The results of Clementi's ab initio calculation for thymine,[7] specifically the MO order, are also in excellent accord with experiment but provide absolute MO energies which are ~2 eV too large.

The photoelectron spectrum of uracil has been reported by Padva et al.[3a] The assignments of these authors were based on a direct correspondence with the results of a semiempirical INDO calculation. The lowest energy ionization potentials, IP(1), of uracil and thymine have been reported by Hush and Cheung.[22] The assignments of these authors were based on direct comparison with the results of ab initio SCF-MO and semiempirical INDO calculations. It is a testament to the value of these calculations that all of them, including our own, provide the same set of assignments for IP(1) through IP(4) and that this set agrees with the empirical one. The one disagreement occurs in IP(5) which is assigned[3a] as $I(\sigma)$ on the basis of INDO calculations and as $I(\pi_3)$ on the basis of CNDO/s calculations; the empirical assignment agrees with the CNDO/s results.

An additive methylation effect on the ionization potentials of simple amides has been shown to occur.[8] We now consider the extent to which such additivity relations are valid for the methylated urea series. As may be verified in Figure 3, additivity of ΔIP(1) obtains within the triads {urea, methylurea, 1,1-dimethylurea} and {1,1-dimethylurea, trimethylurea, tetramethylurea}, but not between triads. Additivity of ΔIP(2) obtains within the triads {urea, methylurea, 1,3-dimethylurea} and {1,1-dimethylurea, trimethylurea, tetramethylurea} as well as between corresponding members of each triad. Thus, additivity behavior does exist, but its existence depends on the choice of sets and is by no means as general as that found in simple monoamides.

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Reaction of Atomic Carbon with Ethylene Oxide. A MINDO/3 Study of Possible Pathways

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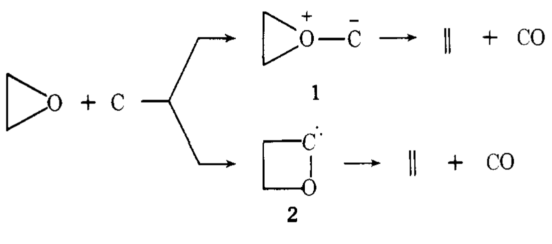
Abstract: A MINDO/3 semiempirical molecular orbital calculation of the energetics of the deoxygenation of ethylene oxide by atomic carbon has been carried out. The results indicate that the most favorable pathway is one in which the carbon strips the oxygen along a reaction coordinate leading directly to carbon monoxide and ethylene without local energy minima. The energetics of insertion of carbon into the C–O bond of ethylene oxide to produce 2-oxacyclobutylidene (**2**) have also been investigated. Carbene **2** is at an energy minimum and has a calculated ΔH_f of 6.7 kcal/mol. The two most likely reactions of **2** appear to be rearrangement to oxetene ($\Delta H^{\ddagger}$ = 36 kcal/mol) and ring contraction to cyclopropanone ($\Delta H^{\ddagger}$ = 39 kcal/mol). The activation enthalpy for the extrusion of CO from cyclopropanone via a nonlinear cheleotropic pathway is calculated to be 41 kcal/mol.

The deoxygenation of epoxides to produce carbon monoxide and an alkene is an extremely facile reaction of atomic carbon (eq 1). This reaction has been observed to occur with arc-generated carbon,[2] with carbon produced by the thermolysis of 5-tetrazoyldiazonium chloride[3] and with nucleogenic carbon-11 atoms.[4] We have recently reported that the deoxygenation of the 2-butene oxides by chemically generated carbon atoms is stereospecific.[5]



(1)

In order to elucidate the pathway by which this deoxygenation occurs, we have carried out a molecular orbital study using the MINDO/3 method recently developed by Dewar and co-workers.[6,7] Dewar, Haselbach, and Shanshal have used the MINDO/2 method to calculate the reaction coordinate for addition of atomic carbon to ethylene.[8] In carrying out the current study, we have made the initial assumption that either the ylide **1** or the carbene **2** is the intermediate in the deoxygenation. Ylide **1,** originally postulated by Skell, results from direct attack of carbon at the oxygen, while **2** is produced by an insertion of carbon into a strained C–O bond of ethylene oxide.

We have investigated the energetics of the formation of **1** and **2** and subsequent reactions of both of these interesting species.

Results and Discussion

Reactions of Carbon at Oxygen. An initial attempt to use MINDO/3 to calculate the energy of **1** led to an unexpected result. An estimate of the geometry of **1** was obtained by placing the carbon atom 1.15 Å from the oxygen of ethylene oxide with C_{2v} symmetry. When this structure was subjected to the geometry optimization procedure of MINDO/3, it surprisingly went immediately to carbon monoxide and ethylene separated by 7 Å.

