

Reaction of O(³P) with Alkenes: Side Chain vs Double Bond Attack

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Received: May 24, 2000; In Final Form: September 12, 2000

O atoms can attack either the double bond or the side chain of an alkene. LIF (laser-induced fluorescence) detection of O(³P) and OH allows separate measurement of the rates of the two types of reactions. The addition to the double bond is by far the more important reaction.

Ground state oxygen atoms react with alkenes by adding to one of the carbon atoms of the double bond forming a triplet ketocarbene. After the addition, a number of processes can take place, including hydrogen atom or radical release, intersystem crossing, and hydrogen atom migration. However, if the alkene has alkyl side chains, an alternate reaction can take place, a simple hydrogen atom abstraction to form a hydroxyl radical.

The rate constants for reactions of O(³P) atoms with the most common alkenes have been measured numerous times and are tabulated in the NIST database.¹ These rate constants are for the total rate of reaction including all product channels. This paper tries to answer the question as to which reaction is more important, addition to the double bond or hydrogen atom abstraction.

The rate constant can be written rigorously as a sum of the rate constants for the two types of reaction:

$$k = k_{\text{OH}} + k_{\text{C=C}} \quad (1)$$

For every alkene, the two rate constants will be different. They can be separated by probing nascent OH radicals from reactions with alkyl-substituted ethenes and comparing the OH signal strengths with that from a reaction with a known rate constant which produces only OH radicals.

Experiment

Detection of OH. O(³P) atoms were made by photolyzing 20 mTorr of NO₂ by a 351 nm (XeF) laser. The pressure of the alkene was 40 mTorr. A Nd:YAG laser pumped a dye laser (R590) which was frequency doubled to produce 280 nm light. This was used to probe OH radicals by exciting the (1,0) band of the A ← X transition. The resulting OH fluorescence, mainly in the (1,1) band was detected after passing through a band-pass filter centered at 313 nm. The delay time between the photolysis and the probe lasers was 1.7 μs. The intensity of the OH emission was defined as the average intensity of four strong rotational lines, R₁(4), R₁(7), Q₁(2), and R₂(2), relative to that of the OH from cyclohexane obtained under exactly the same experimental conditions. Typically, 4–5 spectral scans were made alternating cyclohexane vapor with that of the hydrocarbon. SO₂ is a somewhat richer source of O atoms than NO₂ but the latter was used because SO₂ fluoresces strongly when irradiated at 280 nm.

Removal Coefficients of O(³P) with Alkenes. O(³P) atoms were made by photolyzing 40 mTorr of SO₂ at 193 nm and

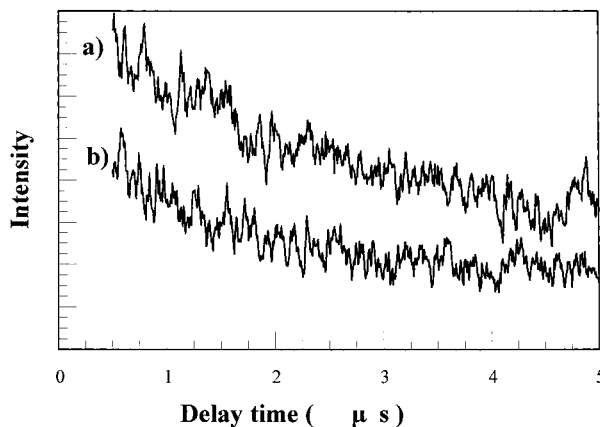


Figure 1. Decay curve of O + 20 mTorr (a) and 50 mTorr (b) of 1-hexene.

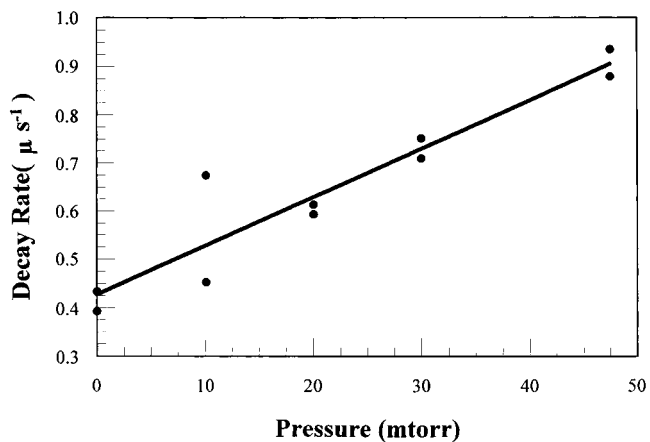


Figure 2. Decay constants plotted against pressure.

were detected by vacuum-UV laser-induced fluorescence at 130.1 nm. The vacuum-UV laser was generated by mixing two photons at 212.56 nm with 578 nm light in Kr at ~40 Torr. The pressure of the alkene was varied between 10 and 50 mTorr. Figure 1 is a plot of O atom concentration vs time for two different 1-hexene pressures. Each curve was fitted by a computer to an exponential and as shown in Figure 2, the decay constants were plotted against pressure. The removal coefficients for the O atoms were derived by least-squares fitting of the decay rate vs pressure plot to a straight line. Given the noise level as shown in Figure 1, the removal coefficients are estimated to be accurate only to 10–15%. This is sufficient for the purposes of this investigation.

