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Reactions of O(^{3}P) with Alkenes: H, CH_2CHO, CO, and OH Channels

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The H, CH_2CHO, CO, and OH products of the reaction of O(^{3}P) atom with alkenes were studied by laser-induced fluorescence (LIF) under single-collision conditions. The average kinetic energies of the H atoms were 10−12 kcal/mol. The CO and OH rotational state populations were characterized by near room temperature Boltzmann distributions. The relative LIF intensities of the various products provide vivid proof of the following mechanism for the reaction of O(^{3}P) atoms with molecules of the form R′RC=CH$_2$, where R′ and R are H or an alkyl group. The O atom attaches itself to the less substituted carbon atom forming a triplet ketocarbene. There is a barrier to the release of an H atom, and the rate of release must compete with the rate of intersystem crossing. If an H atom is not released, following the intersystem crossing an H atom migrates to the adjacent C atom forming an energized aldehyde, R′RCH−CH=O. The aldehyde dissociates unimolecularly forming the pair of radicals R′• and the substituted vinoxy •RCH−CH=O or the pair R′RCH and HCO. Some of the latter have enough internal energy to dissociate to H and CO. In a side reaction O(^{3}P) abstracts H atoms but only from allylic C−H bonds. The most remarkable observation is that chemical reactions that do not involve the side chains such as release of H atoms or breakup of HCO depend sensitively on the length of these chains.

The reactions of ground-state (2^{3}P) oxygen atoms with alkenes have been extensively studied by chemical kinetics techniques.[1] Cvetanovic has shown that the initial step of the reaction consists of an attachment of the electrophilic O atom to the less substituted carbon atom of the double bond, forming a ketocarbene.[2] He found an inverse correlation between the rate constant of the reaction and the ionization potential of the hydrocarbon. The reaction proceeds readily. Of all the alkenes, ethylene has the highest activation energy, 2.6 kcal/mol, and the smallest rate constant. (See Table 1.) Alkyl substitution reduces the already low activation energy and increases the rate constant by up to 2 orders of magnitude. Alkylation at one carbon atom makes the more remote carbon atom more negative and therefore even more likely to attract an incoming O atom. The allylic C−H bonds of the side chains are good targets for O atom abstraction reactions. These OH-forming side reactions will be discussed separately.

After a certain delay, the initially formed ketocarbene falls apart, producing a variety of pairs of radicals. These radicals are highly reactive and when produced in a hydrocarbon flame will speedily be converted into other species. Thus, in general, it is essentially impossible to determine the primary reaction products unless single-collision conditions are used. The only single-collision experiments known to us on these reactions are the crossed molecular beam studies of Schmoltner et al. on O(^{3}P) and ethylene[3] and those of Kanofsky and Gutman and Kleinermanns and Luntz on reactions of O(^{3}P) with ethylene, propene, and 1-butene.[4,5] Schmoltner et al. found two channels:

$$C_2H_4 + O(^3P) \rightarrow CHO + CH_3 \qquad \Delta H_0^\circ = -25.5 \text{ kcal/mol} \tag{1a}$$

$$C_2H_4 + O(^3P) \rightarrow H + CH_2CHO \qquad \Delta H_0^\circ = -13.2 \text{ kcal/mol} \tag{1b}$$

The ratio of the yield of channel 1a to that of channel 1b was found to be 2.5 ± 0.9. Finally, the vinoxy radical (CH_2CHO) product of reaction 1b was peaked in the backward direction relative to the incoming O(^{3}P) atom. On the other hand, the CHO and CH_3 were forward−backward symmetric. Moreover, ab initio calculations showed that the barrier for H atom migration on the triplet surface was too high to be surmounted with the exothermicity of reaction 1b. However, on the singlet surface migration was possible, presumably because the intermediate ethylene oxide configuration is a stable minimum. A general picture emerges that H atoms break off on the triplet surface. Competing with this dissociation is an intersystem crossing to the lower singlet surface on which H atoms undergo a 1,2 shift, ultimately releasing an acyl radical and a companion alkyl radical.

