Theoretical study of the reaction mechanism of the uncatalyzed epoxidation of alkenes by iodosylbenzene†

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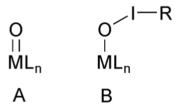
The origin of the barrier for the uncatalyzed epoxidation of alkenes by iodosylbenzene is examined from a computational point of view. The reaction of a monomeric unit with ethylene presents a very low barrier, in disagreement with experimental data indicating the requirement of a catalyst. The polymeric structure of iodosylbenzene was then analyzed and the importance of the presence of a terminal hydration water in its linear structure confirmed. The reaction of a model dimer with ethylene is shown to have a high barrier, in good agreement with experiment. Implications of this result with respect to the nature of the catalytic mechanism are briefly discussed.

Introduction

Olefin epoxidation is by itself a reaction of industrial impact because of the large-scale need for propylene oxide.[1] Although the most commonly applied method is the chlorohydrin process, where the initial attack on the alkene double bond is carried out by a chlorine substituent, the formally simplest approach, direct transfer of one oxygen atom to the alkene, is appealing because of the environmental problems created by the chlorohydrin process. The direct transfer method is furthermore a simple example of the oxygen transfer reactions taking place in a number of biological processes, like those in monooxygenase enzymes.[2] Despite its formal simplicity, the detailed mechanisms of these oxygen transfer processes are complex and they are the subject of intense research both from experimental and theoretical approaches.

There are a variety of experimental systems capable of carrying out an oxygen transfer to an alkene double bond to produce an epoxide. In a number of them, the oxygen added to the olefin comes from a peroxo group,[3] either in the form of an organic peroxide[3,4] or coordinated to a transition metal.[3,5] The essential mechanistic features of these processes have been clarified with the help of high-level *ab initio* computational studies, both in the case of organic peroxides[6–8] and of transition metal peroxo complexes.[9–11]

In contrast, other experimental systems[12–16] do not use peroxo groups as oxygen source, but other donors like iodosylbenzene or sodium hypochlorite. In these cases, the reaction is almost invariably catalyzed by a transition metal complex. Characteristic examples are the metal porphyrin systems[12,13] and complexes with salen ligands.[14] These processes often take place through oxo intermediates (**A** in Scheme 1), where the oxygen atom is separated from the donor and attached through a double bond to the metal center. Further support for the intermediacy of oxo species is supplied by the fact that these compounds have been isolated in a number of cases.[17] Consequently, considerable theoretical effort is being invested in the clarification of the part of the mechanism going from the oxo intermediate to the epoxide product.[18–20]



Scheme 1

However, there are experimental indications that these oxygen transfer reactions do not necessarily go, in all cases, through an oxo intermediate. Koola and Kochi[21] reported as early as 1987 the presence of two different mechanisms in olefin epoxidation by salen complexes, depending on the nature of the oxygen source. Nam and Valentine[22] confirmed through isotope labeling experiments the occurence of these two different mechanisms. They furthermore observed that when the oxygen comes from a peroxide or a peroxyacid the oxo intermediate **A** is formed, but that when iodosylbenzene is used there is no oxo complex and the ethylene is postulated to react directly with a metal-iodosylbenzene complex (**B** in Scheme 1), in which the oxygen is bound through single bonds to both the metal center and the iodine atom. Caradonna and co-workers have found a similar duality of mechanisms[23] for the case of bimetallic complexes modeling monooxygenases.

The presence of a catalytic mechanism without oxo complexes is associated in all the reported cases with the use of iodosylbenzene as the oxygen donor. Iodosylbenzene is one of the most commonly used reactants for oxygen donation.[24] It has already been suggested that iodosylbenzene is a polymeric solid that operates as a heterogeneous catalyst[25] and that the role of the catalyst is to solubilize it as a monomeric form. In any case, its reaction mechanism for epoxidation reactions has not been the subject yet of theoretical analysis. To our knowledge, the only study on related hypervalent iodine compounds was carried out at the semiempirical level on $PhIF_2$ and $PhCl_2$.[26]

In this article we analyze from a theoretical point of view the reaction mechanism of the uncatalyzed epoxidation of alkenes with iodosylbenzene. The characterization of this uncatalyzed mechanism will hopefully help in the understanding of the role of the catalyst and thus of the reaction mechanism for the catalyzed process.

