J. Phys. Chem. A **2002,** *106,* 4137−4144 **4137**

Theoretical Studies of Isomerization Reactions of 2-Pentoxy Radical and Its Derivatives Including the Unsaturated Alkoxy Radicals

Ching-Yeh Lin and Jia-Jen Ho*

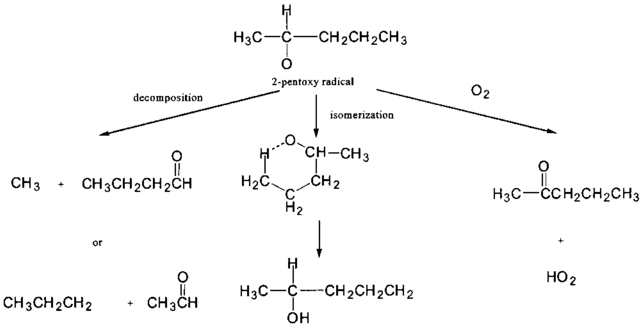
Department of Chemistry, National Taiwan Normal University, 88, Section 4, Tingchow Road, Taipei, Taiwan 117

Received: September 17, 2001; In Final Form: February 28, 2002

This paper deals with the calculation of isomerization reactions of 2-pentoxy radical and its derivatives (including unsaturated alkoxy radicals) by density functional theory. The results indicate that the process via six-membered ring TS calculated at the B3LYP/6-311++G** level for 2-pentoxy had the lowest energy barrier, 8.63 kcal/mol. However, in the unsaturated derivatives, the energy barriers very much depend on the double bond position in the molecule, and that may alter the isomerization processes. The substitution effect on the isomerization barrier was as well investigated. The calculated lowest energy barrier of the substituted compound of 2-pentoxy was 3.77 kcal/mol of 5,5-dimethyl-2-pentoxy radical. We found that the relative stability of the isomerization products was one of the important factors concerning the barrier. Usually, the isomerization takes place via a six-membered TS to have almost free ring-strain energy. Nevertheless, our calculation shows that it is possible to find the substituted unsaturated alkoxy derivatives to proceed via a smaller ring transition structure (five-membered, instead of six-membered) to have lower energy barrier.

Introduction

In urban atmospheres, the alkanes are important volatile compounds which produce alkoxy radicals after reacting successively with the hydroxy radical (OH), oxygen (O_2), and nitrogen monoxide (NO) in the troposphere.[1−10] The alkoxy radical present in the troposphere will further react with oxygen, or decompose via unimolecular decomposition, or proceed isomerization reaction via hydrogen transfer.[11−14] For example, the predicted reactions of 2-pentoxy radical are presented in the following scheme:

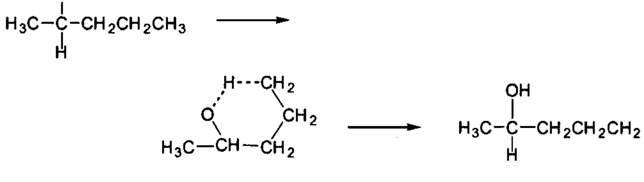


The isomerization reaction via 1,5-H shift involving a six-membered ring transition state produces a δ-hydroxy alkyl radical.[13−17] It was believed that the six-membered TS possesses less ring-strain energy to reduce the isomerization barrier. We are interested in the isomerization reaction of unsaturated alkoxy radicals such as pent-1-ene-4-oxy and pent-2-ene-4-oxy, as well as their substituted derivatives. Whether these unsaturated alkoxy radicals still undergo the familiar six-membered ring TS or via smaller ring configuration will be our major concern. In addition, the substitution effect, such as methyl or chloro-substituted alkoxy radicals, on the isomerization barrier was seldom discussed. The purpose in this study was to examine the factors that dictate the isomerization TS, and from that, we were able to rationalize the isomerization processes and barriers for these unsaturated and substituted alkoxy radicals.

Calculation Method. We carried out the ab initio molecular orbital calculations by using the Gaussian-98 program package. The stationary points on the potential energy surfaces were optimized mainly by density functional theory (DFT) with the Becke three-parameter hybrid method and the Lee−Yang−Parr correlation functional approximation (B3LYP).[18−21] Basis sets with increasing accuracy of polarized split-valence and diffuse functions for heavy and hydrogen atoms 6-311++G** were used in the calculations. The reason for us to adopt this level and basis set was that we were able to calculate the isomerization rate constant of 2-pentoxy via six-membered ring TS to be 1.25 $\times$ 10^5 (s^{-1}) which agreed reasonably well to the experimental data at 298 K of 2.5 $\times$ 10^5 (s^{-1}). [11] Vibrational analyses were carried out at the same level of theory to characterize the optimized structures as local minima or transition states. Zero-point energy (ZPE) correction was also considered.

Results and Discussion

We performed isomerization barrier calculation of 2-pentoxy radical via 1,5-H shift of six-membered ring TS, described as follows:



It first reformed into an intermediate construction (I2, in Figure 1) by passing a transition structure (I1) with the barrier

---

[*] To whom correspondence should be addressed. Phone: (886)-2-29309085. Fax: (886)-2-29324249. E-mail: jjh@scc.ntnu.edu.tw.

