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Mechanism of the Wolff Rearrangement. 6. Ab Initio Molecular Orbital Calculations on the Thermodynamic and Kinetic Stability of the Oxirene Molecule

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Abstract: A nonempirical SCF molecular orbital study using double- ζ quality basis set has been carried out on oxirene and its isomeric ketocarbene, the formylmethylene molecules with full optimization of the geometrical parameters. The total energy of the ground-state oxirene lies 11.8 kcal/mol above ground-state ketocarbene. The reaction path for the interconversion of the two species has also been studied with partial optimization of geometrical parameters. The ring opening reaction of oxirene to yield ketocarbene features an activation energy of 7.3 kcal/mol.

Oxirene and its methyl- and phenyl-substituted derivatives have been shown in recent years to have transient existence and to be implicated as short-lived reactive intermediates in the photolytic and high-temperature thermal decomposition of diazo ketones and ketenes.² The low-temperature thermal decomposition of these molecules, on the other hand, which in most cases leads to the same final products, proceeds via a different reaction path by-passing the oxirene structure. This general kinetic behavior was interpreted as a clear indication that oxirene formation is associated with the presence of excess energy in the reacting system, suggesting that it is thermodynamically less stable than its isomeric ketocarbene. This conclusion appeared to gain further support from theoretical studies. Extended Hückel molecular orbital calculations³ predicted approximately 30 kcal/mol higher energies for oxirene and mono- and dimethyloxirene than for their corresponding isomeric ketocarbene. Also, oxirene and its methyl derivatives were predicted to be inherently unstable with respect to C-O bond cleavage and to exist only as short-lived transients, for their isomerization to ketocarbene was calculated to have zero activation energy.

Further theoretical studies by Hopkinson⁴ and Dewar and Ramsden⁵ culminated in results which were in conflict with the above picture. Thus, Hopkinson, using an ab initio SCF-MO method with a minimum basis, concluded that oxirene is 0.4 kcal/mol more stable than its isomeric formylmethylene, while Dewar and Ramsden from their semiempirical MINDO/3 and NDDO methods computed oxirene to be 18.2 and 20.6 kcal/mol, respectively, more stable than formylmethylene.

The question of the stability of oxirene is of considerable significance on its own merit and also with regards to the mechanistic details of the Wolff decomposition-rearrangement sequence and the decomposition of ketenes. For these reasons we have undertaken another more reliable nonempirical SCF-MO study of the problem using a double- ζ quality basis set.

Method

The individual atomic orbitals used were built up by contraction from 80 primitive Gaussian-type functions (GTF),

and the molecular orbitals were obtained from a 34 contracted double- ζ quality s, p basis set by linear transformation. The basis orbitals associated with the carbon and oxygen ((9^s,5^p) contracted to [4^s,2^p]) and hydrogen atoms ((4^s) contracted to [2^s]) are those originally suggested by Dunning.⁶ The Roothaan-type SCF-MO computations⁷ were carried out on an IBM 360/67 computer using the IBMOL-IV system.⁸ Total energy values associated with the lowest singlet- and triplet-excited configurations of oxirene were computed by the virtual orbital technique.⁹

The geometry optimization was carried out in successive steps. One bond length or one bond angle was varied at a time. To three computed points, along a given mode, a quadratic equation was fitted in order to find the minimum. This fitted minimum point was recomputed in another SCF-MO calculation and that point also served as the first point for the optimization along the next geometrical parameter.

Results and Discussion

The total state energies for the singlet ground state of oxirene and formylmethylene were computed with the full optimization of the geometrical parameters. The results along with the lowest vertical triplet-state energies and dissociation products, C₂H₂ plus O(³P) and O(¹D₂) energies are summarized in Figure 1. The fully optimized geometrical configuration of oxirene lies 11.8 kcal/mol above the fully optimized geometry of formylmethylene. Since the present computation is much more sophisticated¹⁰ than the previous ones and the results are in agreement with all experimental observations on the kinetic features of the oxirene-forming reactions, we conclude that oxirene is thermodynamically less stable than its isomeric ketocarbene, formylmethylene. This result agrees, at least in the qualitative sense, with the earlier extended Hückel calculations, which gave approximately 30 kcal/mol for the stability difference for oxirene and formylmethylene and slightly larger values for mono- and dimethyloxirene. On this basis we also conclude that methyl- and dimethyloxirenes are also thermodynamically less stable than their corresponding ketocarbenes. Thermodynamic instability, of course, does not preclude the possibility of kinetic stability. The earlier extended Hückel calculations, however, predicted no kinetic

