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Computational Prediction of New Mechanisms for the Reactions of Vinyl and Phenyl Radicals with Molecular Oxygen

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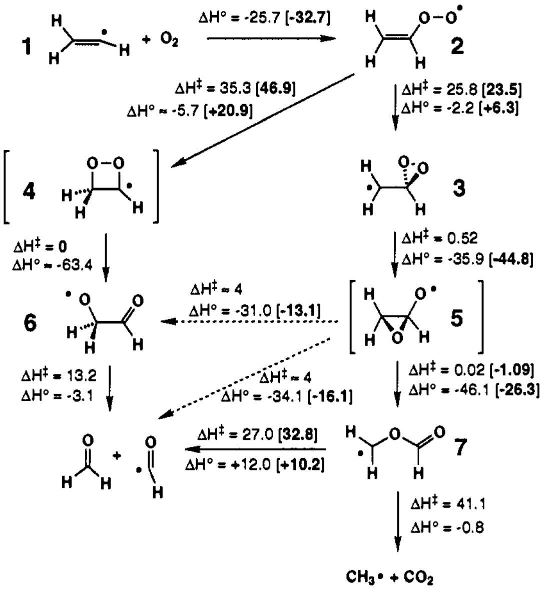
The reactions of vinyl and phenyl radicals with O_2 ($^3\Sigma_g$) play crucial roles in the combustion of hydrocarbons.[1,2] The primary products have been identified as CHO and CH_2O from the vinyl radical (below 900 K)[3] and are believed to be the cyclopentadienyl radical, CO, and O from the phenyl radical.[4] Mechanisms for these reactions have been suggested, and, in the case of the vinyl radical reaction, the activation parameters have been determined.[3]

In this communication are reported the results of quantum mechanical calculations, which lead to the suggestion of new mechanisms and possibly new products for these reactions.

The plausible mechanism that has been proposed for the formation of CHO and CH_2O from the vinyl radical (**1**) and O_2 involves the formation and cleavage of the dioxetanyl radical **4** (Scheme I).[5] However, semiempirical (PM3/UHF)[6] and ab initio (PMP4(SDTQ)/6-311G(d)//UMP2/6-311G(d) with UMP2/6-311G(d) zero-point energy (ZPE) corrections)[7] molecular orbital calculations suggest that formation of the dioxiranylmethyl radical **3** (Scheme I) has a lower activation barrier than does formation of **4**.[8] The lower barrier for formation of **3** can be understood when one recognizes that a 90° C–C rotation is required for formation of **4** from the vinylperoxy radical **2** but not for formation of **3** from **2**. The C–C rotation during formation of **4** leads to loss of π bonding, with a consequent increase in the activation energy.[9]

The hydrocarbon analogues of **2**, **3**, and **4** are respectively 3-butenyl, cyclopropylmethyl, and cyclobutyl. In this manifold, one finds experimentally that the four-membered-ring transition structure[10] has a heat of formation that is about 20 kcal/mol above that of the three-membered-ring transition structure.[11] This fact appears to be consistent with the theoretical analysis just given for the transition structures leading to **3** and **4**.

Scheme I. Predicted Reaction and Activation Enthalpies at 298 K for Conversion of Vinyl Radical and Oxygen to One-Carbon Fragments[a]



[a] The first values quoted come from PM3/UHF calculations. The figures in brackets represent ZPE-corrected potential energy differences from ab initio calculations (see text). All values are in kcal/mol.

In previously proposed mechanisms for the vinyl + O_2 reaction, it was suggested either that formation of **3** would be unfavorable[12] or that it would experience a high barrier to further reaction by intramolecular H shift.[13] The first of these objections has been dealt with above, and the present calculations suggest an alternative to the second. Intermediate **3** can rearrange to the epoxy radical **5** with a negligible activation barrier, according to the PM3/UHF calculations. Structure **5** is a local minimum on the PE surface according to the ab initio calculations; however, there is no barrier to its decomposition to **7** when ZPE corrections are included. The PM3/UHF model also makes the **5** → **7** conversion essentially activationless. Conversion of **5** to **6** or to CHO + CH_2O does have a small (approximately 4 kcal/mol) barrier according to PM3, but there is no structure corresponding to a formal transition state along either of these pathways, and so an exact activation enthalpy cannot be defined.[14]

There appears to have been no previous discussion of the intermediacy of **7** in vinyl radical oxidation. The formation of **7** from CHO + CH_2O would almost certainly have an unfavorable free energy under combustion conditions, and so if vinyl oxidation really occurred via dioxetanyl radical **4**, as previously proposed, it seems unlikely that **7** would play much role. However *direct* formation of **7** from radical **5**, in combination with a kinetic barrier to its fragmentation (as predicted here), would perhaps permit **7** to undergo bimolecular reactions with O_2 or other species.

The semiempirical calculations (and experimental values for heats of formation) suggest that CH_3 + CO_2 would be of lower total enthalpy than CHO + CH_2O, and one can estimate that they would have comparable total entropy. However, the formation of CH_3 and CO_2 from **7** by intramolecular hydrogen transfer is predicted by the PM3 model to have a substantially higher activation enthalpy (and presumably a less favorable activation entropy) than the formation of the observed products, CHO + CH_2O.

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(5) Baldwin, R. R; Walker, R. W. *Symp. (Int.) Combust.* [*Proc.*] **1981**, *18*, 819.