10.1021/jp0135555 CCC: $22.00

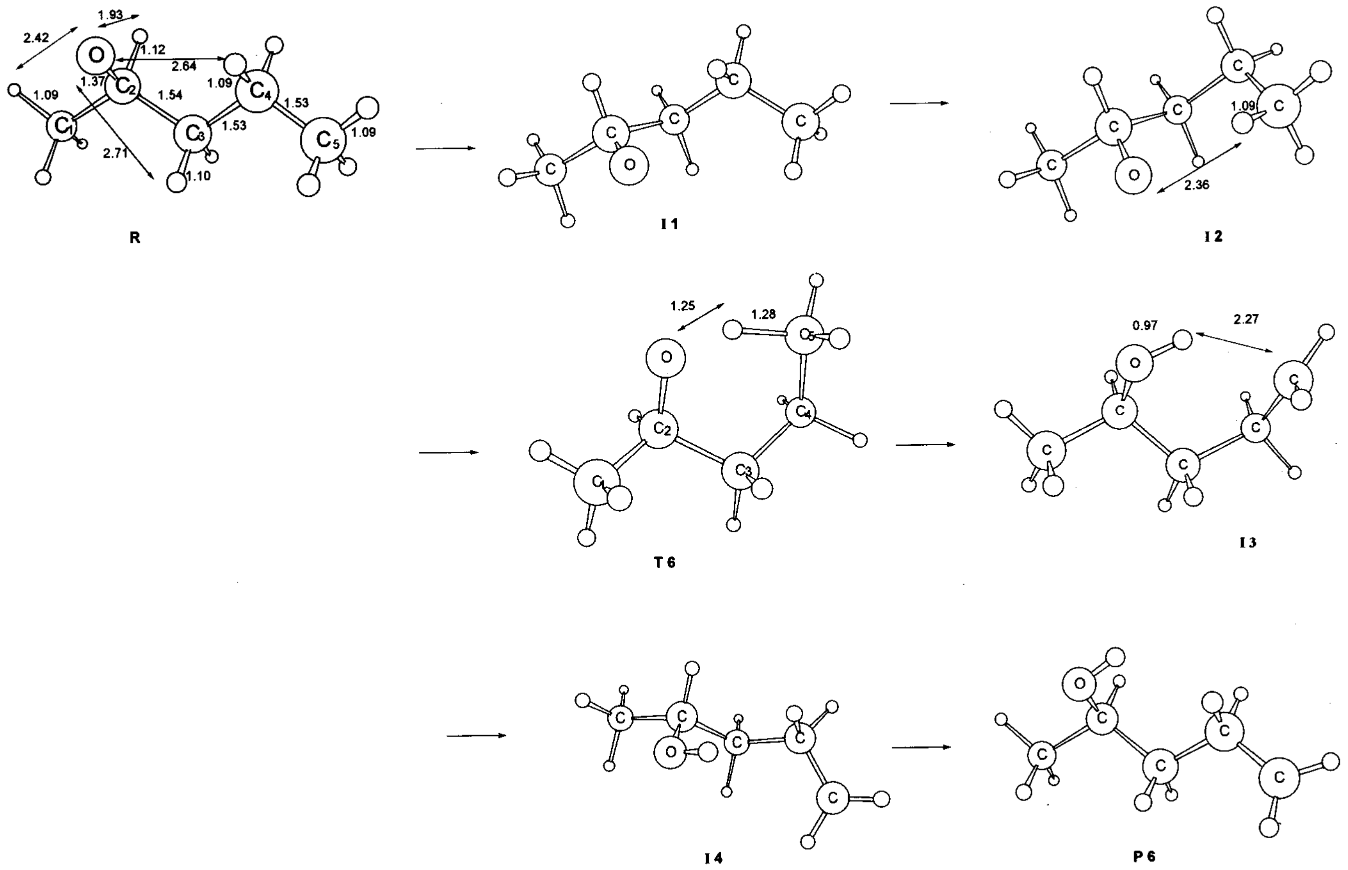


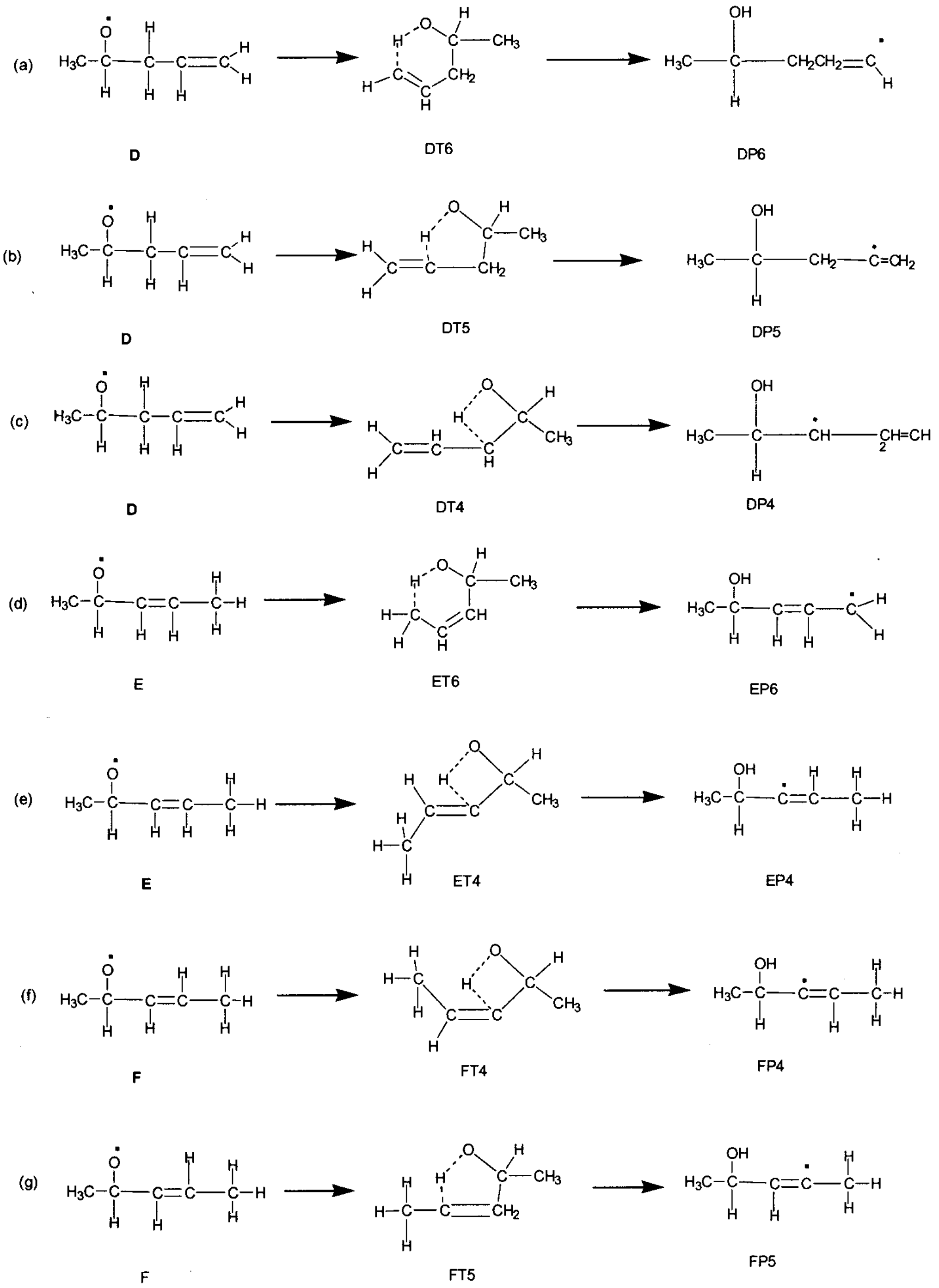
Figure 1. Calculated geometric structures of 2-pentoxy radical, R, its transition structures and the corresponding products via six-membered ring, 1,5-H shift isomerization process.

of 2.44 kcal/mol. The C_3-C_4 bond was turned upward so that the hydrogen on carbon 5 of I2 could be transferred to the oxygen via a six-membered ring transition structure (T6), and finally formed a terminal radical alcohol (P6) by passing through another two intermediates (I3 and I4). The barrier was 8.63 kcal/mol in good agreement with the experimental result (within 5−10 kcal/mol) observed for the Barton reaction.[22] We use this value as a reference for the comparison of isomerization barriers of the unsaturated, and substituted counterparts.