Despite the molecular beam studies referred to, there is not as yet a general picture of the reactions beyond that of O with ethylene. The present paper is a first step in determining the products, their yields, and mechanism of formation. What we find is a general agreement with the overall model just presented together with interesting modifications caused by the additional vibrational and internal rotational modes.

Experimental Section

The technique is identical with that used in previous studies of the reactions of O(^{3}P) with alkynes.[6,7] Briefly, an O atom precursor, usually NO_2 but in a few cases SO_2, was mixed at a pressure of 100 milliTorr with 200 milliTorr of the alkene and flowed through an 8 cm cubic cell fitted with five windows. The reaction was begun by photodissociating NO_2 with a XeF laser at 351 nm or a YAG laser at 355 nm. (SO_2 was photodissociated with an ArF laser at 193 nm.) Probing of H, CO, and OH was carried out after 200 ns by a laser beam which caused one of the products to fluoresce. Probing of vinoxy radicals required a delay of 5 μs until the vibrations of the hot molecule relaxed. H atoms were excited at 121.6 nm, CO molecules near 154 nm, vinoxy radicals in the range 342.2−

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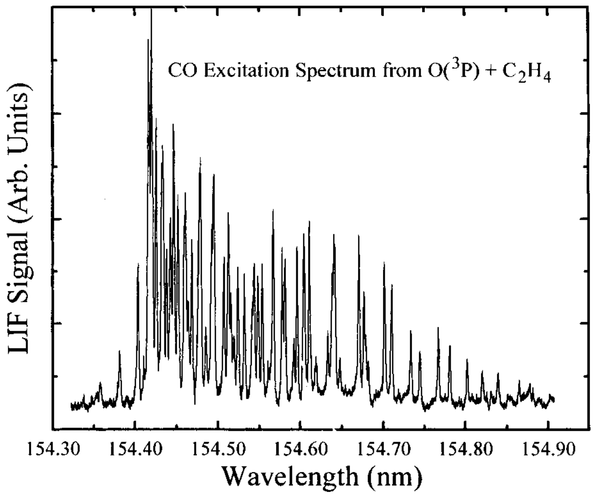

Figure 1. LIF excitation spectrum of the CO product of the reaction of $O(^3P)$ with ethylene.

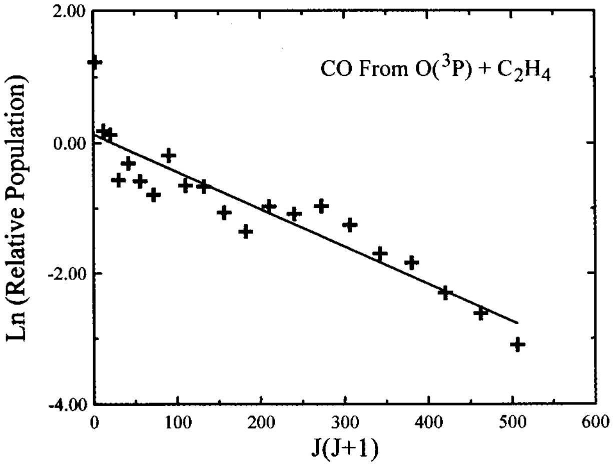

Figure 2. Ln of the corrected Q-band rotational line intensities divided by the Honl–London factor plotted against $J(J + 1)$.

335 nm, and OH radicals at the (1,0) transition near 280 nm. The vacuum-UV radiation was generated by two-photon resonant four-wave mixing in a rare gas. The Lyman α line at 121.6 nm was made by focusing 212.6 and 845 nm light together in 15 Torr of Kr; 154 nm light was made by focusing 249.63 and 650–643 nm light in 30 Torr of Xe. The 212.6 and 249.63 nm radiations were made by frequency doubling in BBO crystals. Alkenes were purchased from Aldrich and used as received.

