3\pi)$ states were computed with the DDCI method. In fact, the only essential energy difference is the one at the TS_2 geometry, but for the sake of a more complete description, calculations were also run for the reactant planar structure and the intermediate geometries.

In the design of the DDCI method particular interest was placed on the use of small reference spaces for the first-order description of the states involved in the computed transition. In the case being studied, the transition from the S_0 to the $^3(3\pi)$ state is a single excitation, so an active space with 2 electrons in 2 orbitals should be enough for results to be reliable, if the active orbitals are well suited. To obtain these orbitals, we used the IDDCI methodology. The initial orbitals came from CASSCF (6,4) for the reactant and intermediate and from CASSCF(6,5) for the TS_2 structure. At the convergence of the

TABLE 2: Energies of the Main Critical Points of the Reaction Path[a]

structure	state	CASSCF		CAS(4,4) SDCI + ACPF		CASPT2 (8,8)		ΔE_{DDCI}	relative[b] SDCI + DDCI	relative[b] CASPT2 + DDCI	relative[b] SDCI/ DDCI + ZPE correction	relative[b] CASPT2/ DDCI + ZPE correction
REAC	S_0	−227.7664	**0.0**	−228.4176	**0.0**	−228.4125	**0.0**				**0.0**	**0.0**
TS_0	S_0	−227.7663	**0.1**	−228.4174	**0.1**	−228.4123	**0.1**					
TS_1	S_0	−227.7369	**18.5**	−228.3893	**17.8**	−228.3876	**15.6**				**16.8**	**14.6**
Interm.	S_0	−227.7473	**12.0**	−228.4036	**8.7**	−228.4037	**5.5**					
TS_2	S_0			−228.4448	**−17.1**	−228.4338	**−13.4**					
	$^3(3\pi)$	−227.7369	**18.5**					0.0479	13.0	16.6	**9.33**	**12.8**

[a] The critical points of the three first structures where located on the ground-state PES; last structure was located on the $^3(3^\pi)$ PES; the energies of the other state correspond to a vertical transition; plain characters in hartrees; bold characters in kcal mol^{-1}. [b] Energies relative to the reactant S_0 energy.

TABLE 3: Energy (in hartrees) of the Structures of the First and Second Transition States on the Potential Energy Surface of the Ground State and Energy Difference (in kcal mol^{-1}) Calculated at the Multireference CASPT2 Level, Using Different Active Spaces

	CASPT2(4,4)	CASPT2(8,8)	CASPT2(12,12)
S_0 TS_1	−228.3868	−228.3876	−228.3863
S_0 TS_2	−228.4390	−228.4338	−228.4344
$\Delta E_{\mathrm{TS1-TS2}}$	32.75	29.00	30.16

TABLE 4: Vertical Transition to the Excited States Potential Energy Surface for Two Critical Points (TS_0 and Intermediate) Localized on the Ground-State PES[a]

		state				
structure	ref	S_0	$^3(3\pi)$	$^3(4\pi)$	$^1(3\pi)$	$^1(4\pi)$
TS_0	this work	0.0	62.9	130.7	86.7	198.5
Intermed.	this work	8.7	15.2	11.2	15.9	13.0
	19b	12.6	14.7			
	21	6.80	6.62			

[a] The values of "this work" have been calculated with the DDCI method.

iterative process, the occupation numbers of the average density matrixes confirmed that a (2,2) active space was enough for a first-order description of the transition, given that only the two active orbitals had occupations significantly different from 0 or 2. The IDDCI energy gaps for the TS_2 are shown in Table 2, and those for the structure of secondary interest are collected in Table 4 together with analogous data of refs 19b and 21.

Finally, to obtain the $^3(3\pi)$ absolute energies, the energy gaps between the S_0 and the $^3(3\pi)$ state were added to the S_0 energies. The final results are also collected in Table 2. Figure 3a summarizes the results when the SDCI method is used to get the reference curve and Figure 3b the results when the CASPT2 method is used.

Let us analyze now the final results. When the SDCI method is used for the ground state, the TS_1 is higher than TS_2 by 4.8 kcal mol^{-1}, and if the ZPE correction (calculated at the CAS-(4,4) level) is added, the energy difference between transition states is even larger (7.6 kcal mol^{-1}). The activation energy of the reaction as a whole corresponds to the energetic barrier of the TS_1, 16.8 kcal mol^{-1} (ZPE corrections added). On the other hand, when CASPT2 is used, the TS_2 is 1.0 kcal mol^{-1} higher than TS_1, but the ZPE correction inverts the energetics to give a TS_1 that is 1.8 kcal mol^{-1} higher than TS_2. The activation energy in this case is lower (14.6 kcal mol^{-1}). Thermal corrections were not calculated but if the ones given in ref 19b were added to our results, the difference in energy between the first and second transition states would be greater (of the same sign). Our theoretical results fully agree with the experimental conclusions about the determinant reaction step, although by a narrow energy margin.