Thus, the calculations indicate that there is no barrier to the decomposition of **1** to CO and ethylene. Further, when the carbon was placed 1.4 Å from the oxygen and the geometry allowed to optimize, the carbon atom moved in to pull off the oxygen and again produced CO and ethylene. We interpret the results of these calculations to indicate that attack of carbon at the oxygen of ethylene oxide gives CO and ethylene by what is essentially a stripping reaction. The carbon simply moves in and strips the oxygen along a reaction coordinate which has no localized minimum. Thus **1** is not a true intermediate in this reaction.

Figure 1 shows the geometries and energies of several points along the coordinate of this stripping reaction. This figure and those which follow were computer generated from geometries and energies calculated by MINDO/3. In all figures, dots have been placed on the oxygen atom for clarity. Figure 1 shows relevant interatomic distances as the stripping reaction proceeds. At the final point of this reaction (not shown in Figure 1) the ethylene and CO are separated by 7.2 Å, and the energy of the system, as expressed by the heat of formation, is 5.7 kcal/mol. Separate MINDO/3 calculations[6] predict that the heats for formation of CO and ethylene are respectively −13.5 and 19.2 kcal/mol, which sum to the 5.7 kcal/mol predicted in this study.

The stereochemical consequences of this stripping reaction are interesting. In order to test the energetics of nonstereospecific ethylene formation, we have calculated the barrier to a 90° rotation about the C(3)–C(4) bond. When this rotation is performed on the 70.5 kcal/mol structure of Figure 1, the energy is raised by 30 kcal. The difficulty of rotation is also demonstrated by considering the Mullikin overlap population[10] between C(3) and C(4) as the stripping reaction proceeds. This overlap population, enclosed in parentheses in Figure 1, increases continuously as the reaction proceeds, indicating little chance for rotation. Since there is no local minimum along the reaction coordinate, there will be minimal time for rotation, and its consequent nonstereospecific ethylene formation. A $\Delta H^{\ddagger}$ of 30 kcal/mol along with a normal Arrhenius A value leads to a rate of $\sim 10^{-9}$ s^{-1} for rotation. Inasmuch as a crude calculation of molecular velocities yields a value of $\sim 6 \times 10^{-4}$ cm s^{-1}, there is insufficient time for rotation to occur during the stripping reaction. The majority of the exothermicity in this reaction should appear as translational energy and be unable to effect rotation.

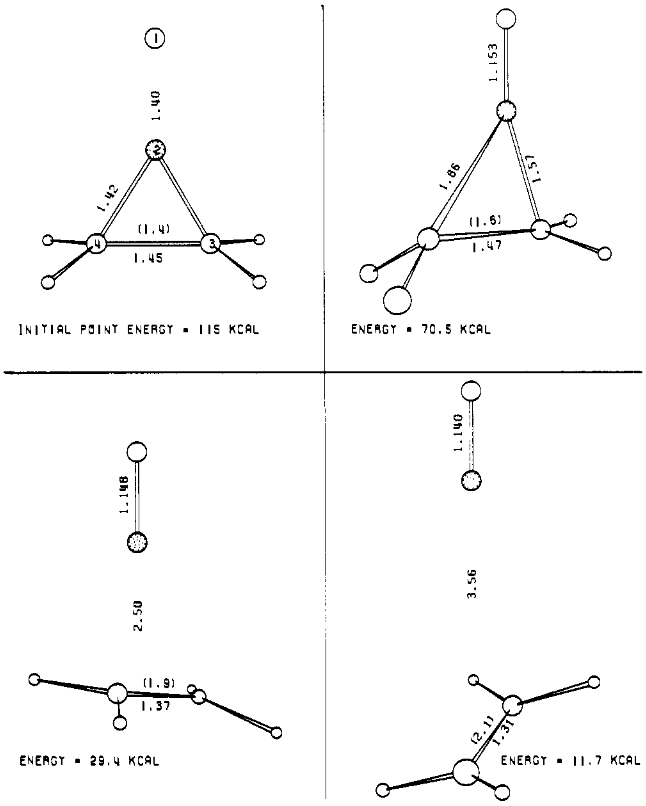


Figure 1. Several geometries along the reaction coordinate for the stripping of oxygen from ethylene oxide by atomic carbon. The numbers on the figure are relevant interatomic distances in angstroms, while numbers enclosed in parentheses are the overlap populations between carbons 3 and 4. Energies are ΔH_f's calculated by MINDO/3.