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† Electronic supplementary information (ESI) available: B3LYP optimized geometries (Cartesian coordinates) and total energies for compounds **1** to **9**. See http://www.rsc.org/suppdata/nj/b2/b203861g/

Computational details

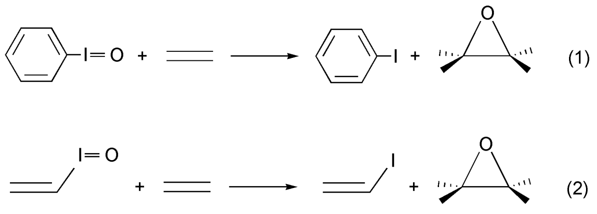
All calculations were carried out with the Gaussian 98 program.[27] Although most calculations were carried out with the density functional B3LYP, calibration calculations presented in the section dealing with the computational method also used the MP2 and CCSD(T) methods. Two different basis sets were used. Basis set I was valence double-ζ with a polarization shell in all atoms except hydrogen. In particular, iodine was described by a pseudopotential and the associated LANL2DZ basis set[28] supplemented with a polarization d shell,[29] while the 6-31G(d) basis was used for C, O, H.[30,31] Basis set II, which calibration calculations presented in the text proved as unnecessarily expensive, was valence triple-ζ and included polarization shells in all atoms, including hydrogens. In the case of iodine this quality was accomplished by splitting the primitives in the LANL2DZ basis set commented above, while the 6-311G(d,p) basis[32] was used for all other atoms. The resulting exponents for the s shell in iodine were 0.7242, 0.4653 and 0.1336 and the exponents for the p shell were 1.290, 0.3180, 0.1053. Except in the calibration calculations, the nature of all the computed stationary points as local minima or transition states was confirmed through analytical second derivative calculations and the energies presented are free energies. Intrinsic reaction coordinate calculations were carried out to confirm the connectivity between transition state **8** and local minima **7** and **9**. Solvent effects were introduced through single-point polarized continuum model (PCM) calculations[33] on frozen gas phase B3LYP/I geometries.

Results and discussion

Computational model

In this section we examine the computational model required for a sufficiently accurate description of the reaction mechanism. Three different parameters are considered: (i) the need to introduce the full aromatic ring of iodosylbenzene, (ii) the computational method and (iii) the basis set. The importance of each of these factors is evaluated through its effect on the exothermicity of the transfer of one oxygen atom from a monomeric iodosyl molecule to an ethylene to yield the corresponding epoxide.

The presence of the phenyl ring increases significantly the size of the system and hence the computational effort required for its study, and computational cost can be critical when considering polymeric forms of the oxygen donor. On the other hand, the presence of the phenyl ring would not be expected to have a very important effect on the key strength of the I–O bond. This effect should be mostly through double bond conjugation and this aspect could be at least approximately described by the use of the much smaller vinyl group. Thus, we considered modeling the iodososylbenzene molecule [depicted in eqn. (1), Scheme 2] by iodosylethylene [eqn. (2), Scheme 2]. The exothermicity of both reactions was computed through full geometry optimizations of reactants and products with two different computational schemes, B3LYP/I and MP2/I, and the results are shown in Table 1. It is clear from the table that iodosylethylene constitutes an excellent computational model for iodosylbenzene, with very small changes in the exothermicity of 0.3 kcal mol^{-1} at the B3LYP level and of 0.2 kcal mol^{-1} at the MP2 level.