The LIF excitation spectrum of the CO product (CO $A^1\Pi(v'=0) \leftarrow X^1\Sigma(v''=0)$) from the C_2H_4 reaction is shown in Figure 1. The Q-branch lines were readily assigned according to the energy levels listed by Lefloch et al.[9] The peak heights of these Q lines, $I(v'J'\leftarrow v''J'')$, were measured directly from the spectrum and corrected to the $^1\Pi$ percentage.[9] Relative populations $P(v''J'')$ can be derived from the equation

$$P(v''J'') \propto I(v'J'\leftarrow v''J'')/\{C_{\Pi}S(J',J'')\} \qquad (2)$$

where C_Π is the component of $^1\Pi$ in the upper state and $S(J',J'')$ is the Honl–London factor which is $(2J'' + 1)$ for the Q-branch of this transition.[10] A plot of ln $P(v'',J'')$ versus $J(J + 1)$ is shown in Figure 2, from which a rotational temperature of 380 ± 25 K is obtained

Results

The principal results are given in Tables 1–3 which list the alkenes and relative yields of H atoms, OH radicals, vinoxy radicals, and CO molecules. A very small yield of OH found for ethylene is believed to be due to the reaction of a small amount of $O(^1D)$ formed by a two-photon process from NO_2[8] at 355 nm. For normalization purposes the yields of CO and H from the ethylene reaction were determined relative to the yields of the same products from the acetylene reaction. The ratio of the CO yields for ethylene was 0.93 ± 0.06, and the ratio of the H atom yields was 1.95 ± 0.05 for ethylene and 1.68 ± 0.10 for propene. The uncertainties are the rms deviations from a set typically of four measurements.

Discussion

Hydrogen Atom Channel. In analogy with the ethylene reaction, H atom release is postulated to take place on the initial triplet potential energy surface; it is therefore natural to start a discussion of the results with this product. The data in Table 1 allow some clear generalizations: (1) If both carbon atoms are alkyl substituted, no H atoms are detected. (2) The presence of an unsubstituted carbon atom, i.e., a CH_2 group, is a necessary but not a sufficient condition for the detection of an H atom. (3) The yield of H atoms drops rapidly with increasing length of the alkyl substituent, becoming zero with 1-hexene.

The first generalization is a result of the fact that a C–C bond has a smaller bond energy than a C–H bond. Thus, when an O atom attaches itself to an alkyl-substituted C atom, the alkyl radical is released in preference to the H atom. A consequence of the second generalization is that the H atoms are derived from vinylic H atoms and not from those of a side chain.

The origin of the third generalization is subtle, and its explanation involves chemical dynamics. In the intermediate ketocarbene molecule, $CHRCH_2O$, what happens at the oxygenated carbon atom apparently depends on the length of the alkyl radical R. To understand this, we postulate two competing processes: release of an H atom and intersystem crossing. From Table 1 we note that the average H atom kinetic energy is in the range 10–12 kcal/mol and does not vary with the radical R. This implies that there is a local repulsion between the H atom and its erstwhile C atom partner. The origin of this repulsion is the change in structure of the oxyradical fragment relative to the same moiety in the ketocarbene and also the repulsion between the two parallel spins on the atom and the radical. The average kinetic energy of 10–12 kcal/mol is not far below the exothermicity of reaction 1b. Thus, the H atom can break away only when most of the molecule's vibrational energy has been concentrated in the reaction coordinate. The rather remote R group should not strongly affect the exothermicity of the reactions analogous to (1b) or the barrier to H atom escape. As the chain length increases, the density of states increases. It increases for the obvious reason that more atoms are in the molecule but also because very low-frequency internal rotation degrees of freedom are being added. In effect, the temperature of the molecule is being lowered, making more infrequent the localization of a relatively large fraction of the available energy in one C–H bond. The rate of intersystem crossing will increase rapidly with increasing density of states. Some of the vibrational frequencies on the initial triplet and the final singlet surfaces are different; quanta in the low-frequency internal rotation modes supply the difference in energy.[11] In conclusion, the H atom yield drops rapidly with increasing chain length because the rate of H atom escape