It should be mentioned that the above calculations are for the closed-shell singlet state. Since our experimental results indicate that triplet carbon is not involved in the deoxygenation reaction,[5] we have not investigated energy surfaces involving C(^{3}P). However, it is possible for this deoxygenation to proceed via an open-shell singlet. Such a reaction coordinate would produce excited CO or ethylene if no crossing to the ground surface occurs. We have carried out limited calculations of the approach of carbon to ethylene oxide using the open-shell singlet surface. As expected, no spontaneous stripping reaction occurs, and the closed-shell energy surface becomes lower in energy when the system reaches the geometry of the 70.5 kcal/mol structure of Figure 1.

Insertion into the Carbon–Oxygen Bond. We have investigated the reaction coordinate for insertion of carbon into the C–O bond of ethylene oxide. Unlike the attack at oxygen, the geometry optimization does not lead spontaneously to CO and ethylene or to carbene **2.** However, if the system is restricted so that the C(1)–C(3)–C(4) angle (Figure 2) is kept constant at 30°, an exothermic pathway to carbene **2** is found as the C(1)–C(3) distance is systematically decreased. Figure 2 shows several geometries and energies along this reaction coordinate. When the C(1)–C(3) distance reached 2.3 Å, the C(1)–C(3)–C(4) angle was allowed to optimize along with the other geometric parameters. This procedure led to carbene **2,** whose equilibrium geometry is shown in Figure 3.

The calculated stability of **2** (ΔH_f = 6.7 kcal/mol) is quite surprising and needs further elaboration. It is clear that the calculated stability of **2** results from interaction with the adjacent oxygen. A calculation of the heat of formation of cyclobutylidene (**3**) (ΔH_f = 81.4 kcal/mol) reveals no special stability for the four-membered ring carbene.

Since molecular orbital indices of bonding, such as bond order and overlap population, reveal little difference between

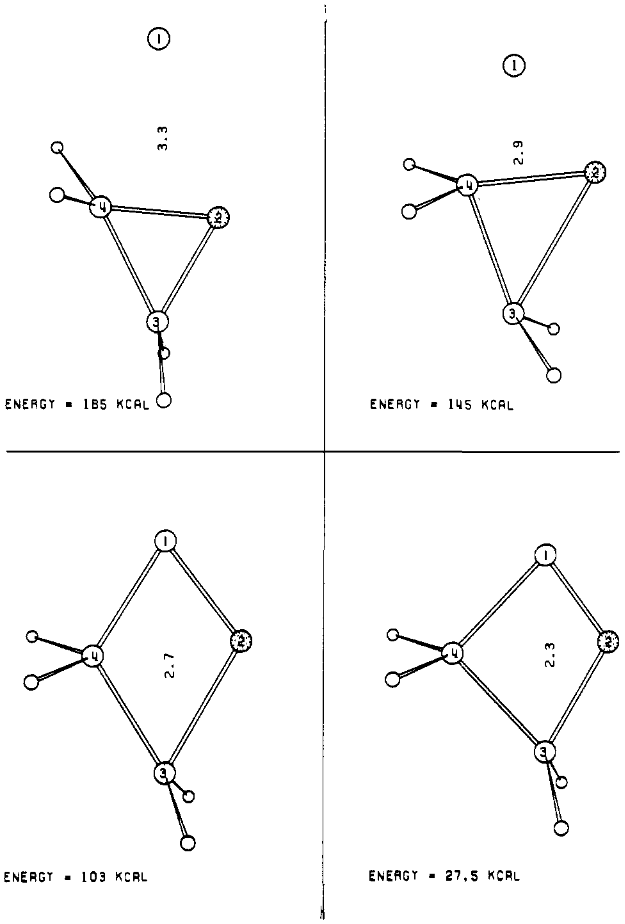


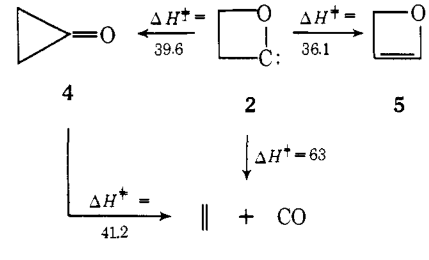
Figure 2. Reaction coordinate for insertion of atomic carbon into the C-O bond of ethylene oxide. The distance between C(1) and C(3) in Å is shown on the figure. When C(1)-C(3) reached 2.3 Å, all geometric constraints were removed, and the system went to carbene **2**, which has a calculated equilibrium geometry as shown in Figure 3. Energies are ΔH_f's calculated by MINDO/3.