A. Unsaturated Alkoxy. The bigger cycles possess less strain. For example, the calculated ring strain energies of the three-, four-, and five-membered relatives to the respective six-membered were 27.7, 26.5, and 6.4 kcal/mol, respectively[23] (MP2/6-31G*). The preference for 1,5-H shift is usually rationalized by analogy: the carbocyclic six-membered cyclohexane ring is strain-free, whereas all other carbocyclic rings have some strain.[24,25,26] Our calculation of the relative energies of the transition states with respect to the reactant (strain free) clearly followed the trend of ring-strain energy in the cyclic hydrocarbons. Could there be other factors besides the ring-strain energy that alter the trend of barriers in the isomerization processes? We were interested in the system containing multiple bond (unsaturated alkoxy) because the relative ring-strains for the five- and six-membered unsaturated rings are very similar to their saturated counterparts.[27] We chose the double bond position to be either in C_4-C_5 (pent-1-ene-4-oxy, designated as **D**) or C_3-C_4 (pent-2-ene −4-oxy, designated as **E** for cis- and **F** for trans-isomers) and drew the possible isomerization processes in Scheme 1.

Isomerization of Pent-1-ene-4-oxy Radical. The calculated geometric structures in the possible processes described in Scheme 1 was drawn in Figure 2. The DI1, DI2, DI3, and DI4 in the figure are the intermediate structures of process (a) analogous to the saturated 2-pentoxy system of Figure 1. The calculated data at B3LYP/6-311++G** are presented in Table 1 where the notation such as DT6 represents a six-membered ring transition structure from its starting reactant **D** to the product DP6. The isomerization reaction of unsaturated alkoxy radical in process (c) via a four-membered ring transition structure (DT4) needs 20.89 kcal/mol to cross over the barrier which is about 4 kcal/mol less than the saturated counterpart. The enthalpy of this process is −18.86 kcal/mol and generates an allylic-like hydroxy radical (DP4), extremely stable, due to its electron delocalization among the molecule. In addition, the bond length of C_1-C_2 increases to 1.38 Å (normal double C=C bond is 1.34 Å), whereas that of C_2-C_3 decreases to 1.38 Å (normal single C−C bond is 1.50 Å), further verifying the electron delocalization between C_1-C_2 and C_2-C_3 bonds. Process (b) is a transfer via a five-membered ring TS; however, its barrier (20.10 kcal/mol) is about 5 kcal/mol higher than the saturated analogue. This unusual high barrier does not follow the previous described trend of ring-strain energies. According to the reported data[27−29] that the difference of ring-strain energy between the 5- and 4-mermbered ring hydrocarbons (regardless of alkane, alkene, or alkoxy) is quite large (about 20 kcal/mol) and consistent. For example, the ring strain energy of cyclopentane is 6.2 kcal/mol compared to that of cyclo-butane, 26.5 kcal/mol; for cyclo-pentene it is 4.4 kcal/mol as to cyclo-butene 28.7 kcal/mol; for oxacyclo-pentene it is 5.4 kcal/mol as to oxacyclo-butene 24.7 kcal/mol. Obviously, the barrier of the isomerization process is not solely dictated by the ring-strain energy. The product in process (b) did not show electron delocalization between C_1C_2 and C_2C_3 bonds and was comparatively less stable. For a six-membered ring process, (a), it

SCHEME 1



needs 13.01 kcal/mol to overcome the barrier, which is about 5 kcal/mol higher than the analogous process of the saturated one, so was the enthalpy, 8.35 kcal/mol, as compared to −1.07 kcal/mol. It also reformed into intermediate structures (DI1, DI2) prior to the migration of hydrogen taking place. The final product, DP6, was less stable and kept the C_1C_2 being double bond (bond length 1.31 Å), C_2C_3 single bond (1.51 Å), no indication of delocalization between these bonds.

Isomerization of Pent-2-ene-4-oxy Radical. There are cis and trans isomers. The energy data of hydrogen transfer of this unsaturated alkoxy compound through four-, five-, and six-membered ring TS calculated at B3LYP/6-311++G** was listed in the lower part of Table 1 and that of the geometric structures were presented in Figure 3. The trans-form, **F**, has the calculated lower energy (2.10 kcal/mol smaller) and was chosen as a reference molecule. If the transfer process of the cis-form took place via a four-membered ring TS (process (e)), it required 33.44 kcal/mol for the barrier, about 12 kcal/mol higher than the analogous process of pent-1-ene-4-oxy, and about 8 kcal/mol higher than the saturated one. It is endothermic ($\Delta H = +4.51$ kcal/mol) in contrast to pent-1-ene-4-oxy ($\Delta H = -18.86$ kcal/mol) and the saturated analogue ($\Delta H = -4.58$ kcal/mol). This big difference is mainly from the degree of unstability of the product generated from the process. The calculated bond length data did not show any effect of electron delocalization between C_1C_2 (1.51 Å), C_2C_3 (1.31 Å), and C_3C_4 (1.48 Å) bonds. The energetic data of process (f), trans-counterpart, are also similar, 34.87 kcal/mol for the barrier and $\Delta H = +7.91$ kcal/mol. If we compared the above three via four-membered ring TS processes (c, e, f) together with the saturated analogue