TABLE 1: H and OH Products from Reaction of Alkenes with $O(^3P)$[a]

alkene	I_H	k	I_H/k	$\langle E_T(H)\rangle$	I_{OH}	I_{OH}/k
ethylene	1.00	0.04	25	11.4 ± 0.8	0.03 ± 0.005	
propene	0.54 ± 0.01	0.23	2.36	12.1 ± 1.4	1.00	4.35
1-butene	0.23 ± 0.01	0.23	1.00	12.0 ± 1.0	0.71 ± 0.05	3.09
isobutene	0.43 ± 0.06	1.0	0.43	10.9 ± 0.7	1.37 ± 0.08	1.37
cis-2-butene	0	0.95	0		1.52 ± 0.07	1.6
trimethylethylene	0	3.17	0		0.96 ± 0.14	0.30
tetramethylethylene	0	4.07	0		0.73 ± 0.02	0.18
1-hexene	0	0.26	0		0.47 ± 0.05	1.81
cyclopentene	0	1.19	0		0.35 ± 0.01	0.29
cyclohexene	0	1.08	0		0.53 ± 0.08	0.49

[a] I_H was obtained by averaging the areas under 4−6 spectra, all relative to the value found for ethylene. The rate constants, k, taken from ref 2 are relative to that for 1-butene. The OH intensity, I_{OH}, was obtained by averaging the peak heights of several rotational lines of the OH LIF excitation spectrum, all relative to the value found for propene.

diminishes and the rate of the competing process, intersystem crossing, increases.

Another process for the formation of H atoms, to be discussed later, is the decomposition of HCO radicals whose C−H bond energy is only 14.2 kcal/mol. These H atoms would be made on the singlet surface. The mechanism of their formation would involve a triplet−singlet crossing and an H atom migration followed by the separation of a hot HCO radical. The formation of an HCO radical requires a CH_2 group, and the probability that it will be formed hot is diminished by the addition of modes. Thus, most of the arguments used above apply equally well to this mechanism of H atom formation. In practice, it is important only for the ethylene reaction.

Vinoxy Radical Channel. Alkenoxy radicals have the general structure $R{-}CH{=}CHO^{\bullet}$. When R = H, the radical is the extensively studied vinoxy radical. It is a planar molecule better described by the structure $^{\bullet}CH_2{-}CH{=}O$ than $CH_2{=}CH{-}O^{\bullet}$. Of particular interest is the $B(^2A'') \leftarrow X(^2A'')$ transition which is used for detection of the vinoxy radical. The fluorescence excitation spectrum begins at the electronic origin at 347 nm and continues only to 334.0 nm, after which it is abruptly cut off. The reason is that the upper levels are strongly predissociated. This phenomenon has been studied extensively by Osborn et al., who showed that predissociation takes place throughout the entire $B \leftarrow X$ absorption which extends to energies considerably above the cutoff energy for fluorescence.[12]

Reaction 1b produces equal numbers of hydrogen atoms and vinoxy radicals. The latter have also been detected as products of reactions of $O(^3P)$ with propene and 1-butene,[7] which is at first surprising. The following mechanism accounts for their formation

$$RCH{=}CH_2 + O(^3P) \rightarrow {}^{\bullet}RCH{-}CH_2O^{\bullet} \rightarrow RCH_2CH{=}O \rightarrow R^{\bullet} + {}^{\bullet}CH_2{-}CH{=}O \quad (3)$$

The triplet-state molecule becomes a singlet-state molecule after which a 1,2 shift of a hydrogen atom occurs, forming an energized aldehyde. The crucial step is the final unimolecular decomposition in which the radical is released rather than a hydrogen atom. A proof of the proposed mechanism depends first of all on the data of Table 2 which shows, at least for two examples, propene and 1-butene, that the yield of vinoxy does not diminish appreciably with chain length. This is in contrast to the H atoms whose yield, as shown in Table 1, diminishes rapidly with increasing chain length. The vinoxy from propene and 1-butene is necessarily a product of H atom migration on the singlet surface.