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TABLE 1: Rate Constants, Removal Coefficients, and Relative OH Yields^a

molecule	$k(298)^b$	$k(\text{fast O})^b$	$k(\text{fast O})/k(298)^b$	OH/ OH(c-C ₆ H ₁₂)
cyclohexane	0.009	<i>c</i>	1.00	
ethene	0.066	<i>c</i>	0	
propene	0.438	7.2 ± 3.6	17 ± 8	0.15
1-butene	0.415	18.1	44	0.24
1-pentene	0.471			0.23
1-hexene	0.519	31.3	60	0.46
isobutene	1.78	25.3	14	0.34
Z-2-butene	1.84			0.24
cyclopentene	1.95	36.6	19	0.49
cyclohexene	2.07	40.2	19	0.50
<i>E</i> -2-butene	2.22	15.9	7.1	0.31
trimethylethene	5.41	34.0	6.3	0.27
tetramethylethene	8.01	61.8	7.7	0.34
cycloheptatriene	4.33	51.7	12	0.51

^a The second column $k(298)$ are from ref 1. ^b In units of $10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$. ^c The rate was too slow to measure.

Results and Discussion

The kinetics literature deals mainly with rate constants, $k(T)$, which are rate constants determined when the reactants are at thermal equilibrium. Under these conditions the signals from hydroxyl radicals are extremely weak. Instead, we use O atoms generated by photodissociation of SO₂ at 193 nm or NO₂ at 351 nm. These atoms have an average of 3–5 kcal/mol of relative translational energy for reaction with a typical hydrocarbon molecule.^{2,3} There is more available energy with SO₂ but this is compensated by the fact that most of the SO molecules are formed in the $\nu = 2$ state.² The rate constants for these hyperthermal O atoms will be called removal coefficients to distinguish them from the thermal rate constants. Removal coefficients were measured by directly observing the decay of O atom concentration in the presence of a large excess of thermal hydrocarbon molecules. Table 1 lists the room temperature rate constants, $k(298)$ (literature) and removal coefficients, $k(\text{fast O})$ (measured here) for a number of O–alkene reactions. Several generalizations can be made. Both rate constants and removal coefficients increase stepwise with increasing number of substituents. The fast O atoms are far more reactive than thermal O atoms and the ratio of the removal coefficient to the rate constant is largest for those molecules with the smallest rate constant.

The OH signal from the reactions of alkyl-substituted ethenes with fast O atoms are also listed in Table 1 but relative to the OH signal from the reaction of O with a reference compound, cyclohexane. A reference compound is one which has OH + a radical as the exclusive reaction channel and has a known removal coefficient. We assume that cyclohexane reacts with O only by abstraction to give cyclohexyl radical:



Let I and r designate hydrocarbon I and the reference compound, cyclohexane, respectively. Then

$$\begin{aligned} k(\text{I}) &= k_{\text{OH}}(\text{I}) + k_{\text{C}=\text{C}}(\text{I}) \\ k(\text{r}) &= k_{\text{OH}}(\text{r}) \end{aligned} \quad (3)$$

If the ratio of OH signals from I and r is measured, eq 1 can be decomposed.

$$k_{\text{OH}}(\text{I}) = \{S(\text{I})/S(\text{r})\}k(\text{r}) \quad (4)$$

Unfortunately, with the present technique the removal coefficient $k(\text{r})$ is too small to be measured and therefore quantitative ratios of side chain attack to double bond attack cannot be obtained. However, an upper limit to this coefficient allows a qualitative answer to the question posed in this paper.

In Figure 2, note that the rate of disappearance of the O atoms, $2 \times 10^5/\text{s}$ in the absence of hydrocarbons is about what one expects for diffusion out of the 2 mm wide vacuum-UV laser beam. Because the rate of decay of the O atoms due to diffusion out of the line of the probe laser beam is fairly fast, only reaction rates significantly faster can be measured. The reaction with cyclohexane was too slow to be measured. Let us examine the ratios between removal coefficients from the fast O atom to the thermalized rate constant as given in the fourth column of Table 1. One sees that the removal coefficients are about 6–10 times larger than the highest rate constants but up to sixty times larger for the smaller rate constants. A conservative upper limit to the removal coefficient for cyclohexane is therefore $0.5 \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$. Thus the removal coefficients of all the alkylethenes are above the upper limit for the removal coefficient for cyclohexane. Their removal coefficients are a factor of 10–100 times greater than the upper limit of that of cyclohexane. On the other hand, as also shown in Table 1, the alkylethenes have OH LIF signal strengths a fraction 0.15–0.50 of that from cyclohexane. This means that the rate of side chain attack compared to that of C=C attack is ≤ 0.02 .