2 and **3**, the calculated stability of **2** over **3** cannot be ascribed to a difference in bond strengths. However, calculated electron densities are quite different in **2** and **3**. An examination of the orbital electron densities in **2** reveals that the out-of-plane p_z orbital contains an electron density of 0.36 (vs. 0.15 in **3**), while the remaining atomic orbitals have a total electron density of 3.44 (vs. 3.85 in **3**).

Thus, the oxygen acts to alter the electron density about the carbene carbon in **2**. Electrons are donated to the empty p orbital, while they are withdrawn from the filled sp^2 orbital. Dewar and Bodor[11] have discussed the effect of substituents on carbene stability in terms of the effect of those same substituents on the stability of the carbonium ion, which is the conjugate acid of the carbene. They postulate that groups which lower the energy of the carbonium ion by electron donation into the empty p orbital have a similar effect on the stability of the carbene. Since oxygen stabilizes an adjacent carbonium ion, a similar effect is observed in **2**.

We now turn our attention to a discussion of the reaction pathways expected for **2**. Scheme I shows various reactions

Scheme I



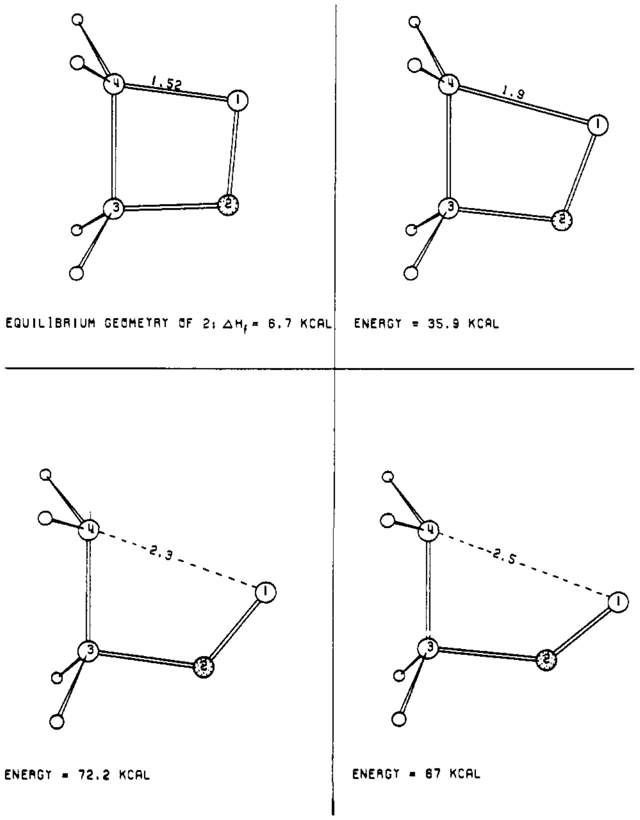


Figure 3. Several geometries along the reaction coordinate for decomposition of **2** to carbon monoxide and ethylene. The figure shows relevant interatomic distances. Energies are ΔH_f's calculated by MINDO/3.

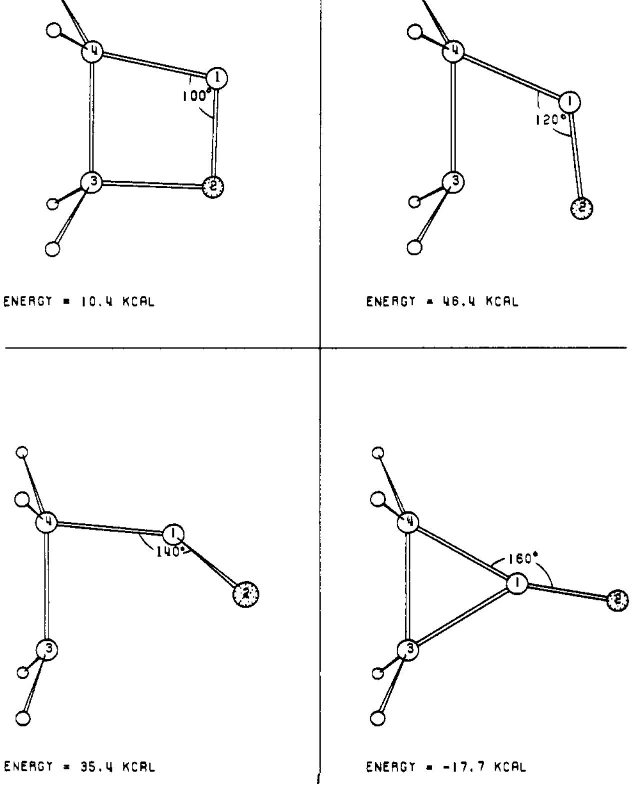


Figure 4. Several geometries along the reaction coordinate for rearrangement of **2** to cyclopropanone. Energies are ΔH_f's calculated by MINDO/3.