Methylvinoxy Radical Channel. Vinoxy was searched for by LIF but not found in reactions of 1,1-dimethylethylene (isobutene) and 1-methyl-1-ethylethylene. Instead, a broad spectrum peaking at 341.4 nm was found as shown in Figure 3. This band is due to methylvinoxy radical, $^{\bullet}CH_3CH{-}CH{=}O$. Part of the proof is that a mechanism for its formation is the same as eq 3:

TABLE 2: Relative Yields of Vinoxy Radical from Reaction of $O(^3P)$ with Alkenes[a]

alkene	I_H	I_H/k	I_{CH_2CHO}	I_{CH_2CHO}/I_H
ethylene	1.00	25	1.00	1.0
propene	0.54	2.36	1.64 ± 0.04	3.0
1-butene	0.23	1.00	1.51 ± 0.02	6.6

[a] The vinoxy intensity, I_{CH_2CHO}, was obtained by averaging the peak heights of several transitions, relative to those in ethylene.

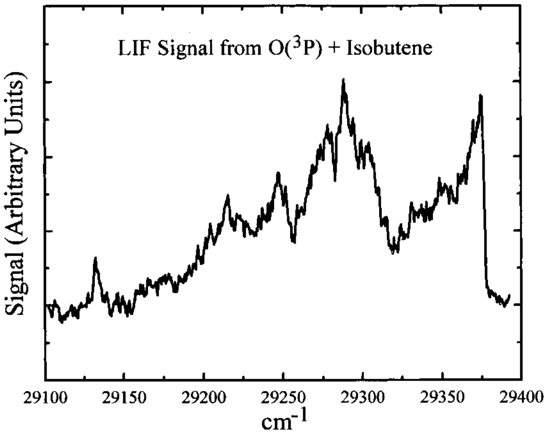

Figure 3. LIF excitation spectrum of the methylvinoxy product of the reaction of $O(^3P)$ with isobutene.

$$R'RC{=}CH_2 + O(^3P) \rightarrow {}^{\bullet}R'RCH_2O^{\bullet} \rightarrow R'RCH{-}CH{=}O \rightarrow R'^{\bullet} + {}^{\bullet}RCH{-}CH{=}O \quad (4)$$

In isobutene, R = R′ = CH_3 and a methyl radical is released rather than a hydrogen atom. However, in 1-methyl-1-ethylethylene, R′ ≠ R and the unimolecular decomposition of the resulting aldehyde intermediate shows exquisite selectivity in that the ethyl radical is preferentially expelled rather than the methyl. Ethyl is a better "leaving group" than methyl by only ∼1−2 kcal/mol. Definitive proof that the spectrum of Figure 3 is indeed due to the methylvinoxy radical is furnished by a comparison of the frequencies of the spectrum with that of a jet-cooled spectrum of the radical photodissociated from methyl propenyl ether recently obtained by J. C. Weisshaar and co-workers.[13] They have also found the spectrum of the radical CH_3COCH_2 in the same wavelength region. We would have observed this radical as a product of the O + isobutene reaction

TABLE 3: CO Yield from O(^{3}P) + Alkenes[a]

alkene	relative CO signal	CO signal/relative rate constant
ethylene	0.36	8.93
propene	1.00	4.35
1-butene	0.35	1.51
isobutene	0.44	0.44
2-butene	0.10	0.11
1-pentene	0.071	(0.290)
2-methyl-1-butene	0.053	(0.053)
1-hexene	0.037	0.142
2-ethyl-1-butene	0.022	(0.022)
trimethylethylene	0.085	0.027
tetramethylethylene	0.037	0.009
cyclopentene	0.313	0.263
cyclohexene	0.022	0.02

[a] Values in parentheses were computed using estimated rate constants. The values in the second column are averages of only two spectra, and so error limits are not given. The intensities are the averages of the peak heights of several rotational transitions relative to that found for propene.

if the O atom had attached itself to the substituted carbon ejecting one alkyl group. The fact that this radical was not observed is further confirmation that the attack of the O atom is selective, i.e., at the less substituted C atom.