Scheme 2

Table 1 Exothermicity (kcal mol^{-1}) of the reactions between ethylene and the two different iodosyl molecules considered with different methods and basis sets. The reactions are indicated in Scheme 2

Energy	//	Geometry	Reaction 1	Reaction 2
B3LYP/I	//	B3LYP/I	−65.3	−65.6
B3LYP/II	//	B3LYP/I	—	−63.2
MP2/I	//	MP2/I	−70.6	−70.8
MP2/II	//	MP2/I	—	−72.4
CCSD(T)/II	//	B3LYP/I	—	−67.9

A second aspect considered was the computational description. Three different methods were considered for reaction 2: B3LYP, MP2 and CCSD(T). B3LYP and MP2 constitute similar cost representatives of the two major theoretical approaches available: density functional theory and Hartree–Fock based methods, respectively. CCSD(T) is a much more accurate and computationally demanding approach, which is used in this case as a benchmark for the quality of the other two methods. Results are summarized in Table 1. Notation is the usual one, with the basis set separated from the method by a single slash and the geometry optimization method separated from the energy calculation method by double slashes. While full geometry optimizations were carried out for B3LYP and MP2, CCSD(T) calculations consisted of single-point calculations on the frozen B3LYP geometries. Results are quite similar for the three computational methods. The difference between B3LYP/I//B3LYP/I and MP2/I//MP2/I is only 5.2 kcal mol^{-1}. This difference, which may be too large for other processes, is a small percentage of the total exothermicity. Furthermore, a qualitatively accurate description will be probably sufficient, because the uncatalyzed reaction that is going to be computed should, after all, have a high barrier. The most accurate CCSD(T) value lies between the B3LYP and MP2 values. We have decided to use the B3LYP method in the calculations because of its more modest requirements in terms of disk space.

The third aspect that has been considered is the basis set. Because of this, the energy difference obtained with basis set I has been recomputed with the significantly more extended basis set II on frozen geometries, at both the B3LYP and MP2 levels. The effect of the basis set is in the range of 2 kcal mol^{-1} in both cases. Therefore, we conclude that basis set I is sufficiently accurate and it will be used in the calculations that follow.

After the tests presented in this section and summarized in Table 1, all calculations in the rest of the article are carried out on the iodosylethylene model, with the B3LYP method and basis set I.

Monomeric system and its reaction profile

The first system we analyze is that presented in eqn. (2), the direct reaction between the iodosyl compound and ethylene. This system has been already discussed in the previous section. It will suffice here to say that at the B3LYP/I level, the free energy of the products is 60.2 kcal mol^{-1} below that of the reactants.

The optimized geometries of reactants (iodosylethylene, **1**; ethylene, **2**) and products (iodoethylene, **3**; ethylene epoxide, **4**) are presented in Fig. 1. The computed bond distances are in all cases reasonable. The C–C distance corresponds to a double bond (between 1.324 and 1.331 Å) in compounds **1** to **3**, while it corresponds to the triangular epoxide arrangement (1.469 Å) in compound **4**. The computed values involving iodine, less known, are in acceptable agreement, taking into

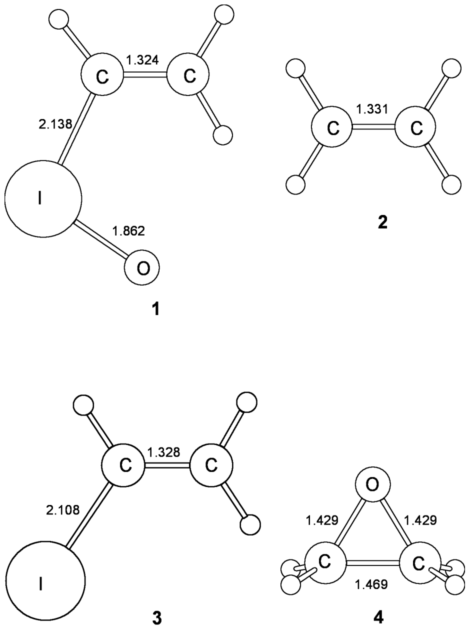


Fig. 1 Optimized B3LYP geometries (distances in Å) for iodosylethylene (**1**), ethylene (**2**), iodoethylene (**3**) and ethylene epoxide (**4**).

account chemical differences, with computed values[34] for iodomethane (C–I, 2.162 Å), and iodosylmethane (C–I, 2.151 Å; I–O, 1.864 Å).