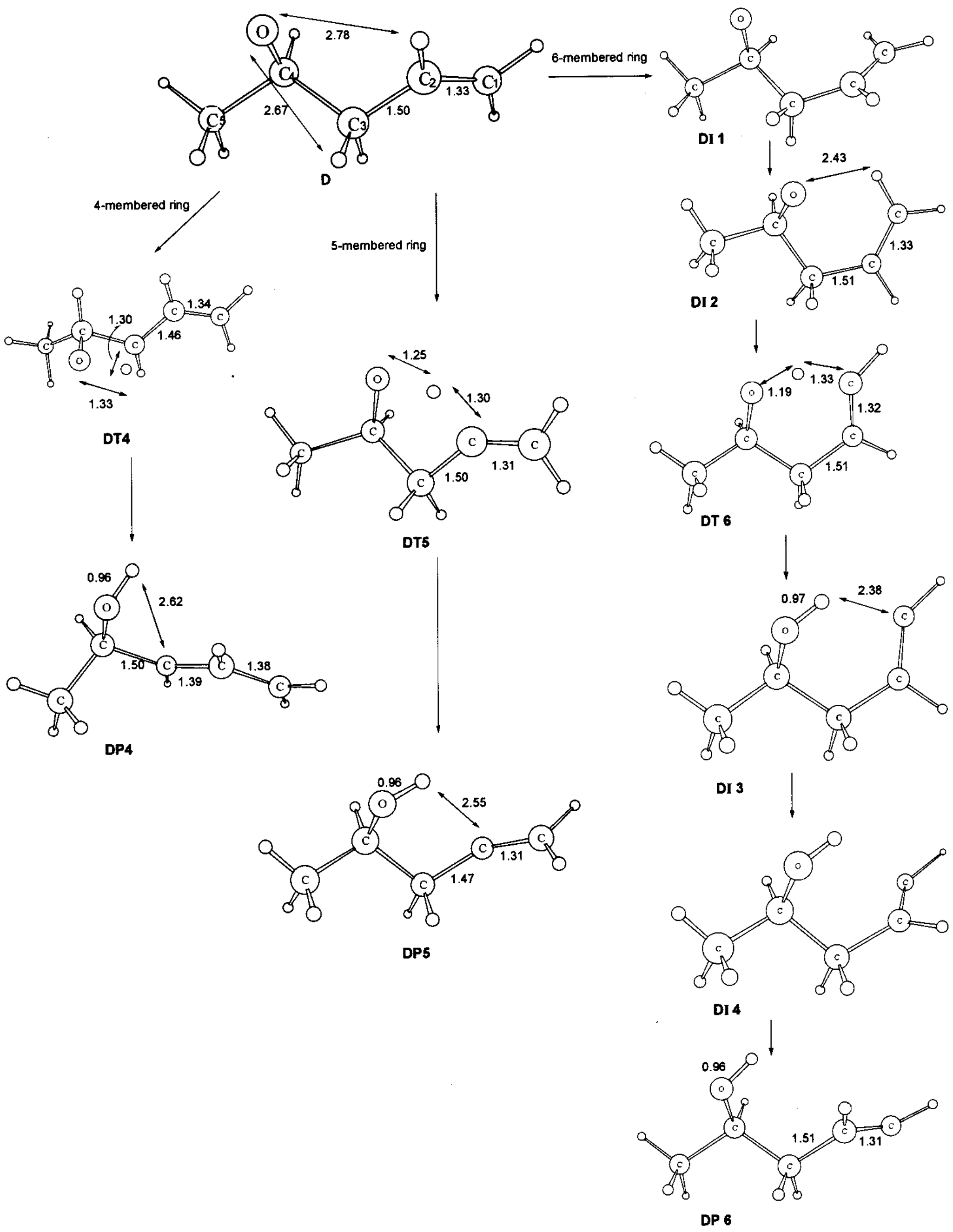


Figure 2. Geometric structures in the isomerization processes described in Scheme 1 of pent-1-ene-4-oxy radical, **D**.

we found that the barriers varied quite a bit (the highest 34.87 kcal/mol, the lowest 20.5 kcal/mol, and the saturated, 26.0 kcal/mol). Although the reported ring-strains of four-membered ring hydrocarbons were quite consistent (26.5 kcal/mol for cyclobutane, 28.7 kcal/mol for cyclobutene, and 24.7 kcal/mol for oxacyclobutene). In addition, the barriers via five-membered ring TS of either process (b) or (g) was calculated to be quite near to each other, around 20 kcal/mol, whereas process (d) via a six-membered ring TS, the barrier was only 6.99 kcal/mol, even smaller than the saturated counterpart. Therefore, there should be other factors as well contributing the isomerization barrier. The transition structure of process (d) is quite different from the saturated counterpart. It is more like a benzene-ring (all in one plane) rather than a chair-form of the saturated one. The reaction through this process releases a lot of heat ($\Delta H = -16.8$ kcal/mol), and the electronic structure in the product is completely delocalized (bond length of C_1C_2 is 1.38 Å, C_2C_3 1.39 Å). Similar phenomenon was observed in process (c) via four-membered ring TS. Therefore, we may conclude that the stability of the forming product is certainly one of the major factors that affect the barrier in these type of radicals, because the barriers in the proposed processes are not strictly proportional to the known ring-strain energies.

B. Substitution Effect. To further understand the effect of substitution on the isomerization barrier we proposed a set of reactions (h) to (m) in Scheme 2.

We changed the substituents in the appropriate positions and restricted that all the reactions proceed via a six-membered ring TS.

Methyl Substitution on the Carbon Atom Bonding to the Oxy-Radical. 1-butoxy radical via six-membered ring TS described in (h) is considered as a parent, unsubstituted alkoxy, whereas 2-pentoxy radical can be thought of as a resultant of methyl substitution of this type on the 1-butoxy radical. And

