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The Reactions of O(^{3}P) with Alkenes: The Formyl Radical Channel

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The HCO product of the reaction of O(^{3}P) with ethene has been detected by cavity ring-down spectroscopy using its A−X transition. For propene a somewhat smaller yield of HCO was obtained but the overall rate constant is much larger. The yield of HCO in this reaction is quite small (∼0.05). Moreover, a large number of other alkenes were tried with negative results. The failure of the 1,2 H atom shift followed by breaking the 1,2 bond implies that the unimolecular decomposition has found a more favorable channel. The proposed mechanism is as follows. For an alkene of the form $RCH_2CH{=}CH_2$ the first step is attachment of the O(^{3}P) to the terminal carbon atom, C_1. Then, intersystem crossing occurs and finally a H atom shifts from C_3 to C_2 and not from C_1 to C_2. In this way a molecule of formaldehyde and an alkene shorter by one carbon atom are formed.

This is the second in a series of papers dealing with the products of the reactions of O(^{3}P) atoms with alkenes.[1] The kinetics of these reactions has been well studied and the rate constants are in standard tabulations.[2,3] These rate constants determine the rate at which an alkene is consumed but give no information on the products nor on the reaction mechanism. This research aims to determine the yields of the various reaction products and to understand the reaction mechanisms as inferred from these yields and from nascent product distributions.

The first paper dealt with the H atom, CO, vinoxy, methylvinoxy, and OH radical channels. The present paper probes the HCO product channel. Following is a review of what is currently known about the O(^{3}P) + alkene reactions. The initial step of the reaction is the addition of the O atom to the double bond forming a hot triplet diradical. The latter can directly decompose or cross to a singlet state, isomerize, and then decompose. The decomposition is complex: even the diradical of the simplest of all alkenes, ethene, does not decompose in a simple fashion. The two principal channels are

$$^3H_2C{-}CH_2O \rightarrow {}^1H_2C{-}CH_2O \rightarrow H_3C{-}CHO \rightarrow H_3C + CHO \quad (1)$$

$$^3H_2C{-}CH_2O \rightarrow {}^{\bullet}H_2C{-}CHO + H^{\bullet} \quad (2)$$

The assignment of spin states follows from two observations by Schmoltner et al.[4] The first is that the products of reaction 1 are isotropically distributed in the center of mass frame whereas the products of reaction 2 are anisotropically distributed. Second, the theoretical barrier for the 1,2 H atom shift is very high in the triplet state and low in the singlet state. It is therefore concluded that the rate of dissociation via channel (2) competes with the rate of intersystem crossing. The latter is followed by the H atom transfer.

In addition there are minor channels with small yields ≤5%. The relative yields of the two major channels has been measured by mass spectroscopy, photochemical modulation spectroscopy, and molecular beam methods with varying results.[4−6] For purposes of discussion we will use the molecular beam result, which gave the branching ratio of channel 1 to channel 2 as 2.5 ± 0.9. The purpose of the present work was to determine the relative yields of HCO when O reacts with different alkenes.

A minor channel observed previously was the CO channel, which we (incorrectly) assumed was correlated with the HCO channel.

Experimental Section

The experiments are carried out by irradiating with pulsed lasers a flowing gaseous mixture of an O(^{3}P) precursor, SO_2, and an alkene in a 2/1 ratio and at a total pressure of 500 mTorr. The absorption coefficients of the hydrocarbons are at most only a few percent of that of SO_2.[7] There are special problems in the detection of HCO in such a system. HCO is commonly probed by its B ← X transition in the UV around 230 nm.[8,9] For probing a product of a reaction in a gas (as opposed to a beam) REMPI is difficult because the gas pressure is too high. LIF is prevented by the strong fluorescence of SO_2, which absorbs and emits in the same spectral regions as CHO. The A state of CHO and the ground state are a Renner−Teller pair, and consequently, the fluorescence yield following the red A ← X transition is only about $\sim 10^{-4}$.[10] CHO must therefore be detected by absorption in the red, and the cavity ring-down technique (CRD) is ideal for this purpose.[11]

Figure 1 is a schematic diagram of the apparatus. The output of a Compex 102 ArF excimer laser (80 mJ/pulse) is led though a nitrogen-purged plastic tube. The shape of the beam is initially a rectangle whose long axis is vertical, but after reflection from two mirrors the long axis is horizontal. The beam crosses the ring-down tube perpendicularly and is reflected back to increase the total absorption. HCO is detected using its transition $\tilde{A}(0,9,0) \leftarrow X(0,0,0)$ in the range 613−618 nm. DCO is detected using the $\tilde{A}(0,11,0) \leftarrow X(0,0,0)$ transition in the range 627−630 nm. The probing light is from a YAG-pumped dye laser with a pulse energy of 20 mJ. The dye solution was a mixture of DCM and Rh640 in methanol whose output can be tuned from 605 to 635 nm.

