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A Quantum Chemical and Classical Transition State Theory Explanation of Negative Activation Energies in OH Addition To Substituted Ethenes

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Abstract: The OH addition to ethene has been modeled using ab initio quantum chemical calculations and classical transition state theory (CTST). The results agree with the hypothesis of Singleton and Cvetanovic (Singleton, D. L.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 6812) that the reaction is not elemental, and that it consists of a reversible first step involving the formation of a prereactive complex, followed by the irreversible formation of an addition adduct. The overall rate depends on the rates of two competitive reactions, i.e., the reverse of the first step and the second step, the former being more favored by an increase in temperature than the latter. Applying CTST to the proposed mechanism, we obtain an overall rate constant of 11.7×10^{-12} cm^3 molecule^{-1} s^{-1}, which agrees very well with the experimental results. New results for the activation energies of the OH addition to a series of substituted ethenes have also been obtained assuming that the above mechanism holds. The activation energies were calculated from projected second-order Moller−Plesset total energies obtained with the 6-311G** basis set. We find that a plot of these data vs the logarithm of the experimental rate constants has a correlation coefficient of 0.996. This seems to imply that the preexponential factor for the series should be approximately constant, in contradiction with the reported values for *A*. Moreover, a plot of our effective activation energies for OH addition vs the activation energies of a similar reaction, the addition of atomic oxygen to the same series of alkenes, also yields a good correlation. Indeed, for this reaction, the reported *A* factors are similar to each other. We suggest that the experimental Arrhenius parameters of the OH addition reaction need to be revised.

1. Introduction

In the troposphere, alkenes participate in a sequence of reactions which ultimately lead to their breakdown into highly toxic aldehydes, at the same time altering the equilibrium ratio of nitrogen oxides and indirectly producing ozone.[1] Alkenes are known to enter the tropospheric reactants pool mainly through one reaction,[1] the addition of an OH radical to the double bond:

$$R_1R_2C{=}CR_3R_4 + OH^\bullet \rightarrow R_1R_2C(OH){-}CR_3R_4^\bullet + R_1R_2C^\bullet{-}CR_3R_4(OH) \quad (1)$$

Rate constants for the OH addition to a large variety of alkenes have been measured.[2] Theoretical work on these reactions has been reported for ethene,[3−5] propene,[6,7] and halogenated ethenes.[5,8] Because so many experimental data are available, they constitute an ideal subject for the theoretical study of radical−molecule reactions.

Reaction 1 is very fast. While for small alkenes the rate of reaction 1 is about one-tenth their limiting rate of diffusion,[1] for larger alkenes it may be about equivalent to it. It is observed that the substitution of a methyl group at one of the carbon atoms of the double bond increases substantially the rate of the reaction, i.e., the rate is three times larger in propene than in ethene, and twice as large in methylpropene than in propene. Substitution of an ethyl (or larger) group has a much smaller effect. Also, the position at which the methyl group is substituted seems to be less important: in fact, isobutene and *cis*-2-butene have similar rates. Thus, a dependence seems to exist between the rate of the reaction and the electronic and polar effects due to the substituents, while steric factors seem to be unimportant. The former can be expected to influence the stability of the transition state and of the β-hydroxyalkyl products. In this context, in previous ab initio work[6,7] on the addition of OH to propene, it was found that the presence of the substituent methyl group, with its positively charged hydrogen atoms, favored, by a dipole−dipole effect, the addition of OH to the central carbon atom, i.e., to the more substituted carbon atom, thus more than

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(1) Finlayson-Pitts, B. J.; Pitts, N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley-Interscience: New York, 1986.

(2) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(3) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 4193.

(4) Villà, J.; González-Lafont, A.; Lluch, J. M.; Corchado, J. C.; Espinosa-García, J. *J. Chem. Phys*. **1997**, *107*, 7266.

(5) Sekusak, S.; Liedl, K. R.; Sabljić, A. *J. Phys. Chem. A* **1998**, *102*, 1583.

(6) Alvarez-Idaboy, J. R.; Diaz-Acosta, I.; Vivier-Bunge, A. *J. Comput. Chem*. **1998**, *88*, 811.

(7) Díaz-Acosta, I.; Alvarez-Idaboy, J. R.; Vivier-Bunge, A. *Int. J. Chem. Kinet*. **1999**, *31*, 29.