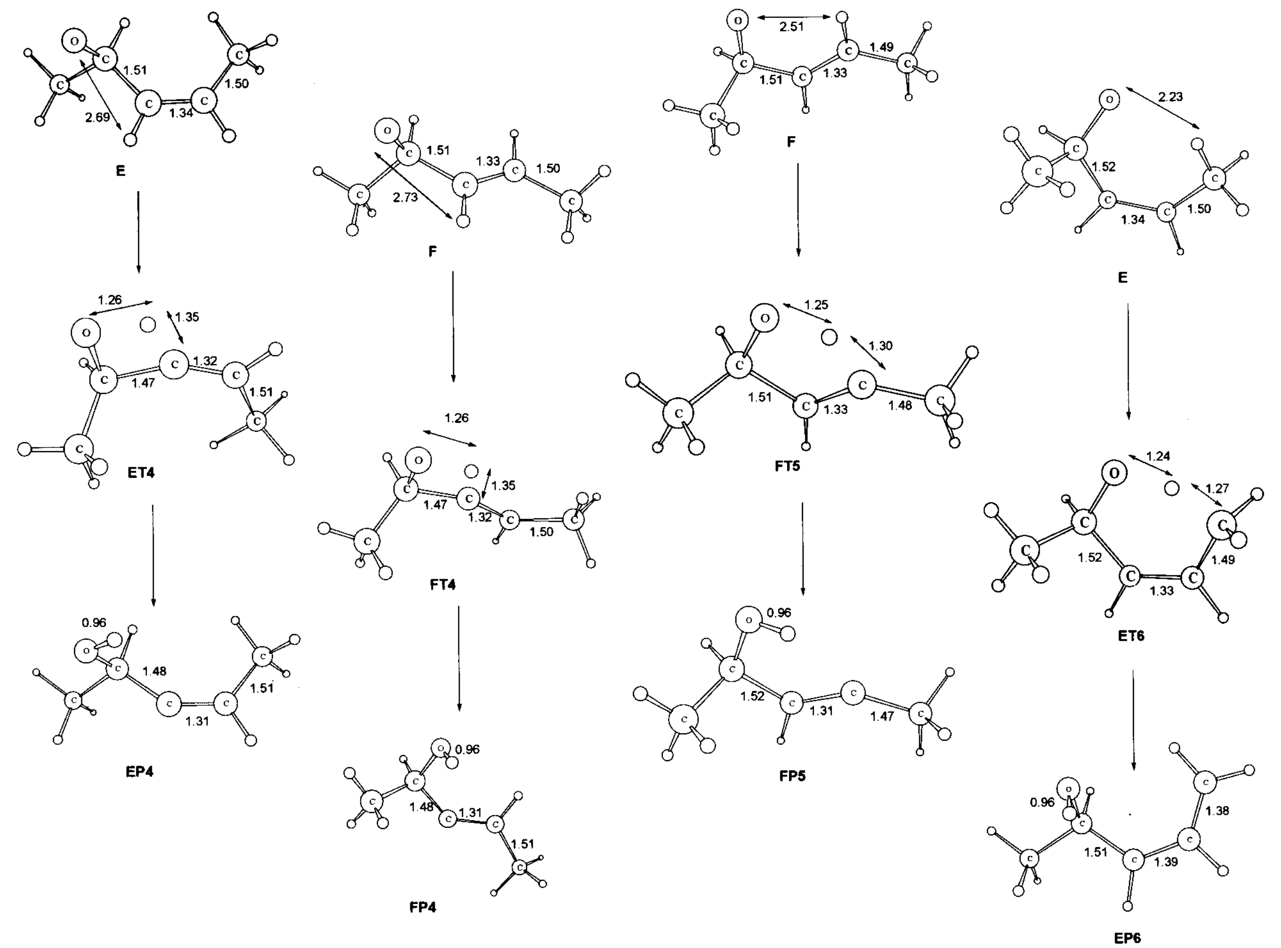


Figure 3. Geometric structures in the isomerization processes described in Scheme 1 of pent-2-ene-4-oxy radical in cis- (**E**) and trans-form (**F**).

that of dimethyl substitution at the same carbon position is presented in reaction i. The calculated energetic data (B3LYP/6-311++G**) are presented in Table 2. The isomerization barriers of methyl-substituted and dimethyl-substituted alkoxies are lowered by about 1 and 2 kcal/mol, respectively, as compared to the parent one. And the relative energies of the products are also lowered with the increasing number of methyl substituents.

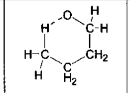
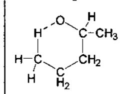
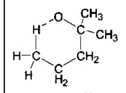
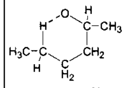
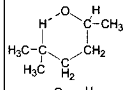
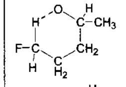
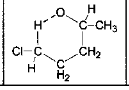
Substitution on the Carbon Atom Bonding to the Transferred Hydrogen. One methyl substitution on the carbon atom of this type (5-methyl-2-pentoxy, reaction j) decreases the barrier to 5.98 kcal/mol, compared to that of 2-pentoxy (8.63 kcal/mol), and for dimethyl substitution (5,5-dimethyl 2-pentoxy, reaction k) it further reduces to 3.77 kcal/mol. Even for electron-withdrawing substituents the barrier also decreases (7.07 kcal/mol for fluoro-substituent (l), and 6.88 kcal/mol for chloro-counterpart (m)). The relative energies of the products follow the trend of stabilities of the degree of alkyl radicals,[30−32] that is, the tertiary radical from (k) is the most stable (−7.69 kcal/mol), then the secondary from (j) (−4.96 kcal/mol), and the least of the primary from 2-pentoxy (−1.07 kcal/mol), listed in Table 2. It looks somewhat disturbing according to the bond dissociation energy of O−H (110.6 kcal/mol) and C−H (98.7 kcal/mol) one would get a very rough of 12 kcal/mol exothermic for this simple H-transfer reaction, compared to our calculated butoxy data of 0.15 kcal/mol endothermic (shown in the table). Nevertheless, this rough prediction does not consider the relative stability of the product formed. In our case, 2-pentoxy as an example, the H-transfer from different carbon position could form different degree of radicals (primary, secondary, and

TABLE 1: Calculated Energetic Data of Unsaturated Alkoxy Species, Their Isomerization Products and the Transition Structures at B3LYP/6-311++G Level Together with the Correction of Zero-Point Energy (ZPE) and the Averaged Spin Square Values ⟨S²⟩**

	B3LYP/6-311++G**			
	E[a]	ZPE[a]	*E* + ZPE[b]	⟨S²⟩
D	−271.1636872	0.127088	0	0.753609
DT4	−271.1261042	0.122791	20.89	0.766439
DP4	−271.1939728	0.127322	−18.86	0.776468
DT5	−271.1267263	0.122166	20.10	0.759583
DP5	−271.1593907	0.126956	2.61	0.758592
DI2	−271.1621038	0.127424	1.20	0.753583
DT6	−271.1379791	0.122118	13.01	0.759123
DI3	−271.1516088	0.126856	7.43	0.759055
DP6	−271.1502329	0.126946	8.35	0.759494
DI1	−271.1588118	0.126604	2.76	0.753836
DI4	−271.1493825	0.126734	8.75	0.759699
E	−271.1648514	0.127161	0.00	0.753613
ET4	−271.1064771	0.122071	33.44	0.760319
EP4	−271.1576988	0.127194	4.51	0.758629
F	−271.1679343	0.126904	−2.10	0.753593
FT4	−271.1073152	0.121841	32.77	0.760283
FP4	−271.1589286	0.127162	3.72	0.758774
FT5	−271.1299231	0.122033	18.70	0.759411
FP5	−271.1602888	0.126375	2.37	0.758514
ET6	−271.1480415	0.121493	6.99	0.756631
EP6	−271.1916616	0.127198	−16.80	0.77721