The transition state **5** for the reaction was also computed. Its geometry is presented in Fig. 2. The geometry is much more similar to that of the reactants than to that of the products, as can be seen in the epoxide C–C distance of 1.353 Å (to be compared with 1.331 Å in **2** and 1.469 Å in **4**), in agreement with the large exothermicity of the reaction. The energy of the transition state happens to be only 17.9 kcal mol^{-1} above that of the reactants. This value was quite unexpected because it would indicate a quite fast reaction at room temperature. If this were the reaction barrier, there would be no need for catalyst! In fact, this computed value for the reaction of ethylene with monomeric iodosylbenzene is of the same order as the computed value for the reaction of ethylene with peroxyformic acid,[7] a reaction that proceeds without catalyst.

The unexpected presence of such a low energy transition state prompted us to further analyze the reaction path to ensure the absence of some unexpected intermediate or the presence of a higher energy transition state in the path from reactants to products. This study was carried out through the computation of the potential energy surface presented in Fig. 3. This surface was obtained by assuming an approach of iodosylethylene to ethylene with the O–I bond perpendicular to the center of the epoxide C–C bond. Single-point calculations were carried out with a variety of values for the I–O and O–(midpoint of ethylene C–C) distances. It can be seen from the surface that there is a clear low energy path connecting the reactants, in the upper left part, with the products, in the lower right part. The values for exothermicity and energy barrier emerging from the graphic are similar, but not exactly identical, to those presented above because of the freezing of coordinates applied in the calculation of the energy surface, and because the surface is in electronic energies instead of free energies.

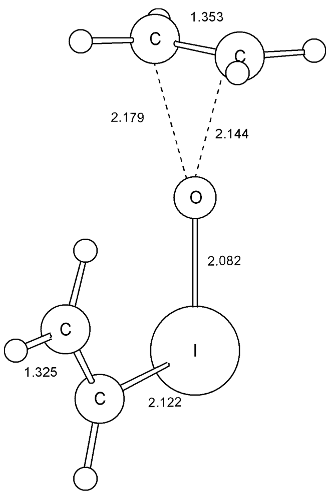


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Fig. 2 Optimized B3LYP geometries (distances in Å) for the transition state (**5**) of the reaction between monomeric iodosylethylene and ethylene.

Structure of the polymeric system

The fact that calculations of the monomeric iodosylethylene system predict a low activation barrier, in poor agreement with experimental data, prompted us to examine the behavior of polymeric units. As mentioned in the introduction, iodosylbenzene is known to be a polymeric solid of low solubility.[24,25] The detailed structure is, however, not known with precision because of the lack of large crystals for analysis by X-ray diffraction.

A combination of X-ray powder diffraction and EXAFS techniques[35] have indicated the solid structure shown in Scheme 3 for iodosylbenzene, a linear polymeric, asymmetrically bridged chain structure, where the iodosyl I–O units of different molecules are bound to each other by what has been labeled as secondary bonds.[25] Experimental bond distances are not very accurate because of the lack of large crystals, but the I–O contact between two units of the chain was estimated to be 2.377 Å, while the best estimation for the I–O intramolecular distance was 2.04 Å (corresponding actually to the average between the I–O and I–C distances).[35]

Our attempts to compute short polymeric units of the type (R–I–O)$_2$ or (R–I–O)$_3$, including a circular trimer, yielded unsatisfactory results. The geometry optimization produced