(6) PM3 calculations (Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209) employed the program package MOPAC 6.0 on an IBM RS/6000 computer. All geometry optimizations were conducted with the PRECISE keyword, and all transition states were identified by the existence of a single imaginary frequency in a harmonic normal mode analysis.

(7) Ab initio calculations were carried out using the Gaussian 92 program: (Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision C; Gaussian, Inc.: Pittsburgh, PA, 1992) on an IBM RS/6000 computer.

(8) According to the semiempirical calculations **4** is not a stationary point—it undergoes O–O cleavage with no activation energy. Rough enthalpies of reaction for conversion of **2** to **4** and **4** to **6** (calculated for purposes of comparison with the ab initio results) came from optimizing the geometry of **4** without the PRECISE keyword. According to the ab initio calculations, **4** *does* represent a stationary point, although the barrier for O–O cleavage has not yet been computed.

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(11) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981.

(12) Westmorland, P. R. *Combust. Sci. Technol.* **1992**, *82*, 151.

(13) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem.* **1993**, *97*, 4427.

(14) Formation of some **6** seems to be required by the observation that photochemically generated vinyl radicals react with excess oxygen to give glyoxal (Gardner, E. P.; Sperry, P. D.; Clavert, J. G. *J. Phys. Chem.* **1987**, *91*, 1922).

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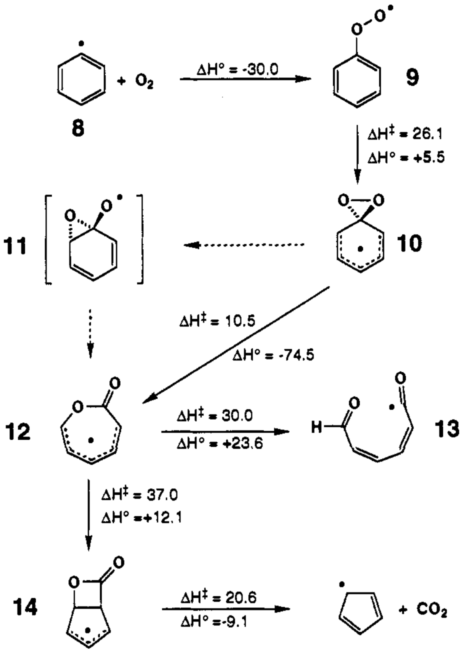
Scheme II. Predicted Reaction and Activation Enthalpies at 298 K for Oxidative Cleavage of Phenyl Radical[a]



[a] All values come from PM3/UHF calculations and are in kcal/mol.

The PM3/UHF calculations suggest that formation of spirodioxiranyl radical **10** (Scheme II) from the phenylperoxy radical **9** has a similar activation barrier to that for formation of **3** from **2**. The rearrangement **10** → **11** has a higher computed barrier than that for **3** → **5**, presumably because of the loss of stabilizing delocalization as **10** is converted to its transition structure. Structure **11** opens without an activation barrier to **12** according to the calculations.

Two unimolecular reactions of **12** were investigated: C–O cleavage to **13** (analogous to the formation of CHO + CH_2O from **7**) and cyclization to **14**, followed by CO_2 expulsion to give the cyclopentadienyl radical. Each of these pathways was calculated to be enthalpically unfavorable and to have a substantial activation barrier, raising the possibility that **12** might be interceptible in bimolecular reactions. Transition structure for the rate-determining step in the conversion of phenyl + O_2 to cyclopentadienyl + CO_2 is computed to be about 4 kcal/mol *below* the reactants in enthalpy, whereas the previously considered formation of the cyclopentadienyl radical + CO + O can be estimated from experimental data[15] to have a rate-determining transition state that is 37 kcal/mol *above* the reactants. If the estimated differences in activation enthalpy between the pathways are approximately correct, it would seem that entropic effects could make the originally proposed mechanism more favorable than the one shown in Scheme II only at very high temperatures.[16]

While the semiempirical calculations cannot be trusted to be quantitatively accurate for these reactions, some modification of the kinetic schemes used to simulate hydrocarbon combustion may be necessary if the predicted mechanisms are even qualitatively correct. In particular, interception of **12**, and possibly **7**, in bimolecular reactions could be significant steps in the oxidative processes.

Acknowledgment. I am pleased to acknowledge important contributions from two of my colleagues: Professor Simon Bauer brought the significance of the title reactions to my attention; Professor David Collum recognized that cyclization of **2** to **4** would contravene "Baldwin's rules" for ring closure (ref 9) and proposed formation and rearrangement of **3** as an alternative. The calculations were conducted using the Cornell National Supercomputer Facility, a resource Center for Theory and Simulations in Science and Engineering (Cornell Theory Center), which receives major funding from the National Science Foundation and IBM Corporation, with additional support from New York State and members of the Corporate Research Institute.

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(15) Lovell, A. B.; Brezinsky, K.; Glassman, I. *Int. J. Chem. Kinet.* **1989**, *21*, 547.

(16) The $\Delta S^{\ddagger}$ for fission of an atom from a molecule is typically about 10 cal/(mol K) (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 90–96). Even if the $\Delta S^{\ddagger}$ for formation of **10** from the phenylperoxy radical were as small as –10 cal/(mol K), and this seems unlikely (PM3 makes the value –4.1 cal/(mol K) at 1000 K and –4.6 cal/(mol K) at 1500 K), the $T\Delta\Delta S^{\ddagger}$ term (*T* times the difference in activation entropy for the two mechanisms) would exceed the $\Delta\Delta H^{\ddagger}$ term only above 1850 K.