The low pressures, typically 60 mTorr, and short times 1.7 μs used in the OH detection experiments suggest that the O atoms were mainly fast. An interesting observation was made with 1,3,5-cycloheptatriene (CHT) whose C–H bond energy is only 73 kcal/mol. When the pressure was increased to 70 mTorr of NO₂ and 56 mTorr of hydrocarbon and the delay time stretched to 16.5 μs , the ratio of the OH signal to that of cyclohexane decreased to 0.13 from 0.51 at short times. On the longer time scale the O atoms will have been thermalized. At room temperature the rate of reaction of CHT with O atoms is 500 times faster than that of cyclohexane. The thermal O atoms can hardly react with cyclohexane while the reaction with CHT is slowed but still very fast. In spite of the relative weakness of the C–H bond of the CH₂ group, the addition reaction is still the major reaction channel.

The central conclusion of this paper might seem obvious when one considers that O atom abstraction reactions of H atoms from alkanes have substantial activation energies ($E_a \sim 5\text{--}10$ kcal/mol), the O + C₂H₄ reaction has an E_a of 2 kcal/mol, the terminal alkenes RCH=CH₂ have $E_a \sim 1$ kcal/mol and ethenes substituted on both carbon atoms have negative E_a 's. However, the rate constant and activation energy are sensitive functions of the C–H bond strength. The bond energies of primary, secondary, and tertiary C–H bonds are 98, 95, and 93 kcal/mol, respectively.⁴ The rate constants and activation energies differ for attack on these different bonds. For example, $k(298)$ for neopentane, cyclohexane and 2,3-dimethyl butane is 6.8×10^{-16} , 8.5×10^{-14} , and $1.9 \times 10^{-13} \text{ cm}^3/(\text{molecule}\cdot\text{s})$, respectively.⁵ The first molecule has 12 primary C–H bonds, the second has 12 secondary C–H bonds, and the third has two tertiary C–H bonds. Allylic C–H bonds, those that are adjacent to a double bond are still weaker, ~ 86 kcal/mol. Weakest of all are the C–H bonds of CH₂ between two double bonds such as in 1,3,5-cycloheptatriene whose CH₂ bond energy is only 73 kcal/mol.⁴ One might have expected an easy abstraction of the allylic H atoms from the alkylated ethenes. This is how the question has arisen of the competition between addition to the double bond and abstraction. The activation energy decreases

from ~7 kcal/mol for neopentane to around 1 kcal/mol for 2,3-dimethylbutane. The O + H-C abstraction process requires collinear alignment of the three atoms during the reactive collision.⁶ The O atom addition to a carbon atom is a result of an attraction of the electrophilic O atom to a slightly negative carbon atom. The reaction probability should be much less sensitive to the angle of attack.

The problem addressed in this paper has been treated by F. Stuhl and co-workers in a different way.⁷⁻⁹ They observed that the Arrhenius plot of $\ln k$ vs $1/T$ was strictly linear for ethylene but was slightly bent for monoalkylethenes. The plot was fitted to a sum of two terms of the form $A \exp(-E_a/RT)$, one for each reaction. The four-parameter fit yielded the results that the fraction of the total rate constant that was due to abstraction was at 298 K 8%, 7%, 19%, and 15% for propene, 1-butene, 1-pentene, and 1-hexene, respectively.⁷ This method could not be applied to ethenes with two or more alkyl substituents because these molecules have a small but negative activation energy in their reaction with O atoms. Although these numbers are very rough, they have the virtue that they do apply to systems at thermal equilibrium.

In summary, the rate constants for the reaction of O atoms with alkylethenes do not increase with increasing substitution because of abstraction from the extra side chains. The extra side chains make it easier to attach an O atom to a carbon atom of the double bond. This may be because of the increase of negative charge at the carbon atom as suggested some time ago by Cvetanovic.^{10,11} This might reduce the already small activation energy. Buchta et al. and Cvetanovic have shown that the ionization potential of the alkene is strongly correlated with the activation energy.^{11,12}

An alternate possibility is that the extra vibrational modes absorb the energy released on attachment of the O atom. The

O atom is attracted to a deep well in the C-O coordinate but unless some energy can be rapidly transferred to other modes, the O atom will bounce off. Replacement of the H atoms in ethene by deuterium does not change the rate constant but alkylation could introduce softer modes which can more easily absorb energy. This would explain why cyclohexene has a larger removal coefficient than cyclopentene. Similarly, 1-hexene has a larger removal coefficient than that of 1-butene which is, in turn, larger than that of propene. A possible test of this explanation is a scattering experiment of O atoms by ethene and propene molecules. Ethene which has such a low reaction probability should scatter like a hard disk, mainly at small angles. With propene there should be considerable intensity at large angles owing to the formation and subsequent fast breakup of a reaction complex.

Acknowledgment. This research was supported by the U.S. Department of Energy.

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