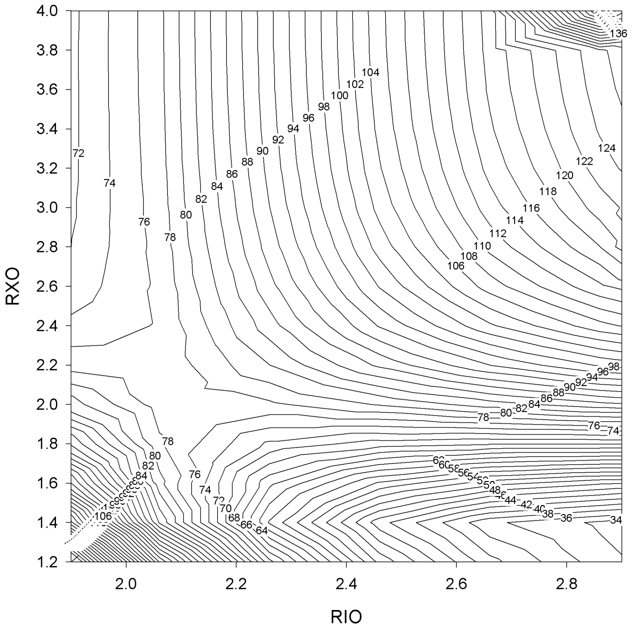
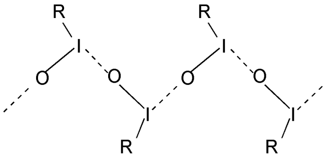


Fig. 3 Energy surface for the interaction between frozen iodosylethylene and ethylene as a function of the RIO (I–O) and RXO (O–midpoint of ethylene C–C) distances, in Å. Energies (in kcal mol^{-1}) are relative to the energy of ethylene epoxide.



Scheme 3

in practice separation of the system into its monomeric units, which were bound to each other only through weak van der Waals interactions. Things were very different when we added one hydration water to our system, having structures of the form HO–(RIO)$_n$–H. In this type of structure, the hydration water is divided in two pieces: the hydroxyl group goes to one end of the chain and it is attached to a iodine; while the remaining hydrogen goes to the other end, and it is attached to an oxygen. This type of arrangement has been suggested from experimental data on aqueous solutions of iodosyl species.[36] When we introduced the hydration water in our calculation of the dimeric HO–(RIO)$_2$–H system, we obtained structure **6**, shown in Fig. 4.

Structure **6** has a strong interaction between both monomers, which in fact practically lose their identity. The central oxygen atom shows nearly identical bond distances to both iodine atoms (2.072 and 2.080 Å). The terminal hydroxyl groups are also in a very symmetric arrangement with respect to the iodine atoms (I–O bond distances of 2.093 and 2.094 Å). The substantial change in the computed structure of the dimer upon addition of the hydration water gives strong support to the experimental suggestions of its importance.[25,36]

The thermodynamic stability of **6** with respect to the separate fragments can be evaluated through the following reaction:

$$2 \cdot H_2C{=}CHIO + H_2O \rightarrow HO{-}(H_2C{=}CHIO)_2{-}H$$

The products lie 19.5 kcal mol^{-1} below the reactants, further confirming the hypothesis that polymeric chains must be completed by a hydration water at its ends.

Agreement between our computed geometry and experimental data is, however, not perfect. The interaction in our structure is so strong that it becomes more symmetrical in the I–O bond distances (all values between 2.05 and 2.10 Å) than the experimental EXAFS data (two different values of 2.377 and *ca.* 2.05 Å).[35] We do not consider this discrepancy to be critical, since it is probably related to the fact that we are computing only a 2-member chain. The asymmetry in the experimental study is likely related to the existence of much longer chains, where the symmetrizing effect of the hydration water is probably damped throughout the chain. Furthermore, we think that our dimeric system may be a good model of short polymeric units that may dissolve from the solid polymer and act as the reactant for the epoxidation reaction.

The comparison of structure **6** with the geometry of the monomer **1** (Fig. 1) shows that the I–O distance is noticeably longer by 0.2 Å (*ca.* 2.07 *vs.* 1.862 Å) in the dimeric structure, while the I–C distance is slightly shorter by 0.01 Å (*ca.* 2.125 *vs.* 2.138 Å).

For the sake of completeness, and following the suggestion from one referee, we have also optimized the geometry of the hydrated monomer, HO–(RIO)–H. It has a quite symmetric arrangement of the two hydroxyl groups around iodine, with I–O distances of 2.089 and 2.083 Å. More significantly, its free energy is 10.4 kcal mol^{-1} below that of the monomer plus water. This value is significantly smaller than the 19.5 kcal mol^{-1} stabilization reported above for the dimer, and it indicates that, even when bound to the fragments of a dissociated water molecule, the system prefers the polymeric to the monomeric form.