(8) Donovan, W. H.; Famini, G. R. *J. Phys. Chem.* **1994**, *98*, 7811.

10.1021/ja993693w CCC: $19.00

Table 1. Rate Constants, at 298 K and 760 Torr Total Pressure, and Arrhenius Parameters, for Alkene Reactions, According to Atkinson[2] [a]

reaction	$10^{12}k$ (cm^3 molecule^{-1} s^{-1})	$10^{12}A$ (cm^3 molecule^{-1} s^{-1})	E_a (kcal/mol)
	Alkene + OH		
ethene	8.52	1.96	−0.87
propene	26.3	4.85	−1.00
methylpropene	51.4	9.47	−1.00
cis-2-butene	56.4	11.0	-0.97
2-methyl-2-butene	86.9	19.2	−0.89
2,3-dimethyl-2-butene	110		
trichloroethene	2.36	0.56	−0.85
tetrachloroethene	0.17	9.64	+2.40
	Alkene + O(^{3}P)		
ethene	0.73	10.6	+1.59
propene	4.00	10.1	0.56
methylpropene	16.9	15.9	−0.03
cis-2-butene	17.6	11.0	−0.28
2-methyl-2-butene	51.0	28.2	−0.40
2,3-dimethyl-2-butene	76.9	24.9	−0.60

[a] The Arrhenius parameters for the alkene + O reaction have been obtained from ref 9, those for the chloroethenes + OH reaction, from ref 1, p 432.

compensating for the increased stability which would be expected for the terminal OH-substituted radical due to hyperconjugation and inductive effects.

In Table 1, the Arrhenius parameters for reaction 1 with different alkenes are given, as reported by Atkinson.[2] It can be observed that the preexponential factor in Table 1 increases with the rate of the reaction, i.e., as the number of substituents on the C atoms increases, in apparent contradiction with the fact that the steric effect on a more substituted C atom is expected to be larger. Since these systems are planar around the double bond, one may suppose that the steric effect is not very important. However, to explain the observed increase in the *A* factor it would be necessary to assume that there is a very large increase in the overall ΔS in going from one substituted alkene to a more substituted alkene. The latter is not expected to occur. In fact, the preexponential Arrhenius parameters of 1- and 2-butene should then be very similar, which is not the case.

In Table 1 we have also included the Arrhenius parameters for the alkene + O(^{3}P) reaction.[9] Reactions of alkenes with O and with OH are expected to have similar preexponential factors and to obey similar trends, differing essentially in the values of the activation energies. On the contrary, the numbers in Table 1, for both reactions, show quite different trends. While for alkene + OH all the activation energies lie close to −1 kcal/mol, large differences are observed in the case of alkene + O. In addition, all *A* factors are very similar in alkene + O, but very different in alkene + OH. An ab initio calculation of the activation energies could throw light upon these apparent contradictions.

Reaction 1 is also characterized by having a so-called negative activation energy, i.e., the rate at which OH is consumed decreases with increasing temperature. If reaction 1 were elemental, a negative activation energy would imply that the reaction occurs with no energy barrier, in obvious contradiction with the fact that different alkenes have different reaction rates and, moreover, that large substituents increase the rate rather than decrease it, as might be expected from the fact that larger molecules are slower to diffuse.

The behavior of reactions having a negative temperature dependence has been successfully described, for systems at low pressures, by Mozurkewich and Benson,[10] who used RRKM theory to develop quantitative expressions to calculate the rates of these reactions as a function of temperature. The method was tested on the gas-phase reaction of the hydroxyl radical with carbon monoxide. For systems at high pressures, several explanations have been proposed, which are summarized in ref 1. Three of them maintain the idea of an elementary reaction but suggest a modification of the preexponential factor in the Arrhenius equation to allow for a term $T^{-1.5.}$ According to a recent experimental article by Weber et al.[11] on the temperature dependence of the rate constants of the reactions of oxygen atoms with 2-pentene, the preexponential factor would rather have a T^n dependence, with n positive and slightly larger than 1 (1.12 and 1.14 for *cis*- and *trans*-2-pentene, respectively). On the other hand, Singleton and Cvetanovic[12] propose a different mechanism and explain the occurrence of these negative activation energies as being due to the reversible formation of a loosely bound prereactive complex which is formed without activation energy, followed by a second reaction whose transition state energy is lower than the energy of the separated reactants and which is irreversible:

$$R_1R_2C{=}CR_3R_4 + OH^\bullet \rightleftharpoons [R_1R_2C{=}CR_3R_4]\cdots OH \rightarrow \text{products} \quad (2)$$