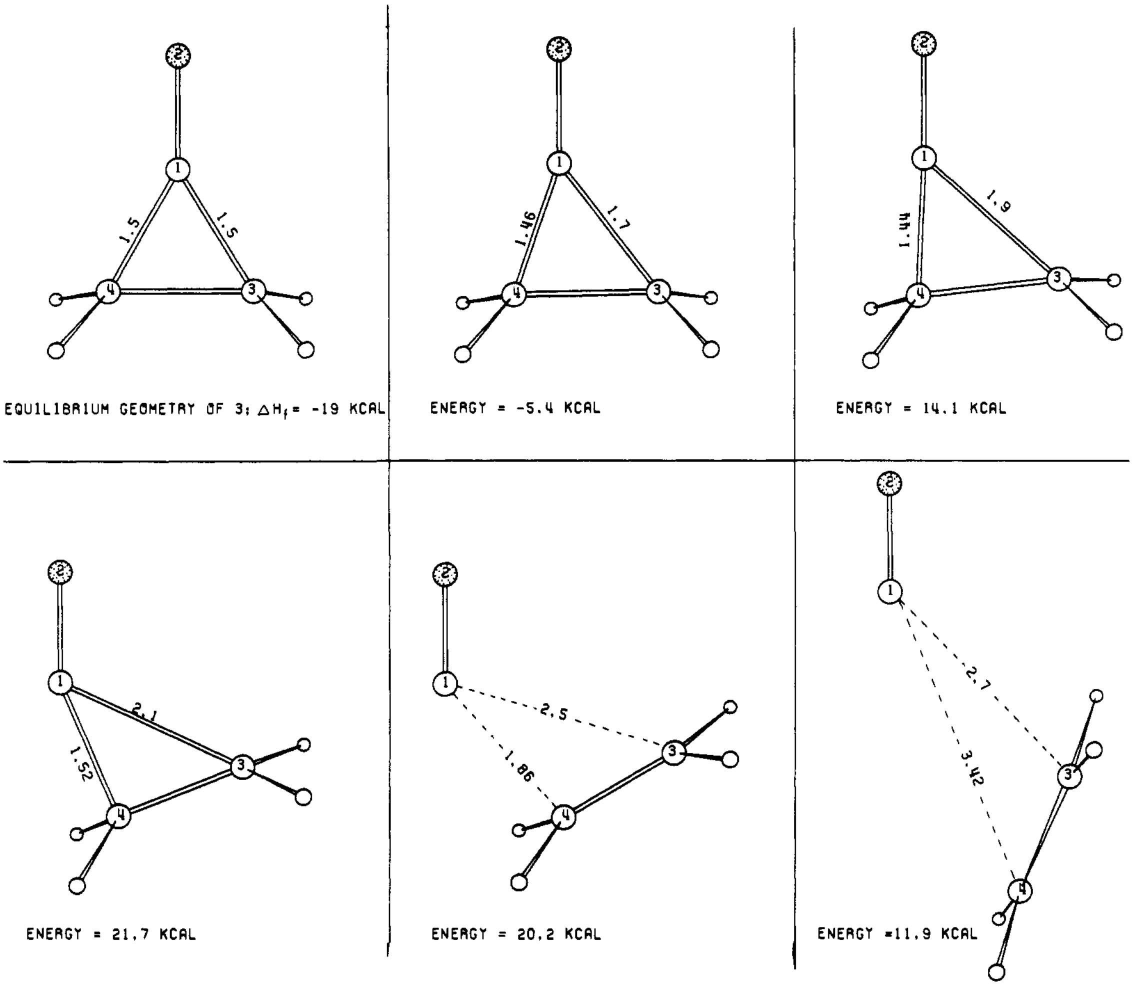


Figure 5. The calculated nonlinear cheleotropic pathway for extrusion of ethylene from cyclopropanone. Energies are ΔH_f's calculated by MINDO/3.

of **2** along with activation enthalpies that have been calculated using MINDO/3. Each of the reactions shown in Scheme I will be briefly discussed.