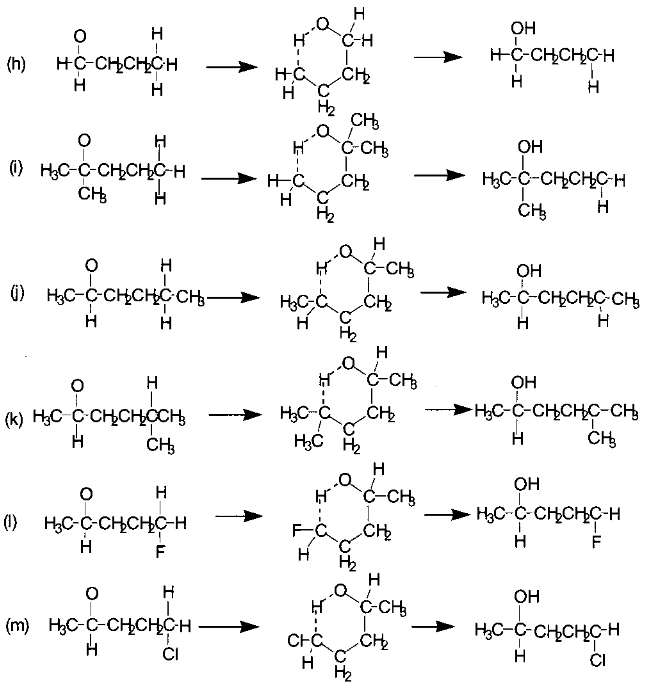
[a] The unit is in a.u. [b] The upper half of the table are relative energies considering ZPE with respect to the pent-1-ene-4-oxy radical (**D**), and the lower half of relative energies are with respect to the *cis*-2-ene-4-oxy radical (**E**).

TABLE 2: Calculated Energetic Data and the Relative Energies at B3LYP/6-311++G Level for Isomerization Reactions from (h) to (m)**

Reaction	TS structure	Reactant[a]	TS[a]	Product[a]	Barriers[c]	Relative energy of products[b]
h		-232.9502430	-232.9346597	-232.9500092	9.78	0.15
2-pentoxy		-272.2498818	-272.2361349	-272.2512630	8.63	-1.07
i		-311.5474041	-311.534595	-311.5501848	8.04	-1.74
j		-311.5459849	-311.5364628	-311.5538915	5.98	-4.96
k		-350.8418725	-350.8358699	-350.8541295	3.77	-7.69
l		-371.5224152	-371.5111562	-371.5282481	7.07	-3.66
m		-731.8814557	-731.8704966	-731.8890015	6.88	-4.74

[a] B3LYP/6-311++G** level with zero-point energy corrections (a.u.). [b] The relative energy of product with respect to its own reactant (kcal/mol). [c] The unit is kcal/mol.

SCHEME 2



tertiary), and the stabilities of these radicals affect the energy released. Our calculated data (not shown in the table) gives the tertiary formation to be −9.83 kcal/mol, secondary −5.91 kcal/mol, and primary −1.07 kcal/mol, which is in the correct qualitative order. Similar calculated result was shown in the Houk's work.[24] Obviously, Our calculated tertiary product was closer to the above rough prediction based simply on the O−H and C−H bond dissociation energies, and that was the best agreement we could get from our calculation level. The relative energies of the products from halo-substituents are also lower due to strong inductive effect[33] from the halogens. That the Cl-substituted being lower than the F-substituted counterpart could be due to the larger electron density of the F-atom, which produces greater repulsion force between carbon radical and the F atom, making product more unstable.

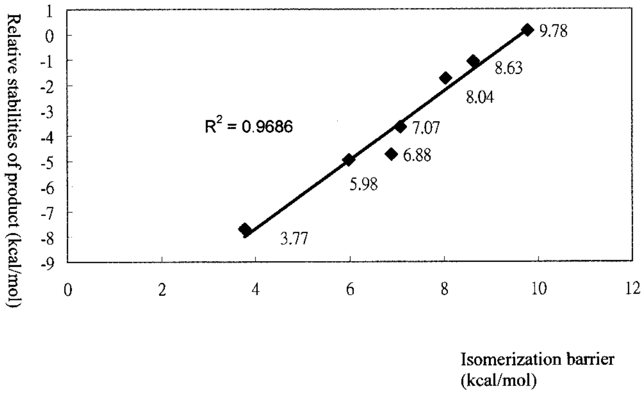


Figure 4. Linear regression diagram of product relative energies vs isomerization barriers.

Effect of Cl-Substitution Position on the Barrier. We have shown that the isomerization barrier of the substituted reactant could be greatly reduced if the substitution position were on the carbon atom bonding to the transferred hydrogen rather than to the oxy radical. We also found the close relation of the relative stabilities of the isomerization products to the variation of barriers. A linear regression diagram between these two calculated variables is shown in Figure 4 with $R^2 = 0.9686$, highly linearly correlated. This fact implies that the transition structures are more close to the product-oriented constructions, in good agreement to the Hammond postulate. Now we are ready to change substitution positions other than the two carbon positions discussed above to see the effect on the barrier. We performed calculations of chlorine substituent on carbon 3 and 4 positions of 2-pentoxy and also focused the study via six-membered ring TS. Because these two positions become chiral centers after chlorine substitution, there are S- and R-form optical isomers in each substitution position. The structural

SCHEME 3

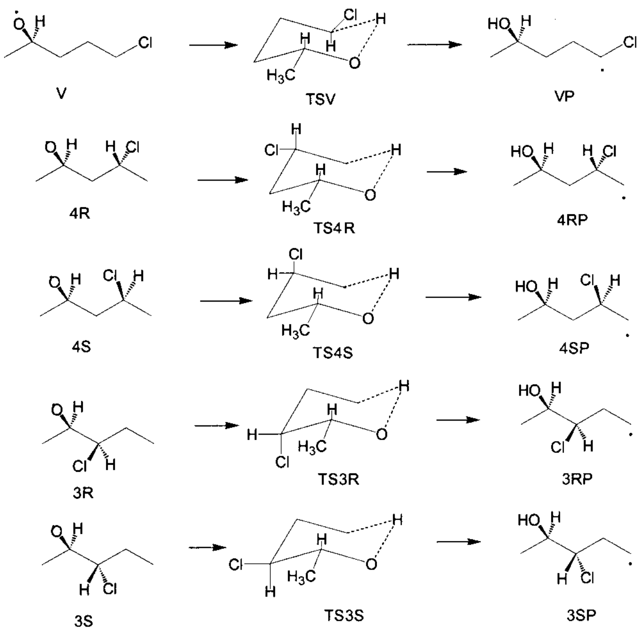


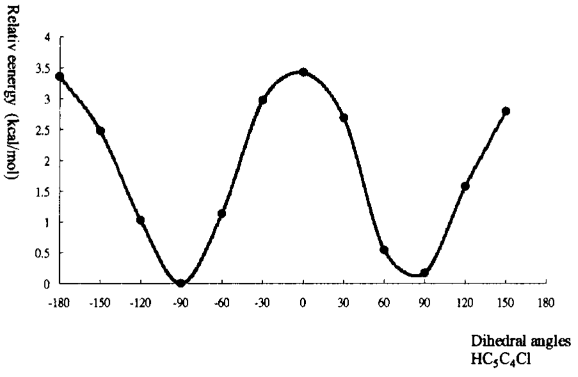
TABLE 3: Calculated Energetic Data and the C−C1 Bond Lengths of Chlorine Substituted 2-pentoxy Derivatives, Transition States, and Their Isomerization Products