Reaction of the dimeric system

The interaction of dimer **6** with ethylene was studied. Three different stationary points were located in the potential energy hypersurface. All of them were characterized through calculation of the second derivatives. Two of them correspond to local minima (zero imaginary frequencies) and the remaining one is the transition state connecting them (one imaginary frequency).

The first geometry computed for this system, labeled as **7**, is an adduct corresponding to the initial approach of ethylene to **6**. The distance between the fragments is still large, with the ethylene carbon closer to the central oxygen of the dimer still 3.511 Å away from it. Consequently, the geometry of the dimer part in **7** is very similar to that in **6**, and, in fact the free energy of **7** is 6.2 kcal mol^{-1} above that of the separate reactants, because of the unfavorable entropic effects.

The second geometry computed for this system is transition state **8**, shown in Fig. 5. **8** has one single imaginary frequency, with a value of 339*i* cm^{-1}. Its connectivity to reactant **7** and product **9** (Fig. 6) was confirmed through intrinsic reaction coordinate calculations.[37] The most remarkable characteristic of **8** is its free energy, which is 57.6 kcal mol^{-1} above the reactants. This high value is in agreement with the practical absence of uncatalyzed reaction. The breaking of the polymeric chain is therefore at the origin of the large energy barrier for this reaction and the main role of catalysts will be therefore the breaking of the chain.

There are several aspects in the geometry of **8** that merit discussion. The breaking of the two oxygen–iodine bonds takes place in a synchronous manner. The oxygen atom being transferred is still symmetrically bound to the two iodine atoms to which it was attached in reactant **7**. The I–O distance increases significantly when going from the reactant (*ca.* 2.1 Å) to the transition state (*ca.* 2.6 Å). This means essentially that the oxygen must be completely separated from the two iodine atoms before completing the formation of the epoxide. This is

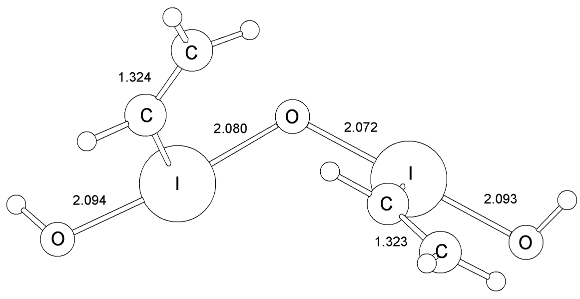


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Fig. 4 Optimized B3LYP geometries (distances in Å) for the dimeric system (**6**).

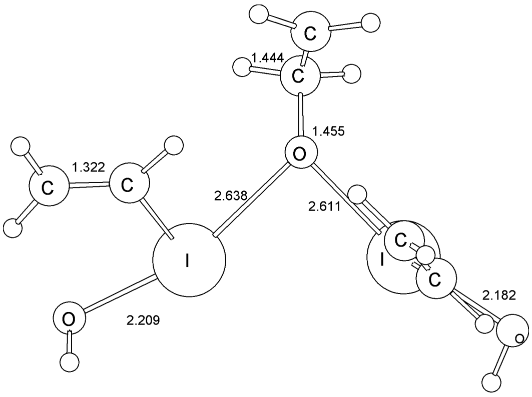

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Fig. 5 Optimized B3LYP geometry (distances in Å) for the transition state **8**.