The cavity itself is 60 cm long, bounded at the ends by two 2 cm diameter spherical mirrors of 99.997% reflectivity obtained from Los Gatos Instruments. The ring-down decay signal is detected with a red-sensitive photomultiplier protected by a filter

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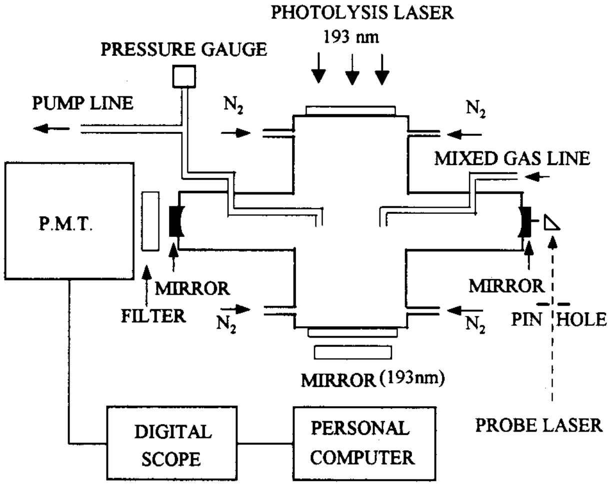

Figure 1. Schematic diagram of the cavity ring-down apparatus.

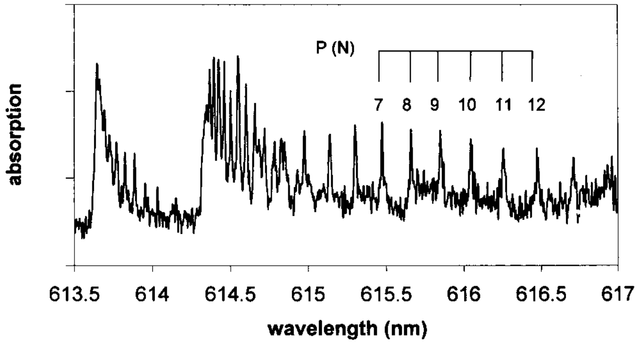

Figure 2. Cavity ring-down spectrum of the HCO product of the reaction of O(^{3}P) with ethene.

that absorbs scattered 193.3 nm light. The probe laser beam passes through several irises and is about 1.5 mm wide when it enters the cavity. It is delayed from the excimer laser pulse by 11 μs. The signal is digitized and displayed on a LeCroy 400 MHz digital oscilloscope. The data are transferred through a National Instruments (GPIB-AT) IEEE-488 interface to a PC. A program, furnished to us by D. Robie, averages the early parts of three cavity ring-down curves and then least-squares fits them to an exponential decay function to yield the ring-down decay rate. When the dye laser is scanned, the decay rate as a function of wavelength is the CRD spectrum (Figure 2). In the absence of absorber the cavity ring-down time should be ~70 μs. However, with daily cleaning with methanol the ring-down time increased to over 100 μs, increasing the sensitivity of the detection. However, only the early part of the decay was used so that the total time in which the reaction was studied varied between 20 and 40 μs. All chemicals were from Aldrich except CD_3CDO, which was from Cambridge Isotope.

In initial experiments using a 193 nm laser and SO_2, a pale yellow powder, believed to be sulfur, deposited on both transverse windows, making them quickly opaque to incident 193 nm light. The problem was solved by placing the quartz windows at the ends of extended arms and flowing nitrogen at a pressure of 20 Torr across the inner surface of the windows. This had the unexpected effect of increasing the signal, presumably because the reacting gases were concentrated nearer the center line of the cavity.

TABLE 1: Yields of HCO in O(^{3}P) + Alkene Reactions[a]

alkene	k_{rel}	I_{rel}	fractional yield of HCO
$CH_2{=}CH_2$	1	1	0.71 ± 0.06^4
$CH_3{-}CH{=}CH_2$	5.75	0.44 ± 0.04	0.05 ± 0.02
other alkenes		0	0

[a] k_{rel} of the second column are from ref 2.