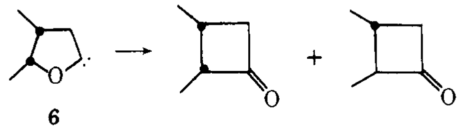
Decomposition of 2 to Carbon Monoxide and Ethylene. An initial attempt to use the C(3)-O(2) distance as the reaction coordinate failed to bring about the decomposition to CO and ethylene. Instead, the molecule was calculated to rearrange to cyclopropanone via a high-energy pathway. The use of the C(1)-C(4) distance as reaction coordinate carried the system toward carbon monoxide and ethylene. Every other atomic coordinate of **2** was free to seek its optimum value. The equilibrium geometry of **2** along with several points along this reaction coordinate are shown in Figure 3. Once the maximum-energy geometry of Figure 3 is passed, spontaneous decomposition to ethylene and CO occurs.

The rather high energy barrier calculated for this reaction is characterized by the unassisted breaking of the C(1)-C(4) bond. Basic orbital symmetry considerations dictate the nonconcerted pathway, which is calculated by MINDO/3.

It is obvious that the breaking of the C-C bond can lead to an open-shell singlet biradical. MINDO/3 calculates that the energy of the open-shell singlet corresponding to the geometry of the maximum lies only 6 kcal/mol above that of the closed-shell singlet. Thus, it appears likey that a crossing of energy surfaces in the vicinity of the maximum will lower the calculated activation energy. It should be noted, however, that the open-shell singlet surface leads ultimately to the extremely endothermic formation of either CO or ethylene in an electronically excited state.

Rearrangement of 2 to Cyclopropanone. The lowest energy pathway for this rearrangement is calculated when the O(2)-C(1)-C(4) angle is chosen as the reaction coordinate. A plot of several geometries along this reaction coordinate is shown in Figure 4. The equilibrium geometry calculated for cyclopropanone is shown in Figure 5.

Again this reaction coordinate is characterized by its nonconcerted nature. Complete breaking of the C(3)-O(2) bond occurs before substantial bonding can occur. The lack of concert in the rearrangement of the five-membered ring carbene **6** to *cis*- and *trans*-2,3-dimethylcyclobutanone has been demonstrated experimentally.[12]



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Decomposition of Cyclopropanone to Carbon Monoxide and Ethylene. Since the activation energy for rearrangement of **2** to cyclopropanone is considerably lower than that for its decomposition to ethylene and CO, an alternate pathway by which **2** can produce carbon monoxide and ethylene is via cyclopropanone decomposition. Although the activation energy for the extrusion of CO from cyclopropanone has not been measured, there is ample experimental evidence that this reaction occurs.[13,14]

Several geometries along the calculated reaction coordinate for decomposition of **4** to CO and ethylene are shown in Figure 5. According to Woodward and Hoffmann,[15] this reaction represents an example of a nonlinear cheleotropic reaction. The MINDO/3 calculted reaction path bears out this prediction exactly. An examination of the structures of Figure 5 shows

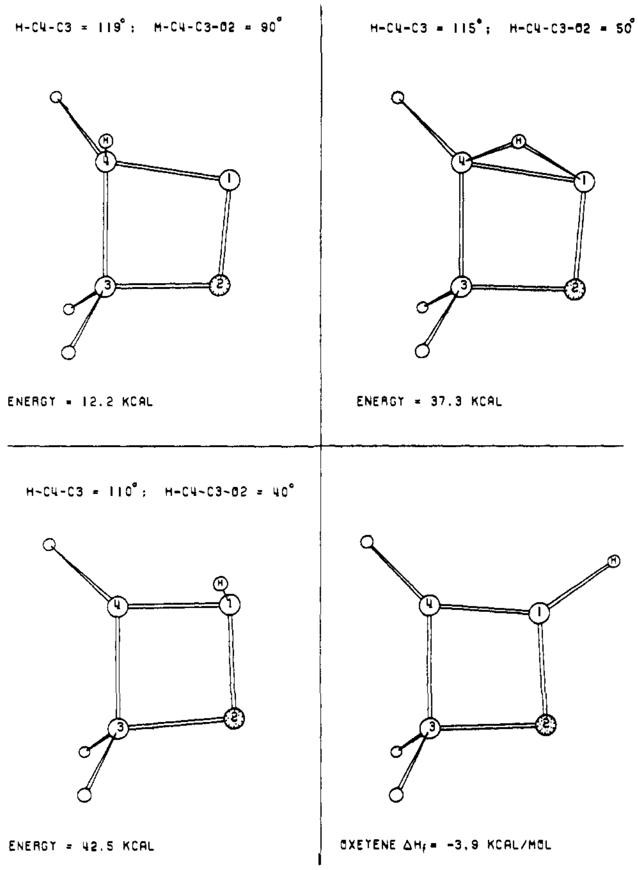

Figure 6. Several geometries along the reaction coordinate for rearrangement of **2** to oxetene **5.** Energies are ΔH_f's calculated by MINDO/3.

a beautiful nonlinear cheleotropic pathway with a rather high barrier of 41 kcal/mol. A glance at the figure reveals the origin of this energy barrier. The molecule distorts itself until it is sufficiently removed from the original C_{2v} symmetry. At this point the reaction is no longer symmetry forbidden and occurs spontaneously. The figure shows that most of the activation energy is expended in destroying the C_{2v} symmetry rather than in removing the CO. It is interesting that a MINDO/3 calculation of the linear cheleotropic pathway, in which C_{2v} symmetry is retained, gives an activation energy of 86 kcal/mol.