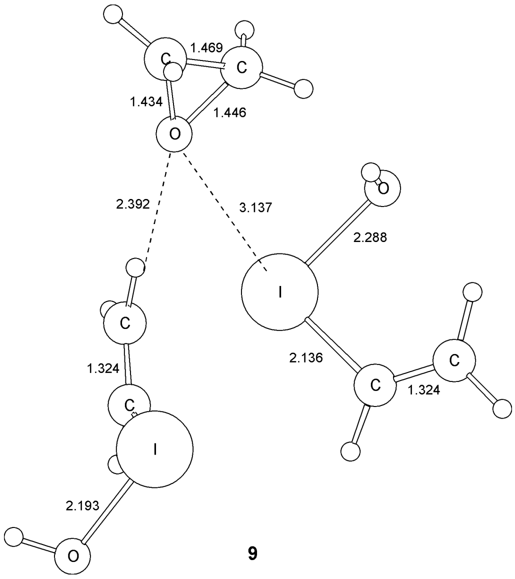

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Fig. 6 Optimized B3LYP geometry (distances in Å) for the product **9**.

consistent with the high barrier: old bonds are completely broken before the new ones are formed. The formation of the two oxygen–carbon bonds is in contrast completely asynchronous. While one of the ethylene carbons is already practically at the epoxide distance (1.445 Å), the other is still very far from the oxygen (2.054 Å). The arrangement of the substituents around the first carbon is practically tetrahedral, while the second one is almost planar. This suggests that the ethylene is donating its π-electron pair to the oxygen atom, which consequently must break its two other chemical bonds. The computed asymmetry in the transition state with respect to the C–O bonds probably corresponds to chemical reality because the B3LYP method applied is not affected by the bias of the MP2 method favoring the asymmetric structures reported for epoxidation reactions with other agents.[38] It is worth noticing that calculations with the same computational method indicate a synchronous formation of both C–O bonds in the permitted reaction of unsubstituted alkenes with peroxyformic acid.[7]

Our calculations prove that the geometry of **8** corresponds to a transition state connecting species **7** and **9**, but are not conclusive in the sense that this is the only possible transition state. Other conformations could exist with different orientations of the ethenyl substituents around the single I–C bonds, the case becoming even more complex if the real phenyl groups were considered. We have not found such alternative structures, but we would like to mention here that even if they existed, they would have little impact on the overall picture. The main result is the high energy of the transition state above the reactants, a result which will not be affected by small energy changes in the range of a few kcal mol^{-1}, which is what one could expect from such conformational changes.

The third structure optimized for this system is product **9**. As mentioned above, this structure has been shown to be related to transition state **8** through an IRC calculation. **9** can be viewed as composed of three nearly independent fragments: ethylene epoxide and two independent $H_2C{=}CH(IOH)$ units. The identification of the reaction product, ethylene epoxide, is clear from a variety of geometrical parameters. The oxygen has been completely transferred to the epoxide, with C–O distances of 1.434 and 1.446 Å, and taken away from the dimer, the closer distances to the other two fragments being an O–H distance of 2.392 Å and an I–O distance of 3.137 Å, both of them clearly non-bonding. The energy of this product is 9.8 kcal mol^{-1} above that of the separated reactants.

The fact that the energy of this product is above that of the reactants can seem surprising, but it can be easily understood by looking at the rather peculiar nature of the product. There are two $H_2C{=}CH(IOH)$ fragments, which in principle should not be expected to be very stable. In fact, since these fragments should have a radical character, compound **9** would be better described as a diradical and the restricted closed shell approach used throughout this work is not appropriate. **9** does not appear thus to be in its ground electronic state. Further proof is provided by the fact that the free energy of two separated $H_2C{=}CH(IOH)$ radical fragments plus epoxide is 24.0 kcal mol^{-1} below that of **9**. However, in this work we are not particularly interested in describing accurately the electronic features of **9**, but in showing that it contains the epoxide product and that it is connected to the reactants through a high energy barrier.

In order to estimate the overall thermodynamics of the reaction, it is still necessary to observe that these $H_2C{=}CH(IOH)$ molecules are probably going to evolve in solution to produce more stable products. In particular, we have considered the reaction:

$$2\cdot H_2C{=}CH(IOH) \rightarrow H_2C{=}CHI + H_2C{=}CHIO + H_2O$$

The free energy of this reaction is 28.4 kcal mol^{-1} in favor of the products. The overall change in free energy of the whole process can be therefore estimated as −42.6 kcal mol^{-1}, which is the sum of the 9.8, −24.0 and −28.4 kcal mol^{-1} reported above. The epoxidation reaction with a dimeric iodosylethylene is therefore quite exothermic, but with a high reaction barrier of more than 50 kcal mol^{-1}.