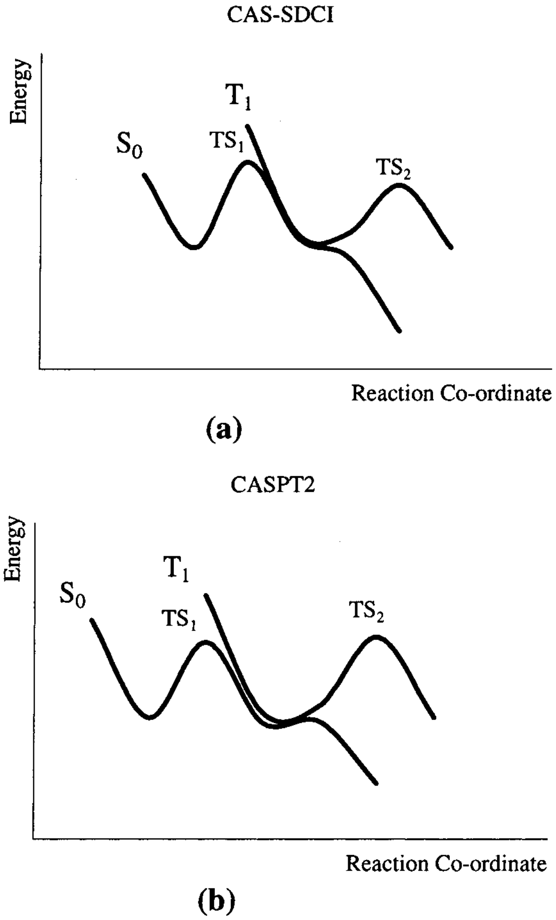


Figure 3. Schematic representation of the reaction profile along the PES of the S_0 and $^3(3\pi)$ states. (a) Reference state calculated with SDCI, (b) reference state calculated with CASPT2.

The experimental value for the activation energy[10b] is 22.7 kcal mol^{-1}, which is in better agreement with the SDCI-DDCI value than with the CASPT2-DDCI one, but none of the results can be considered quantitatively satisfactory. For this particular study, it should be pointed out that because the SDCI reference space is a CAS (4,4) while the CASPT2 space is a CAS (8,8), the quality of the CASPT2 results should be better than the SDCI ones, and so the agreement with experimental results. These discrepancies indicate that one of the main sources of uncertainty in the results is the inaccurate description of the reference state. This problem may arise from not including the dynamical correlation in the geometry optimizations or from the unavoidable limitations in the energy calculation (size of active space and basis set used).

A comparison must also be made with the latest and more conventional theoretical calculations. First of all, let us compare the vertical energy difference for the intermediate obtained in this work with the energies obtained in refs 19b and 21 (Table 4). The considerable differences between the results of comparable methods are surprising but the discrepancies are not only due to the energy calculation but also to the differences in the optimized structures (e.g., in ref 19b the S_0 minimun could not be located without restrictions).

Regarding the relative energies of TS_1 and TS_2, the SDCI-DDCI and CASPT2-DDCI results compare well with those of ref 21 and are a clear improvement on the CAS(12,10)+MP2 results in ref 19b which do not reproduce the energetic order (TS_2 lower than TS_1) suggested by the experimental results. The best activation energies of refs 19b and 21 (16.5 and 17.89 kcal mol^{-1}, with ZPE but without thermal correction) are almost coincident with the SDCI-DDCI one, and in a fair agreement with the CASPT2-DDCI one.

All these data seem to indicate that the results obtained with the strategy used in this study are of the same or better quality than the results provided by other standard methods. The level of confidence in the quantitative character of the results depends mainly on how reliable the calculation of the reaction path projection over the ground state is; that is, it depends on the accuracy of the standard methods used. Nevertheless, a more extensive study on the applicability of the DDCI method to reactivity problems should be carried out.

Conclusions

The modeling of the reaction mechanism of the thermal decomposition of dioxetane is used to test the applicability of the DDCI method to the quantitative study of reactivity problems. The main aim of this study is to compare the energy of the two transition states of the reaction path of the thermal decomposition of dioxetane. Species of quite different geometries that are also in different electronic states are compared. The order of magnitude of the energy difference (of a few kcal mol^{-1}) makes the problem even more difficult. Despite the ambitious goal to be achieved, the results are quite satisfactory, as they fully agree with the experimental conclusions in the establishment of the determinant reaction step, although our second aim, quantitative precision, seems not to have been completely attained. It has been shown that the DDCI method, which was used to calculate the energy difference between the ground and excited states, provides the same or better results than conventional high level methods, but at lower cost.

We have shown that the DDCI method is capable of studying reaction mechanisms when excited states are involved, but a more extensive study should be carried out to check the level of applicability and the reliability of the method at the quantitative level.

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