	E (a.u.)[a]	*E* (kcal/mol)[b]	*D* (Å)[c]	*D* (Å)[d]
V	−731.881456	0.00	1.82	−0.08
VP	−731.889002	−4.73	1.74	
TSV	−731.870497	6.89		
4R	−731.886760	−3.33	1.85	+0.08
4RP	−731.890753	−5.83	1.93	
TS4R	−731.869901	7.25		
4S	−731.881391	0.04	1.84	+0.11
4SP	−731.889082	−4.79	1.95	
TS4S	−731.868978	7.83	-	
3R	−731.882045	−0.37	1.84	+0.01
3RP	−731.886848	−3.38	1.85	
TS3R	−731.867948	8.48	-	
3S	−731.883582	−1.33	1.84	0.00
3SP	−731.884006	−1.60	1.84	
TS3S	−731.869654	7.41	-	

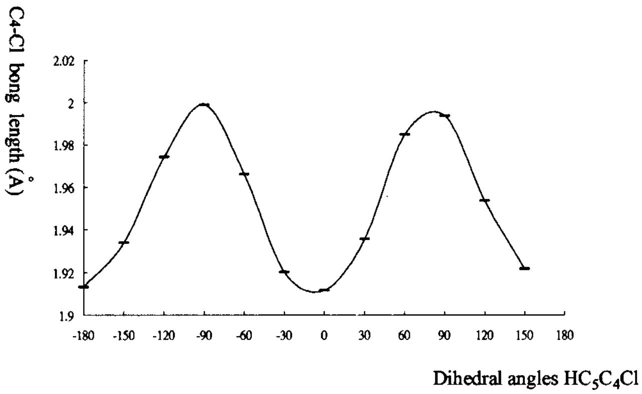
[a] The calculated absolute energies of chlorine substituted 2-pentoxy radicals. Each block lists the data of starting derivative, its isomerization product and the transition state. [b] The calculated relative energies for all the isomers and their transition states with respect to the reference molecule, V, 5-chloro-2-pentoxy radical. [c] The calculated C−C1 bond lengths of chloro-substituted 2-pentoxy radicals together with their isomerization products. [d] The difference of C−C1bond lengths between the chloro-substituted 2-pentoxy radical and its isomerization product. The positive value indicates the increase of the C−C1 bond length after the isomerization, and vice versa.

representation of isomerization processes for these isomers are depicted in Scheme 3.

In Scheme 3, the first isomer, **V**, describes the Cl-substitution on carbon 5 as a reference and the rest represent the Cl-substitution on carbon 4 and 3 to have 4R, 4S, and 3R, 3S optical isomers. The calculated energetics data at B3LYP/6-311++G** level are listed in Table 3. It is interesting to notice that the sequential order of the relative energies of the isomers correlates with their geometrical constructions in the transition states. That is, the 4R and 3S isomers together with their transition structures locate at lower relative energies, in which the transition structures have their chlorine substituents at the equatorial position, whereas 3R and 4S together with their transition structures locate at relative high energies with their chlorine substituents situating at the axial position. It is obvious that the axial position is relatively more unstable due to the steric effect. We also found that the products of 4RP and 4SP are relatively more stable than 3RP and 3SP due to electron delocalization occurred in 4RP and 4SP. The C−Cl bond, which is parallel to the unpaired p orbital of the carbon atom, becomes an acceptor of the delocalized electron in the molecule. It can be proven from the variation of the C−Cl bond lengths between the reactant and the product, listed in the right-hand part of Table 3. The positive value indicates the increase of the C−Cl bond length after the isomerization, and vice versa. It is interesting to find that the difference between **V** and **VP** is about −0.08 Å, indicating the reduction of the C−Cl bond length after the isomerization. On the contrary, that between 4R and 4RP, 4S and 4SP increases 0.08 and 0.11 Å, respectively, whereas that between 3R and 3RP, 3S and 3SP remains almost the same. This interesting phenomenon can be rationalized as follows. The decrease of C−Cl bond length in **VP** as compared to **V** is due to the change of bond hybridization in the terminal carbon atom. It was sp^3 in **V** but reformed between sp^2 and sp^3 in **VP**. Whereas the increase of C−Cl bond lengths in 4RP and 4SP is due to the electron delocalization that goes into the antibonding orbital of C−Cl bond (σ^*). This effect stabilizes the system yet weakens the C−Cl bond (decreasing the bond order) and, thus, extends the bond lengths, whereas those of remaining constant the C−Cl bond being too far to the terminal radical neither electron delocalization nor change of bond hybridization occurs in the C−Cl bond. The explanation may be supported by the result of NBO (Natural Bond Orbital) calculation in which the acceptor−donor interaction between C−Cl σ^* orbital and the unpaired p-orbital of the terminal carbon becomes greatest in the 4RP and 4SP. If the chlorine atom were replaced by methyl group or hydrogen atom then the interaction reduced. The proportional ratio of the interaction energy for Cl, CH_3, and H atoms is approximately 22:5:6. This delocalization effect is substantial and nontrivial in the chlorine substituent. In a careful look we also found that this interaction energy was affected by the direction of C−Cl bond. Several dihedral angles HC_5C_4Cl were performed from −180° to 180° for each increment of 30° to calculate the relative energies at HF/6-31G level and the result was drawn below.



The lowest relative energy occurs at both 90° and −90°, in which the unpaired p-orbital is parallel to the C−Cl bond to have the maximum overlap (best delocalization occurs). As compared to the least overlap orientations (−180° and 0°) the energy difference is around 3.5 kcal/mol less. The extent of delocalization can also be read from the calculated spin densities in C_5, C_4, and Cl atoms at several dihedral angles of HC_5C_4Cl. Our calculation shows that at the least overlap orientation the C_5 atom has the greater spin density, supporting that the electron is more localized at the C_5 atom. As the orientation shifts to −90° or 90°, the spin densities at C_4 and Cl atoms increase tremendously, whereas that in C_5 atom decreases proportionally, indicating a greater amount of delocalization spread within C−Cl bond. We also plotted the C−Cl bond lengths with respect to the change of dihedral angles in the following result.