If k_1 and k_{-1} are the rate constants for the first step and k_2 corresponds to the second step, a steady-state analysis leads to a rate constant for the overall reaction which can be written as

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \quad (3)$$

Even though the energy barrier for k_{-1} is about the same size as that for k_2,[6] the entropy change is much larger in the reverse reaction than in the formation of the products. Thus, one can expect that k_{-1} be considerably larger than k_2. With this assumption, first considered in ref 12, one obtains

$$k = \frac{k_1 k_2}{k_{-1}} = \left(\frac{A_1 A_2}{A_{-1}}\right) e^{-(E_1 + E_2 - E_{-1})/RT} \quad (4)$$

Since E_1 is zero, the net activation energy for the overall reaction is

$$E_a = E_2 - E_{-1} = (E_{TS} - E_{P-R}) - (E_{P-R} - E_R) = E_{TS} - E_R \quad (5)$$

where P-R stands for the prereactive complex, TS is the transition state, and R is the sum of the reactants.

Prereactive complexes, or molecular associations, are, indeed, common in most chemical reactions involving bond breaking, and they are due to the long-range interactions between the reactant molecules. They can be observed in most quantum mechanical representations of reaction profiles, but they are normally ignored because they are not relevant for the reaction paths. However, when the sum of the energies of the reactants is very close to the transition state energy, prereactive complexes may play an important role if the reaction occurs at pressures high enough for these complexes to be collisionally stabilized. Reactions in the gas phase which only involve the formation

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(9) Cvetanovic, R. J. *J. Phys. Chem. Ref. Data* **1987**, *16*, 261.

(10) Mozurkewich, M.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6429. Mozurkewich, M.; Lamb, J. J.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6435.

(11) Weber, M.; Hake, A.; Stuhl, F. *Int. J. Chem. Kinet.* **1997**, *29*, 149.

(12) Singleton, D. L.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 6812.

of bonds, such as radical recombination, have an energy reaction profile which decreases monotonically and which does not have any intermediate stationary points between reactants and products.

Using quantum chemical methods, it is possible to calculate energies of intermediate structures and transition states with a reasonable degree of precision, and thus to model the reaction path of a reaction. In previous work of our group on the addition of the OH radical to propene,[6,7] a stabilization of the P-R by about 4 kcal/mol was obtained, as well as an overall negative activation energy of about −1.5 kcal/mol, calculated according to eq 5. In recent publications by Villà et al.[4] and by Sekusak et al.,[5] accurate calculations of the ethene + OH addition reaction have been reported at several levels. Using classical transition state theory or even a more accurate theory such as Truhlar et al.'s variational transition state theory[13] to calculate reaction rate constants, it would then, in principle, be possible to calculate k_1, k_{-1}, and k_2 for the individual elementary reactions and then to obtain k for the overall reaction. In the first part of this work, the OH + ethene reaction shall be characterized using several methods and large basis sets, to obtain an accurate reaction profile and to reproduce the experimentally observed negative value of the activation energy (−0.87 kcal/mol).[2] With the corresponding partition functions an effective rate constant will then be calculated, using classical transition state theory and assuming the mechanism in eq 2.

It is also possible to take advantage of the trends in a series of similar compounds, and of systematic cancellations of errors, to obtain valuable information about reaction mechanisms from energy calculations alone. According to eq 5, the effective activation energy of reaction 1 is equal to the difference between the energies of the transition state and the reactants, and thus it can be calculated without having to obtain the energy of the prereactive complex. If the mechanism in eq 2 is valid, a plot of these calculated energies vs the experimental values (Table 1) should be linear. In this work, several substituted alkenes will be used to model, with accurate ab initio methods, the initial addition of OH to a double bond. We shall report new results for the energetics of the reactants and transition states of the OH−alkene reaction for eight substituted ethenes. Trends and correlations will be analyzed. Although the occurrence of reactions with negative activation energies is frequent and has been widely discussed, the fact that additional methyl substituents increases the reaction rate in OH addition to alkenes has not, to our knowledge, been explained.