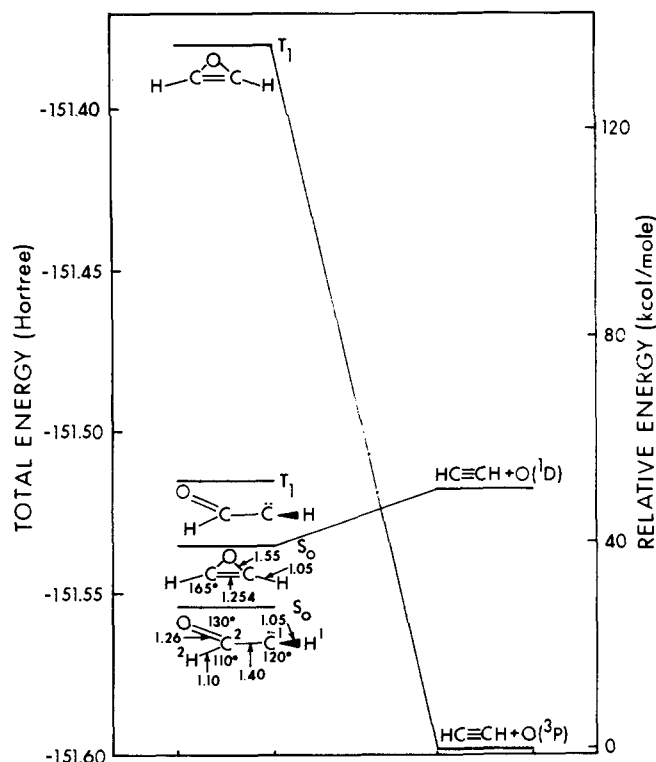


Figure 1. Computed total energies and geometries. The acetylene energy was calculated for the experimental geometry and the oxirene and formylmethylene are fully optimized with geometrical parameters indicated.

stability either for oxirene or mono- and dimethyloxirenes, since their ring-opening isomerization to ketocarbene revealed no energy barrier for the process. Therefore, we reexamined the isomerization reaction path using the present ab initio method. Before proceeding further, however, it should be noted that the lowest vertical triplet excitation energy of oxirene is considerably higher than that of formylmethylene. Also, the energy manifold of the ketocarbene and oxirene should be lowered relative to the acetylene plus oxygen atom manifold, since the addition of triplet oxygen atom to acetylene to yield the lowest triplet state of formylmethylene should be an exothermic process. This distortion of the energy manifold is due to the neglect of correlation energies. In the adduct, there is one more electron pair than in the dissociated reactant. The average value of correlation energy is 0.06–0.10 hartree per electron pair and, therefore, the adduct manifold should be

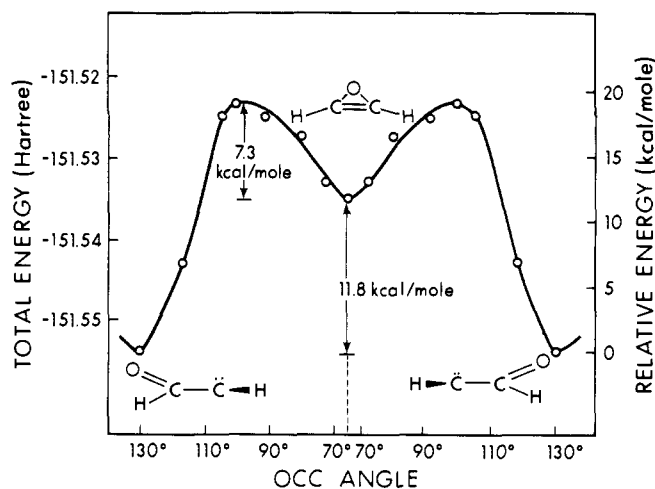


Figure 2. Computed total energy variation for the interconversion of oxirene and formylmethylene. For further details cf. Table I.

lowered by about 36–60 kcal/mol to give the correct values for the enthalpy changes of the addition–dissociation reaction.

In order to elucidate the kinetic stability of the oxirene molecule, the OCC bond angle was varied between the oxirene and ketocarbene values and the bond lengths and CH bond angles were partially optimized, bracketing but not precisely identifying the energy minimum. The resultant potential energy curve is depicted as a function of OCC angle in Figure 2 and the data are given in detail in Table I. As seen, the oxirene–formylmethylene isomerization reaction features an activation energy of 7.3 kcal/mol. From this the lifetime of oxirene at room temperature when formed from thermalized formylmethylene can be estimated to be shorter than 10^{-8} s. This result, when considered in conjunction with the predictions of the earlier extended Hückel calculations giving zero activation energy for the alternative, competing isomerization of formylmethylene to ketene explains why oxirene could not be trapped chemically or stabilized by matrix isolation techniques. Of course it would be erroneous to conclude from the present computational results that all derivatives of oxirene should be unstable or unscavengeable. Appropriate substituents could conceivably lower the energy of oxirene below the ketocarbene and/or increase the energy barrier of the ketocarbene \rightarrow ketene process relative to the ketocarbene \rightarrow oxirene process.