HCO Channel. Probing HCO by LIF using the B ← X transition around 235 nm not effective. SO_2 is strongly fluorescent when excited at this wavelength and emits in the same region as HCO. NO_2 must be dissociated around 355 nm, which is near the peak of the HCO emission. During the time required for the photomultiplier tube to recover from the strong pulse of dissociating light, NO_2 rapidly reacts with HCO.[1] After 10 μs a very small HCO LIF signal was seen. We plan to probe HCO by cavity ring down spectroscopy.[14]

CO Channel. CO molecules in the $v = 0$ state were detected in the reaction of every alkene examined. However, the yields as shown in Table 3 were very small except for ethylene, propene, 1-butene, and cyclopropene. The minor yields may be derived from small amounts of acetyl radical, CH_3CO. As the number of carbon atoms in the substituent alkyl groups increases, the CO yield decreases sharply. The explanation is that in those hydrocarbons with an unsubstituted carbon atom HCO and an alkyl radical are the primary products. As the O atom attached itself to the C atom, initially almost the entire exoergicity was localized in the CO bond. As they separate, some of the HCO molecules may retain a sufficient amount of the initial energy to decompose into an H atom and a CO molecule. The cooling off of the CO bond is faster the more vibrational modes are present in the molecule. Thus, the alkyl side chains act as energy reservoirs that alter the nature of the products by removing energy from a somewhat distant site. Exactly this phenomenon was seen in the H atom channel.

In the reactions with ethene and propene no $v = 1$ CO molecules were detected by LIF using the (0,1) transition near 160 nm. The LIF excitation spectrum of the CO product from the C_2H_4 reaction is shown in Figure 1, and the plot in Figure 2 shows a typical Boltzmann plot from which the rotational temperatures were extracted. The rotational temperatures were all in the range 300−400 K. If the CO molecules are really derived from a parent HCO molecule, one might have expected more rotational energy. As the carbon−carbon bond breaks, it would be natural to expect that a twist would be applied to the HCO molecules. However, the HCO parents of the CO molecules are not representative. A total of 14.2 kcal/mol is required to break up an HCO molecule; for ethylene this is more than half of the reaction exothermicity. Thus, the CO molecules are derived from HCO molecules for which there is less energy available for translation and rotation. A real test will come from probing of HCO molecules directly.

The measured product ratios for the ethylene (E) and acetylene (A) reactions allow an indirect determination for the ethylene reaction of the fraction of HCO dissociated into CO + H. Three ratios are used. ($k^A{}_{CO}/k^A{}_H$) is the branching ratio in the acetylene reaction of the CO and the H atom channels which is 1.5 ± 0.15. ($k^E{}_H/k^A{}_H$) and ($k^E{}_{CO}/k^A{}_{CO}$) are the ratios of the H atom and CO signals observed under otherwise identical conditions in the ethylene and acetylene reactions. They are 1.95 ± 0.10 and 0.67 ± 0.06, respectively.

$$k^E{}_{CO}/k^E{}_H = (k^A{}_H/k^E{}_H)(k^E{}_{CO}/k^A{}_{CO})(k^A{}_{CO}/k^A{}_H) \qquad (5)$$

Substituting the values quoted above for the ratios on the right side of eq 5, one finds 0.5 for the ratio; in other words approximately half of the H atoms are products of the decomposition of HCO. This is an important third channel of the O(^{3}P) + ethylene reaction.