2. Computational Methodology

Electronic structure calculations have been performed with the system of programs Gaussian94 (G94).[14] Restricted Hartree−Fock theory (RHF) was used for closed shell systems, and unrestricted Hartree−Fock theory (UHF) for radicals. The correlation energy corrections were introduced with Moller−Plesset perturbation theory up to second order, and results from spin-projected calculations were used (PMP2).

All geometries were fully optimized at the MP2/6-311G** level, and the character of the transition state was confirmed by a frequency calculation, performed at the same level, and presenting only one imaginary frequency corresponding to the expected transition vector.

Table 2. Activation Energies (in kcal/mol), Calculated with Different Methods[a]

method	E_a	E_a^{corr}
PMP2/6-311G++(d,p)	−1.50	1.35
PMP4(SDTQ)/6-311G++(d,p)	−0.92	1.92*
CCSD(T)/6-311G++(d,p)	0.51	3.35*
PMP2/6-311G++(3df,2p)	−2.70	−0.11
PMP2/aug-cc-pVTZ	−3.13	−0.54*

[a] For each method, the uncorrected E_a is given first, and the E_a^{corr}, calculated including the ZPE corrections, is indicated in the third column. The asterisk indicates that the ZPE was taken from the closest lower level calculation.

In the case of the ethene + OH reaction, other methods of calculation were also used (PMP4 and CCSD(T) as well as PMP2 with large basis sets up to the aug-cc-pVTZ, which is Dunning's correlation-consistent triple-ζ basis set,[15] augmented with diffuse functions. In fact, single-point MP2 calculations with this basis set have already been performed by Sekusak et al.[5] They found that this method gave the best agreement between theoretical and experimental activation energies.

We assume that the reaction occurs according to the two-step mechanism proposed in eq 2, involving a fast preequilibrium between the reactants and the prereactive complex followed by an internal rearrangement leading to the formation of the adduct. The rate constant may then be written as

$$k = \frac{k_1 k_2}{k_{-1}} = K_{eq} k_2 \tag{6}$$

and it may be expressed in terms of the partition functions of the reactants (Q_R), of the prereactive complex (Q_{P-R}), and of the transition state (Q_{TS}). The equilibrium constant can be obtained from the total partition functions of the prereactive complex and of the reactants, while k_2 can be calculated from the classical transition state theory expression. Thus,

$$k = \frac{Q_{P-R}}{Q_R} \exp^{E_{-1}/RT} \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_{P-R}} \exp^{-E_2/RT} \tag{7}$$

where κ is the tunneling factor (which is not important in this reaction) and k_B is Boltzmann's constant.

3. Results and Discussion

The Ethene + OH Reaction. The MP2, MP4, and CCSD(T) methods have been used to calculate the energies of the reactants, prereactive complex, transition state, and product along the reaction path between the reactants and the OH−ethene adduct. The zero-point vibrational energy corrections (ZPE) have been calculated at the MP2 level using the 6-311G++(d,p), and these values were used in the calculation of the PMP2, PMP4, and CCSD(T) activation energies. In addition, a frequency calculation was performed with an extended basis set, the 6-311++G(3df,2p). The activation energy of the ethene + OH reaction, calculated according to eq 5, is given in Table 2 for all the methods employed. As already observed in ref 5, the increase of the basis set size, especially the addition of diffuse and polarization functions, decreases deviations from experimental data. Introducing the ZPE corrections yields, in some cases, an activation energy which agrees less well with experiment than when no corrections are introduced. Both the corrected and uncorrected activation energies are reported in Table 2. However, when a large enough

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(13) See, for example: González-Lafont, A.; Truong, T. N.; Truhlar, D. G. *J. Chem. Phys.* **1991**, *95*, 8875.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(15) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