Intramolecular C–H Insertion by 2. A third possible reaction of **2** is a 1,2-hydrogen migration to give oxetene (**5**). This is perhaps the most common reaction of carbenes with β protons.[16]

Several geometries along the reaction coordinate for hydrogen migration are shown in Figure 6. The search for a suitable reaction coordinate was more difficult in this case than in those discussed previously. A preliminary calculation with MINDO/2 had indicated that the H-C(4)-C(3)-O(2) twist angle would be a suitable reaction coordinate. However, the use of this angle with MINDO/3 led to difficulties when a twist angle of 30° was reached. At this point the H-C(4)-C(3) angle opened until it was greater than 180°, and the hydrogen was taken to the opposite side of the C(1)-C(4) axis. From this point the system approached the geometry of **2**. For this reason, the calculation was repeated for a fixed H-C(4)-C(3) angle and H-C(4)-C(3)-O(2) twist angle. The angles chosen were those calculated along the MINDO/2 reaction coordinate. The remaining degrees of freedom were allowed to optimize, the only restriction being that the protons on C(3) were treated as mirror images of one another.

The striking feature of the calculated reaction coordinate is its high activation energy. Calculations of the activation energy for this reaction in alkyl carbenes have revealed extremely low barriers.[11,17] Experimentally the reactions of various alkyl carbenes bear out this prediction quite nicely.[15] Although there is less experimental evidence concerning the reactivity of carbenes analogous to **2**, it has been shown that ring contraction in **6** is competitive with hydrogen migration.[12] The activation energies calculated here indicate that ring contraction and hydrogen migration are also competitive processes in reactions of **2**.

Figure 6 reveals that the maximum point along the reaction coordinate is quite close to the geometry of the product. In other words, there is a late energy barrier. Hydrogen migration in ethylcarbene is exothermic by close to 60 kcal/mol, while the exothermicity associated with hydrogen migration in **2** is calculated to be only 10 kcal/mol. Since we are dealing with a late energy barrier, this barrier is superimposed on the exothermicity of the reaction. This results in a minimal barrier for the highly exothermic rearrangement of ethylcarbene, but a considerable barrier in the far less exothermic rearrangement of **2** to oxetene **5**. Thus, we propose that the unusual stability of **2** combined with the strain energy of **5** renders the rearrangement of **2** to **5** less exothermic than expected, bringing about the development of a rather high activation energy.

We may now briefly inquire into the fate of oxetene formed by this reaction. Although oxetene itself has not been synthesized, tetramethyloxetene undergoes electrocyclic ring opening to 3,4-dimethyl-3-penten-2-one with an activation enthalpy of 25 kcal/mol.[18] We have used MINDO/3 to calculate that the enthalpy of activation for the electrocyclic ring opening of **5** is 30.7 kcal/mol. This calculation was quite straightforward. A reaction coordinate involving the simultaneous opening of the C(1)-C(3)-C(4) and the O(2)-C(4)-C(3) angles in oxetene carried the molecule smoothly to acrolein.

Conclusions

The MINDO/3 method distinguishes three pathways for the deoxygenation of ethylene oxide. The first is the stripping reaction having no activation energy. The two other pathways involve the intermediacy of **2**. Direct decomposition of **2** to ethylene and carbon monoxide has a calculated activation enthalpy of 63 kcal/mol. The alternative ring contraction of **2** to cyclopropanone, followed by extrusion of carbon monoxide, has a $\Delta H^{\neq}$ of 41 kcal/mol.

We interpret the results of these calculations to indicate that the deoxygenation of ethylene oxide proceeds via the direct stripping reaction. The lack of any energy barrier renders this an extremely attractive pathway. If carbene **2** were an intermediate, one would expect to see acrolein as an additional product. We have been unable to isolate any acrolein in our reactions of chemically generated carbon with ethylene oxide.[3] Acrolein has not been reported in other studies of this reaction.[2,4]

Because of the intriguing results obtained in this preliminary study, we are continuing to investigate the utility of MINDO/3 in studies of carbon atom reactions. Experiments directed toward the production of carbene **2** are also underway in these laboratories.