Finally, a study using the minimal basis set of Klessinger¹¹ has also been made of the conformational hypersurface of formylmethylene, searching for additional minima corre-

Table I. Structural Parameters of the Reaction Intermediates for the Oxirene–Formylmethylene Isomerization

	Oxirene	I	II	III	IV	V	VI	Formylmethylene
$R(C(1)-C(2))$, Å	1.254	1.269	1.275	1.275	1.275	1.342	1.371	1.400
$R(C(2)-O)$, Å	1.550	1.521	1.380	1.380	1.350	1.376	1.318	1.260
$R(C(2)-H(2))$, Å	1.050	1.055	1.070	1.070	1.070	1.080	1.090	1.100
$R(C(1)-H(1))$, Å	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
$\angle OC(2)C(1)$, deg	66.14	72.53	80.00	91.68	100.00	104.46	117.23	130.00
$\angle C(1)C(2)H(2)$, deg	165.00	159.50	155.00	143.00	135.00	132.00	121.00	110.00
$\angle C(2)C(1)H(1)$, deg (in plane)	165.00	166.50	180.00	180.00	180.00	174.00	177.00	180.00
$\angle C(2)C(1)H(1)$, deg (out of plane)	180.00	174.00	180.00	180.00	180.00	144.00	132.00	120.00
Total energy S_0 (hartree)	-151.53502	-151.53281	-151.52740	-151.52500	-151.52341	-151.52484	-151.54278	-151.55386

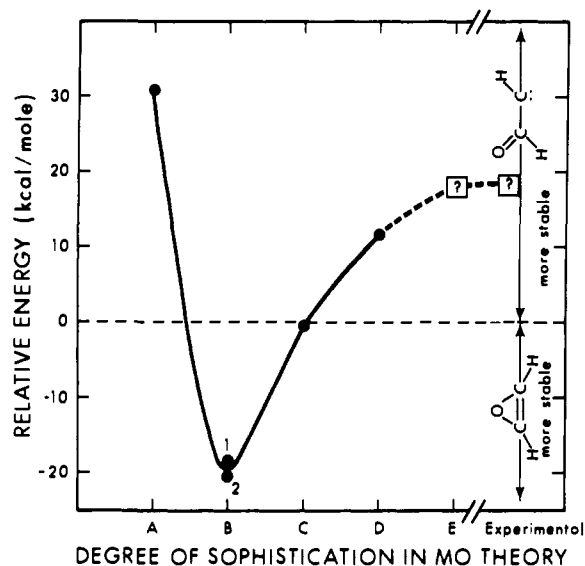
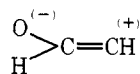


Figure 3. Improvement in relative energies of formylmethylene and oxirene as a function of degree of sophistication in the MO theory used: (A) Extended Hückel molecular orbital (EHMO) theory; (B) (1) MINDO/3 and (2) NNDO molecular orbital theory; (C) Ab initio SCF-MO theory with minimal basis set; (D) Ab initio SCF-MO theory with extended basis set (present study); (E) Ab initio SCF-MO theory with extended basis set + polarization function (future study).

sponding to the zwitterion structure:



Although the minimal basis set SCF-MO method tends to exaggerate the stability of ionic structure, no additional minimum could be located in the hypersurface, indicating that the ketocarbene with the geometry given in Figure 1 is the only stable structure for formylmethylene.

In conclusion, some remarks would perhaps be in order in connection with the noticeable discrepancy obtained by the MO theory at the varying level of sophistication. This discrepancy is associated with the fluctuation of the calculated relative stability:

$$\Delta E = E(\text{oxirene}) - E(\text{formylmethylene})$$

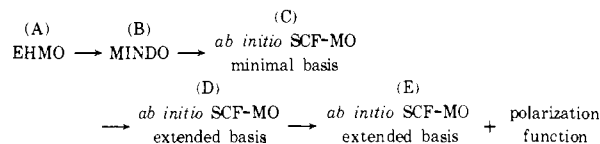
which in turn is a consequence of the fact that although the Variation Theorem guarantees for all molecular species that an improvement in our calculation will lower (i.e., improve) our computed total energy (E) it says nothing about the rate

of improvement. In other words, the rate of improvement may be greater for one species and smaller for the others. Consequently, this will change ΔE not only in magnitude but in sign as well, as illustrated in Figure 3. Thus, sometimes a little improvement in the method will spoil the relative stability obtained by the less sophisticated method and one has to go a long way to ensure that we are converging not only to both of the E values, but to the exact ΔE value as well. Undoubtedly further improvement in the computation would change our present relative stability ($\Delta E = 11.8$ kcal/mol), but accumulated experience would suggest that the final value should be within ± 5 kcal/mol.

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Clearly the present wave function obtained by basis set D is more sophisticated than that obtained by either A, B, and C. However, wave function D may be superceded in the future by wave function E, but it is not expected to alter the present results markedly. More important is the fact that all of these (from A to E) represent SCF-MO computations, while the wave function of the latter four (B, C, D, and E) may further be improved by configuration interaction (CI) calculation. The inclusion of CI is important in all those cases where electron pairs are unpaired, but in our case the pairing scheme is conserved throughout the process investigated and for this reason we are confident that method D will yield at least semiquantitative results. (Cf. Figure 3 and accompanying discussion at the end of this paper.)

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