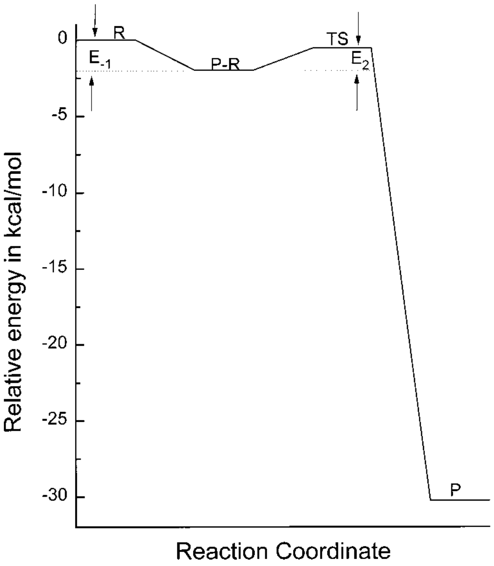

Figure 1. Energy profile of the OH + ethene addition reaction, as calculated at the PMP2/aug-cc-pVTZ//MP2-311++G(3df,2p) level.

Table 3. Calculation of the Rate Constant at 298 K of the OH + Ethene Addition Reaction Using the Data Obtained at the PMP2/aug-cc-pVTZ//MP2/6-311++G(3df,2p) Level[a]

$Q_{OH} = 6.00625 \times 10^7$	$K_{eq} = 0.00396$
$Q_{ethene} = 3.97810 \times 10^9$	$k^2 = 2.94 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}
$Q_{P-R} = 2.72477 \times 10^{13}$	$k = 11.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}
$Q_{TS} = 8.84603 \times 10^{13}$	$A = 3.82 \times 10_{12}$ cm^3 molecule^{-1} s^{-1}
$E_a = -0.54$ kcal/mol	$k_{exp} = 8.52 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}

[a] The transition state partition function has been corrected for internal rotations (see text).

basis set is used, the ZPE-corrected, projected MP2 results yield the best activation energy (as compared with the experimental value). A cancellation of errors probably occurs. As already observed by Sekusak et al.,[5] the single-point coupled-cluster method does not give satisfactory results, probably due to the fact that the geometry is not optimized at this level and that spin contamination is not eliminated.

The energy profile obtained for the ethene + OH reaction using the PMP2/aug-cc-pVTZ//MP2/6-311++G(3df,2p) energies is shown in Figure 1. The formation of a stable prereactive complex followed by a transition state whose energy is lower than the energy of the reactants is clearly observed. Such a profile agrees with the hypothesis of Singleton and Cvetanovic and implies the existence of a mechanism of the type of eq 2.

Three low frequencies are present in the transition state, in addition to the imaginary frequency. Of these, two can be viewed as internal rotations. Thus, in the partition function of the transition state, their harmonic contributions have been replaced by those of free rotors.[16] The calculated rate constant is in excellent agreement with the experimental result, (Table 3).

Substituted Alkenes. Next, the following eight molecules were selected for our calculations: ethene, propene, *cis*-2-butene, methylpropene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, trichloroethene, and tetrachloroethene. They include ethenes in which one, two, three, and four hydrogen atoms have been substituted by methyl groups, and also two molecules in which hydrogen atoms have been substituted by chlorine atoms, to study both electron donor and electron acceptor groups. Experimental rate constants have been reported for all of these molecules (see Table 1). The activation energies are negative except in the tetrachlorine-substituted compound.

Table 4. Activation Energies (in kcal/mol) of the Alkenes + OH Addition Reaction, Calculated using eq (5)

alkene	E_a
ethene	−1.08
propene	−2.06
methylpropene	−2.93
cis-2-butene	−3.41
2-methyl-2-butene	−3.92
2,3-dimethyl-2-butene	−4.45
trichlorethene	+0.64
tetrachloroethene	+3.37

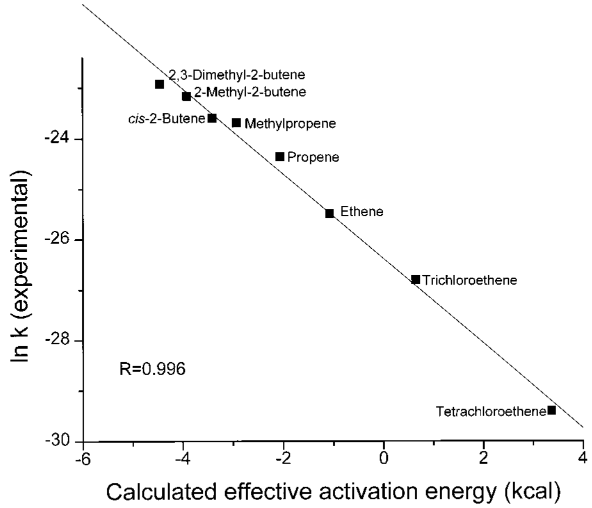

Figure 2. Experimental log *k* values vs E_a for the OH + alkenes addition reaction.