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Conversion of Hydroxyphenyl to Phenoxyl Radicals: A Radiolytic Study of the Reduction of Bromophenols in Aqueous Solution[1]

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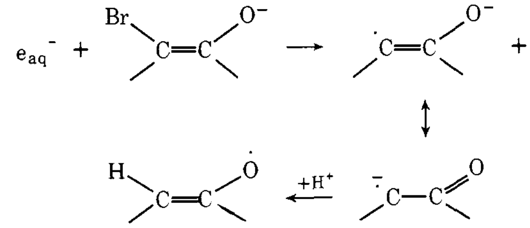
Abstract: Both steady-state ESR and spin trapping experiments demonstrate that hydroxyphenyl radicals are produced in the reaction of hydrated electrons with the bromophenols. Conductometric and optical pulse radiolysis studies show that the anionic forms of the ortho and para hydroxyphenyl radicals protonate rapidly at the radical site to produce phenoxyl radical. At pH 11.5 the protonation periods are respectively 14 and 4.1 μs. The meta isomer protonates at least an order of magnitude more slowly. Protonation is not observed for the neutral forms of these radicals. The important feature required for protonation appears to be the existence of appreciable negative charge density at the radical site. The rapid protonation of the *p*-hydroxyphenyl radical anion observed here provides a reference with which to compare other reactions of this radical and it has been possible to estimate a rate constant of $6 \times 10^5\ M^{-1}\ s^{-1}$ for its abstraction of H from *tert*-butyl alcohol and $4 \times 10^7\ M^{-1}\ s^{-1}$ for its addition to nitromethane. In the case of *p*-bromophenol, the phenoxyl radicals resulting from the initial protonation undergo a tertiary electron transfer reaction with *p*-bromophenoxide with a rate constant of $2.0 \times 10^8\ M^{-1}\ s^{-1}$, so that the optical absorption spectra of the three bromophenoxyl radicals produced by OH reactions were also examined and are reported here. Because of this tertiary transfer, phenoxyl radicals cannot be observed in steady-state ESR experiments on these systems. Studies of the dependence of the width of the ESR lines of phenoxyl radical produced from phenol on the phenol concentration show that electron transfer between the radical and the substrate occurs with a rate constant of $1.9 \times 10^8\ M^{-1}\ s^{-1}$.

Introduction

Studies[2] of the attack of e_{aq}^- on bromotetronate anion make it clear that the radical anion initially produced by the reductive elimination of Br^- protonates very rapidly at the radical site. Presumably this protonation results from appearance of appreciable negative charge at the radical carbon, i.e., as shown in the reaction below. Similarly, in the radicals produced as the result of electron attack on *p*- and *o*-bromophenolate, but not in the case of the meta isomer, one expects that there will be appreciable negative charge at the radical site and protonation seems likely. It was, therefore, decided to carry out optical and conductometric pulse radiolysis studies on the radiation chemistry of solutions of the bromophenols to examine for protonation of the radicals produced initially. It was indeed found that in their anionic forms the *p*- and *o*-hydroxyphenyl radicals protonate rapidly on the ring carbon to form phenoxyl radical. Protonation of the meta isomer is at least an order of magnitude slower. It was also found that in their neutral forms, these radicals do not observably undergo protonation. These observations explain the fact that hydroxyphenyl radicals were observed in steady-state ESR experiments on *m*-bromophenol,[3] but not in the cases of the other isomers. The results of pulse radiolytic and steady-state ESR experiments on the three bromophenols are described in the following. The studies on *p*-bromophenol make it apparent that electron transfer between phenoxyl radicals and phenoxide is fairly rapid ($k \sim 10^8\ M^{-1}\ s^{-1}$), so that information on this transfer reaction is also included.



Experimental Section

p-Bromophenol (Eastman Chemical Co.) and *o*- and *m*-bromophenol (Aldrich Chemical Co.) were used without further purification. Phenol, *tert*-butyl alcohol, and the inorganic compounds used were Baker Analyzed Reagents. For studies involving the reaction of e_{aq}^-, the water used was triply distilled from basic permanganate and acid dichromate with a final distillation in a quartz system. Oxygen was removed by purging with nitrogen containing <0.01% oxygen.

The optical pulse radiolysis system described by Patterson and Lilie[4] was used. The software used in this system has now been modified to make it feasible to average a large number of experiments and to store and display 100 points on each trace for a more detailed examination of the overall kinetics. Dosimetry was by measurement on the N_2O