It shows that the longest C−Cl bond length occurs at both −90° and 90°, whereas these two extremes correspond to the lowest relative energies in the previous diagram. All these calculated results support the fact that the delocalization is due to the good match of acceptor−donor interaction of the C−Cl σ^* antibonding orbital with the unpaired p orbital of the terminal carbon atom.

Combination of the Effect of Substitution and Unsaturated Double Bond to the Barrier. From the result of our calculation and others, the isomerization of 2-pentoxy radical and most of its derivatives would carry out via a six-membered ring TS owing to its smaller ring strain. The difference of ring-strain energies between five- and six-membered is around 6 kcal/mol, whereas the electron delocalization in the allylic-like structure reduces the barrier around 4.5 kcal/mol. By adding the substitution effect, it seems possible to find an substituted unsaturated-alkoxy undergoing an isomerization reaction via a five-membered ring TS instead of six; that is, could the isomerization barrier via five-membered be lower? We sought the possibility of finding the molecule whose isomerization process follows five-membered instead of six's. In hexa-1-ene-5-oxy molecule when it undergoes similar isomerization the calculated barrier via six-membered is still lower by 1.27 kcal/mol, although the TS via five-membered could form an allylic-like radical. However, in the combination of substitution effect (we substituted a chlorine atom at the 4th carbon position to form hexa-1-ene-4-chloro-5-oxy radical ($CH_3HCOCHClCH_2CH{=}CH_2$)) the similar isomerization prefers five-membered TS. The calculated barrier is smaller by 1.05 kcal/mol (9.43 kcal/mol, B3LYP/6-311++G**) than the six-membered one (10.48 kcal/mol). In addition, the relative energy of the five-membered product is about 26 kcal/mol more stable than the six-membered analogue. Our calculation proves the possibility for the substituted unsaturated-alkoxies to proceed the isomerization via five-membered TS.

Summary

We concluded the energy barriers of isomerization reaction involving hydrogen transfer of saturated and unsaturated alkoxy radicals and their substituted derivatives as follows:

(1) The electron delocalization in the allylic-like radical effectively stabilizes the transition structure as well as the product, and hence greatly reduces the isomerization barrier in the proper process.

(2) The substitution position on the carbon atom bonding to the transferred hydrogen has stronger effect on the decrease of the barrier, regardless of the type of the substituents. The decrease of the barriers caused by this effect may be as large as 5 kcal/mol (the barrier for dimethyl substituent is only 3.77 kcal/mol as compared to the unsubstituted, 8.63 kcal/mol).

(3) It is possible to obtain a less isomerization barrier via five-membered ring TS as compared to the six-membered one in an appropriate substituted-ene-alkoxy such as hexa-1-ene-4-chloro-5-oxy.

Acknowledgment. Support for this research from the National Science Council of the Republic of China (NSC-89-2113-M-003-023) is gratefully acknowledged. We are also grateful to the National Center for High-Performance Computing where the Gaussian package and the computer time were provided.

References and Notes

(1) Kwok, E. S. C.; Arey, J.; Atkinson, R. *J. Phys. Chem.* **1996**, *100*, 214.

(2) Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Hendry, D. G. *J. Phys. Chem.* **1977**, *81*, 2483.

(3) Carter, W. P. L.; Darnall, K. R.; Lloyd, A. C.; Winer, A. M.; Pitts, J. N., Jr. *Chem. Phys. Lett.* **1976**, *42*, 22.

(4) Cox, R. A.; Patrick, K. F.; Chant, S. A. *Environ. Sci. Technol*, **1981**, *15*, 587.

(5) Finlayson, B. J.; Pitts Jr., J. N. *Science* **1976**, *192*, 111.

(6) Aschmann, S. M.; Chew, A.; Arey, J.; Atkinson, R. *J. Phys. Chem. A* **1997**, *101*, 8042.

(7) Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. *J. Phys. Chem. A* **2001**, *105*, 1020.

(8) Tuazon, E. C.; Aschmann, S. M.; Atkinson, R.; Cater, W. P. L. *J. Phys. Chem. A* **1998**, *102*, 2316.

(9) Atkinson, R.; Arey, J. *Acc. Chem Res*, **1998**, *31*, 574.

(10) Lei, W.; Zhang, R. *J. Phys. Chem. A* **2001**, *105*, 471.

(11) Atkinson, R. *Int. J. Chem. Kinet*. **1997**, *29*, 99.

(12) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem. A* **1981**, *85*, 2698.

(13) Atkinson, R. *J. Phys. Chem. Data* **1997**, *26*, 227.

(14) Atkinson, R. *Atmospheric Environment* **2000**, *34*, 2063.

(15) Dóbé, S.; Bérces, T.; Márta, F. *Int. J. Chem. Kinet.* **1986**, *18*, 329.

(16) Atkinson, R. *J. Phys. Chem. Data* **1994**, *2*, 1.

(17) Atkinson, R.; Carter, W. P. L. *J. Atoms. Chem.* **1991**, *13*, 195.

(18) Lee, C.; Yang, W.×*c1F*Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(19) Becke, A. D. *J. Chem. Phys.* **1992**, *97*, 9173.

(20) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155.

(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(22) Barton, D. H. R.; Beaton, J. M.; Geller, L. E.; Pechet, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 2640.

(23) Haake, P. C.; Westheimer, F. H. *J. Am. Chem. Soc.* **1961**, *83*, 1102.

(24) Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 2195−2197.

(25) Dorigo, A. E.; McCarrieck, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508.

(26) Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 5421.

(27) Dudev, T.; Lim C. *J. Am. Chem. Soc.* **1998**, *120*, 4450.

(28) Eigenmann, H. K.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 1687.

(29) Wiberg, K. B. *Angev. Chem, Int. Ed. Engl.* **1986**, *25*, 312.

(30) Carey F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 4th ed.; Kluwer Academic/Plenum: New York, 2000; p 12.

(31) Solomons; *Fundamentals of Organic Chemistry*, 5th ed.; Wiley: New York, 1997; Chapter 10.

(32) Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1996**, *118*, 3761.

(33) Pérez-Casany, M. P.; Sánchez-Marín, J.; Nebot-Gil I. *J. Am. Chem. Soc.* **2000**, *122*, 11 585.