As shown in Table 3, the only reactions that give appreciable yields of CO are with ethylene, propene, 1-butene, and cyclopentene. Cyclopentene and cyclohexene reacting with O(^{3}P) have almost the same rate constant (Table 1); cyclohexene has a higher yield of OH radicals consistent with the fact that it has an additional CH_2 group. However, cyclopentene has an order of magnitude higher yield of CO product. Cvetanovic observed that cyclopentene was unique among alkenes in that it produced a high yield of ethylene on reaction with O(^{3}P). The partner of the ethylene molecules, of course, must be CO molecules. Clearly the two cycloalkenes must have very different reaction mechanisms. The fact that the overall rate constant is the same only means that the rates of attack on the double bond and the allylic O−H bonds are the same. The subsequent rearrangements and decompositions must be quite different. At first sight one might have thought that the reaction mechanism would have been the same for these two cycloalkenes. An addition of an O atom would be followed by an H atom migration to form a cycloalkanone and then extrusion of the CO with the simultaneous formation of a cycloalkane. This might be the mechanism for cyclopentene. The heat of formation of cyclopentanone is 113 kcal/mol less than that of the reactants O and cyclopentene; similarly the heat of formation of cyclohexanone is 112 kcal/mol less than that of the reactants O and cyclohexene. While 25 kcal/mol is required to convert cyclopentanone into cyclobutane and CO, only 9 kcal/mol is required to convert cyclohexanone into cyclopentane and CO. The release of CO from a hot cyclohexanone should be even more facile than from cyclopentanone. We conclude that the cyclohexene reaction does not, for the most part, involve cyclohexanone formation.

Hydrogen Atom Isotope Effects. As has been observed with acetylene and deuterioacetylene, the overall rate constant for the reaction of O(^{3}P) with ethylene is the same as that for perdeuterioethylene.[15] If the hydrogen mass plays no role in the formation of the initial reaction complex, then the point of attack of the O atom must be at one of the C atoms and not at the hydrogen atoms. A second question is whether the branching ratio of the two channels, reactions 1a and 1b, is affected by isotopic substitution. To answer this question, the LIF excitation spectra were measured of hydrogen atoms resulting from the reaction of an equimolar mixture of C_2H_4 and C_2D_4. The relative abundance of the H and D atoms is given by the ratio of the areas under the excitation curves. The average kinetic energy is obtained from the second moment of

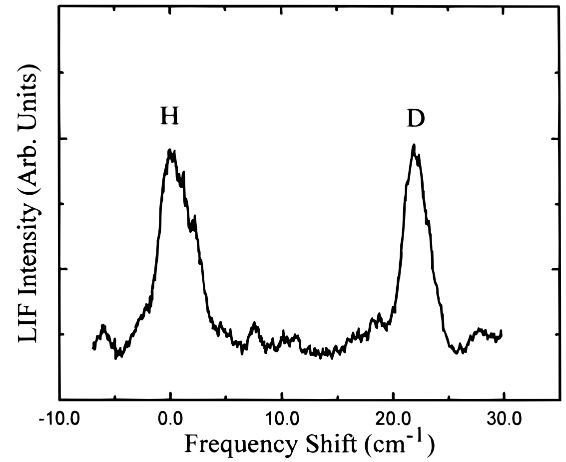

Figure 4. LIF excitation spectrum of the H and D atom products of the reaction of O(^{3}P) with an equimolar mixture of ethylene and perdeuterioethylene.

the excitation curve. In Figure 4 the H and D peaks have similar heights, but the D peak is narrower and therefore the H/D ratio is greater than one. The average of six spectra like that in Figure 4 yields H/D = 1.30 ± 0.10. Similarly, the CO spectra from the reaction of O(^{3}P) with C_2H_4 and C_2D_4 were compared with the CO from O(^{3}P) the reaction with C_2H_2 . The two ratios were 0.67 ± 0.06 and 0.93 ± 0.02. Thus, the ratio of CO yields from ethylene and deuterioethylene is 0.72 ± 0.05. We see that in the reaction with C_2D_4 fewer hydrogen atoms are released but more CO molecules are formed than with C_2H_4.