Consideration of an extended solvent

It has been shown in the previous section how the presence of one water molecule, divided into one hydrogen atom at one end of the chain and a hydroxyl group at the other end, is critical for the stability of HO–(RIO)$_n$–H polymer chains in solution. We analyze here the effect of the bulk of the solvent on the chemical equilibria. The solvent was introduced through PCM calculations, which treat it as a polarizable continuum. The solvent used is water, which because of its high dielectric constant is expected to have the largest effects. The free energies of solvation obtained with this method for each of the compounds **1** to **9** were −3.6, 1.6, 0.9, −2.8, −0.3, −6.3, −1.7, −6.1 and −8.1 kcal mol^{-1}, respectively. These results are logical, the solvation energies being always rather small for neutral molecules and positive, disfavoring solvation in water, for the organic ethylene (**2**) and iodoetylene (**3**) molecules. The most relevant result is nevertheless that all energies lie within a span of 9.7 kcal mol^{-1} (between 1.6 and −8.1 kcal mol^{-1}), which is clearly insufficient to affect significantly the results presented in the previous sections. The absolute values would be even smaller if solvents different from water were considered. Therefore, we can conclude that the effect of the bulk of the solvent is relatively small in this system and it has a minor effect on the relative reactivities of the monomeric and dimeric forms of iodosylbenzene with respect to epoxidation.

Discussion

Our calculations indicate that the monomeric form of iodosylethylene would be able to carry out the epoxidation with a small barrier. On the other hand, the dimeric form, which constitutes a more realistic model of the experimental polymeric compound, yields a barrier of over 50 kcal mol^{-1}. It is therefore clear that the barrier is intimately related to the existence of the polymer. Therefore, the main role of any catalyst will be to provide a low energy mechanism for the breaking of the polymeric structure. The catalyst can act either by producing a soluble species with a monomeric unit of iodosylbenzene, by altering the surface chemistry of the solid to produce a local concentration of olefin accesible iodosyl groups or by abstracting an oxygen atom directly from the solid.

This result provides a simple explanation to the presence of two different mechanisms, depending on the particular catalyst, in the epoxidation of olefins by iodosylbenzene.[16,21,22] The difference between these two mechanisms, described in the Introduction and depicted in Scheme 1, is the nature of the reaction intermediate, which can be an oxo compound in which the oxygen is completely separated from iodine (**A**), or it can still contain an iodine attached to the oxygen (**B**). The existence of these intermediates corresponds to a stage where the polymeric structure, with the oxygen attached to two iodine atoms, is already broken. Because of this, the particular nature of the intermediate, **A** or **B**, is not as critical as its existence and the reaction can take place through quite different intermediates. The existence of "monomeric" soluble derivatives of iodosylarene,[25] stabilized by intramolecular interactions, looks therefore to be a promising way to convert these species into oxygen donors without the need for catalysts.

The behavior described in this work is likely characteristic of iodosylbenzene and cannot be directly extrapolated to other oxygen donors, where the abstraction of oxygen from the donor may be concerted with its transfer to the epoxide.

Concluding remarks

Theoretical B3LYP calculations on a iodosylethylene model allow to understand the main features of the reactivity of iodosylbenzene towards the uncatalyzed epoxidation of olefins and provide significant clues on the mechanism of catalysis. A monomeric iodosylbenzene would produce the epoxidation reaction with a very low barrier and the experimentally observed high barrier appears only when the polymeric nature of the iodosyl species is taken into account. This computational study has also allowed a better understanding of the polymeric structure, emphasizing the important role of the presence of a hydration water on the chain ends.

The origin of the barrier for the uncatalyzed epoxidation with iodosylbenzene is precisely the extraction of oxygen from the strongly bound polymer. Because of this, seemingly different catalysts able to break the polymer but forming different types of intermediates afterwards are efficient in this process.

Acknowledgements

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