A full geometry optimization was carried out at the MP2/6-311G** level for the isolated reactants and for the transition states, for the eight reactions considered. Relative energies, in kcal/mol, calculated with respect to the sum of the energies of the corresponding alkene and of OH, are given in Table 4. According to eq 5, the latter are the overall activation energies.

From Table 4, it can be seen that, as the number of substituted methyl groups increases, the calculated activation energy becomes more negative, while the reverse situation is observed when the electron acceptor chlorine atom is substituted at the double bond. If these data are compared with the experimental data in Table 1, three observations can be made:

(i) On the one hand, smaller calculated activation energies correlate with larger experimental rate constants.

(ii) No regularity is observed when calculated and experimental activation energies are compared.

(iii) A clear correlation is found between the calculated activation energies of the OH + alkene reaction and the experimental activation energies of the alkene + O(^{3}P) reaction.

In order for the above relationships to be quantified, they have been plotted in Figures 2−4.

Figure 2 represents a linear fit between the logarithm of the measured rate constants and the activation energies calculated in this work for the series of alkenes. A very good correlation is obtained, with a correlation coefficient of 0.996. From this graph, some important conclusions can be drawn, concerning the mechanism of the reaction. First of all, the rate constant seems to depend essentially on the energy difference between the isolated reactants and the transition state, implying that the preexponential factors must be very similar for all the alkenes considered. The linear fit obtained could mean that the reactivity

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(16) Benson, S. W. *Thermochemical Kinetics*; Wiley & Sons: New York; 1976; p 43.

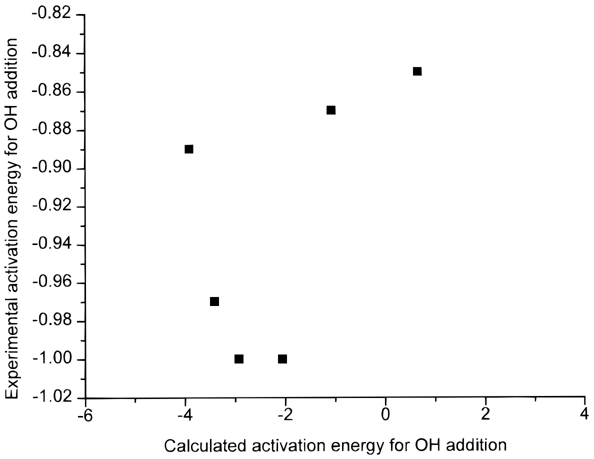

Figure 3. Experimental vs theoretical activation energies for the OH + alkenes addition reaction.

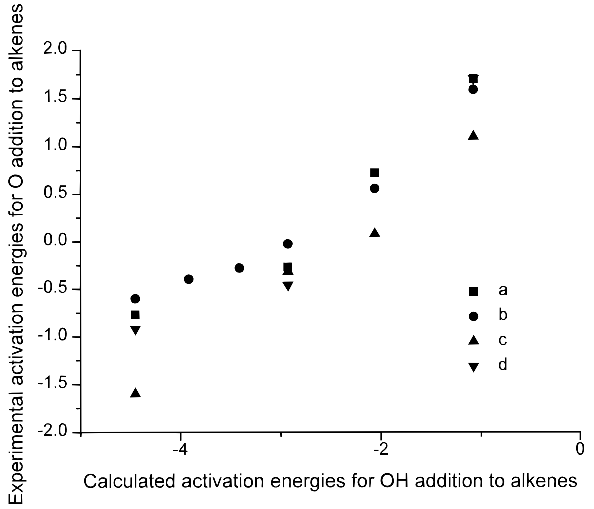

Figure 4. Experimental values of E_a for the O + alkenes addition reaction vs calculated values of E_a for the OH + alkenes addition reaction. The experimental values indicated by a dot have been taken from ref 9. All other values are from ref 12.

of different alkenes is approximately proportional to the stability of their transition states, the latter being the result of the inductive and dipole−dipole effects due to the presence of methyl groups attached to the double bond. In the second place, the reaction cannot be elemental, since the effective activation energy has been calculated assuming that the mechanism proposed by Singleton and Cvetanovic[12] holds.