OH Radical Channel. OH radicals in the $v = 0$ state were found in the reactions of O(^{3}P) with all the alkenes investigated except for ethylene. The quantum-state distribution was, within experimental error, the same as that found by Andresen and Luntz in the reaction of O(^{3}P) with alkanes, i.e., low rotational temperatures and equal population of the Λ doublet states.[17] The low rotational temperature implies a collinear C−H···O transition state.

The relative OH LIF intensities presented in Table 1 lead to the following generalizations: (1) There is a high selectivity in the site of OH production. O(^{3}P) cannot attack vinylic C−H bonds because they are stronger than O−H bonds (110 vs 104 kcal/mol). Of all the C−H bonds in an alkyl chain attached to a C atom of a double bond, only the allylic C−H bonds appear to be attacked. They are the weakest C−H bonds (88 kcal/mol) in the molecule. For example, the OH signal from ethylethylene (1-butene) is weaker than that from methylethylene (propene). Even propargylic C−H bonds are not attacked. Propene gives a strong OH signal, but with propyne no OH is observed. (2) Methyl groups attached to the same carbon atom sterically hinder each other. For example, the OH yield from isobutene is less than twice the OH yield from propene. (3) The OH yield decreases a little with increasing substitution but to a much lesser extent than the H atom or CO yields.

The reactions have been initiated with photolytically produced O(^{3}P) atoms which have more than thermal translational energy. This was necessary in order to create single-collision conditions in a bulb on a nanosecond time scale. We believe that the conclusions derived from these experiments nevertheless apply also to reactions of thermal O atoms because (a) when NO_2 is dissociated at 351 nm much of the available energy goes into vibrational and rotational energy of the NO product, (b) the relative energy of O and the alkene is less than the laboratory kinetic energy, and (c) the translational energy, a few kcal/mol, is small compared to the exothermicity of these reactions.

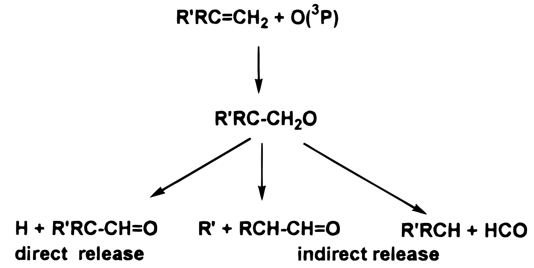

Figure 5. General scheme for the reaction of O(^{3}P) with an alkene.

Conclusions

The alkenes can be divided into two groups: those in which at least one of the carbon atoms of the double bond is bonded to two hydrogen atoms, i.e., R′RCH=CH$_2$, and those in which both carbon atoms are attached to alkyl groups. For the former group a major product channel of the O(^{3}P) reaction is HCO$^•$ and R′RCH$^•$ which we have not probed directly. However, a large amount of circumstantial evidence has been collected to support the reaction scheme shown in Figure 5. The H atom release channel is important only for ethylene and propene (see Table 1) and is believed to take place on the triplet surface. The other two channels follow a migration of a H atom from the oxygen bound carbon to the alkylated carbon. In the special case that R′ = R = H, the products in the second channel are identical with those of the first although they were formed in a different way. The two channels could be distinguished from each other, in principle, by partial deuterium substitution. In case R′ ≠ R, as with 1-methyl-1-ethylethylene, the radical that will be released is the one whose channel is most exoergic.

Less is known about the alkenes, both of whose double-bonded carbon atoms are bound to alkyl groups. The variety of products will be greater because the O atom will have approximately equal probability of attacking either carbon atom. One product pair will result from a breaking off of a radical attached to the oxygen-bonded carbon atom. If the radical does not separate, an H atom, if present, will migrate, and afterward either the original C−C double bond will break or one of the alkyls on the second carbon will separate.

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