In Figure 3, the experimental activation energies have been plotted vs the calculated values in Table 1. Points are spread about the graph, and no correlation is found.

It may be reasoned that the reaction of O(^{3}P) with alkenes occurs following a mechanism which is similar to the one for the OH radical, although the OH + alkene reaction is expected to be faster. In Figure 4, several sets of experimental activation energies reported by different authors and taken from refs 12 and 9 for this reaction are plotted against our calculated values. It can be seen that they all fall approximately along a line, even though the dispersion is not negligible. However, it is surprising to find that our results for the calculated activation energies of the OH + alkene reaction correlate so poorly with the corresponding experimental data. We suggest that the experimental Arrhenius parameters of the OH + alkene reaction need to be revised.

4. Conclusion

From the above discussion we conclude that, when the OH−alkene reaction occurs at atmospheric pressure, the following hold:

(i) The reaction is not elemental.

(ii) The overall addition of OH is irreversible, due to the large thermal effect of reaction 1 (ΔH is usually larger than −30 kcal/mol).

(iii) The overall rate depends on the rates of two competitive reactions (the reverse of the first step and the second step in reaction 1), the former being more affected by temperature than the latter.

We claim that only Singleton and Cvetanovic's hypothesis[12] is compatible with the above three points, i.e., the existence of a relatively stable prereactive complex, in equilibrium with the reactants, and from which the addition adduct is formed irreversibly. However, the activation energy of the OH−alkene reactions at high pressures can be calculated as the difference between the energy of the TS and that of the reactants, without having to obtain the prereactive complex.

The proposed mechanism provides a clear explanation of the experimental behavior. If E_{-1} is larger than E_2, the former will be relatively more favored by an increase in temperature and the overall rate will decrease. This explanation was predicted by Singleton and Cvetanovic a long time ago.[12] It is also interesting to note that, although mathematically the effective rate constant may be written as that of an elemental reaction, albeit with a negative activation energy, the latter has no physical meaning. In particular, in reactions in which the tunnel effect is important (as is the case in the hydrogen abstraction from alkanes[17] and small aldehydes, for example[18]), only E_2 must be considered.

In the global rate equation, eq 7, the temperature is present both in the preexponential term and in the exponent, but in the case of very small barriers, the latter are relatively less important than usual, which may explain why, in this type of reaction, a non-Arrhenius behavior is observed over a large temperature range.

Finally, we would like to point out that, according to Singleton and Cvetanovic's hypothesis, k_2 is expected to be much smaller than k_{-1}. When methyl groups are added to the double bond, however, comparative results for ethene and propene[7] indicate that the prereactive complex becomes more stable, meaning that E_{-1} increases. At the same time, experimental results indicate that the overall rate increases, implying that E_2 must decrease. Thus, the $k_2 \ll k_{-1}$ condition may not be true any more, and the temperature dependence of the rate constant may become more complex.

The fact that the methyl substitution at the double bond increases the reaction rate appears to be due to the stabilization of the transition state structure, due to inductive and dipole−dipole effects.

A discrepancy is observed when the experimental data for the Arrhenius parameters of a series of alkene + OH reactions are compared with those reported for the alkene + O reaction. Although these two reactions are expected to have similar mechanisms, their reported Arrhenius parameters obey very different trends. The results obtained in this work for the OH + alkene reaction agree with the trends observed by the O + alkene parameters (Figure 3). When our activation energies, calculated using eq 5, are compared directly with the experi-

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(17) Sekušak, S.; Sabljić, A. J. *Chem. Phys. Lett.* **1997**, *272*, 353.

(18) Alvarez-Idaboy, J. R.; Mora-Diez, N.; Vivier-Bunge, A. Unpublished.

mental rate constants, a linear correlation of 0.996 is obtained (Figure 1). It appears that the experimental activation energies and preexponential factors of the OH + alkene reactions might have to be revised.

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Supporting Information Available: Tables of total energies and zero point correction energies, in hartrees (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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