Results

The CRD spectrum of the CHO reaction product of the O(^{3}P) reaction with ethene is shown in Figure 2. The S/N ratio of the CHO formed by photodissociation of acetaldehyde is even greater. A somewhat weaker signal is seen with propene. However, because of the presence of 20 Torr of N_2 all HCO spectra were identical in shape and thermalized. No signal was seem with 1-butene ($C_2H_5CH{=}CH_2$), *cis*-2-butene (CH_3-$CH{=}CHCH_3$), isobutene ($(CH_3)_2C{=}CH_2$), 1-pentene (C_3H_7-$CH{=}CH_2$), allene ($CH_2{=}C{=}CH_2$), 1,3-butadiene ($CH_2{=}CH{-}CH{=}CH_2$), cyclopentene, and cyclohexene. Table 1 summarizes the results obtained. As mentioned earlier, the total time of observation of the reaction did not exceed 40 μs. By this time almost all of the oxygen atoms have reacted. For these reasons, secondary processes reducing the concentration of HCO such as reaction of O(^{3}P) with HCO or HCO dimerization with the help of a third body did not have to be considered.

Discussion

The absolute signal strengths listed in Table 1 are less meaningful than the signal strengths relative to the rate constants. These are also listed in the table. The rate constant of propene is 5.75 times that of ethene, but its signal is less by a factor of 0.44. Considering the variety of all the other alkenes and alkadienes, it is safe to say that ethene and propene are the only alkenes that are sources of HCO.

The central result is that the production of HCO (and CH_3) is the major channel of the reaction of O with ethene, a minor channel of the reaction of O with propene, and not observable in the reaction of O with any other alkene.

To try to understand these facts, consider first an alkene that has an alkyl group attached to each of its two doubly bonded carbon atoms, $HR_1C{=}CR_2H$. When an O atom is bonded to either carbon atom, previous work showed that no H atom is released. Presumably, one of the two alkyl radicals is released because the C$-$C bonds are typically weaker than C$-$H bonds, by about 40 kJ/mol. The fact that no HCO is formed is explained if one assumes that radicals are ejected faster than they can migrate.

Now consider an ethene with only one of its hydrogen atoms replaced by an alkyl group, $HRC{=}CH_2$. In general, the electrophilic O atom is more likely to attach itself to the C atom with the larger negative charge. A recent SCF calculation found that in propene, 1-methylethene, C_1 and C_2 have Mulliken-defined charges of -0.25 e and -0.08 e, respectively.[12] Therefore, we expect that more reactive collisions will result in an O atom attached to C_1 than to C_2. If, nevertheless, the O atom attacks C_2, the alkyl group, R, will be preferentially released. If the O atom attacks C_1, a H atom can be released directly but the yield of this process diminishes rapidly with the increasing length of R. A competing process is an intersystem crossing to a lower singlet state followed by a H atom migration, a "1,2 shift" in the language of organic chemists. The result of the H atom migration is a hot aldehyde molecule.

$$R{-}CH{=}CH_2 + O \xrightarrow[\text{addition}]{} R{-}CH{-}CH_2O \xrightarrow[\text{1,2 shift}]{} R{-}CH_2{-}CHO \quad (3)$$

This energized molecule could dissociate either by breaking the $C_1{-}C_2$ bond or the $C_2{-}C_3$ bond. In each case a pair of radicals

TABLE 2: R−CH−CH$_2$O Decomposition Products[a]

R	ΔH, kJ/mol			ϕ_{HCO}
	RCH + CH$_2$O	R + CH$_2$CHO	RCH$_2$ + HCO	
H	+15	−47	−115	0.71
CH$_3$	−323	−89	−116	0.05
C$_2$H$_5$	−336	−103	−110	0.00

[a] $\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{O}(^3\text{P}) + \text{RCH=CH}_2)$.

are formed. Why does the probability of the C$_1$−C$_2$ breaking become negligible as the chain length increases? Table 2 lists the exothermicity of these two bond-breaking channels.[13,14] In the O + C$_2$H$_4$ reaction the HCO channel is dominant. In this case there is a pronounced thermodynamic bias for the breaking of the C$_1$−C$_2$ bond rather than the C$_2$−C$_3$ bond. However, as shown in the bottom two rows of Table 2, there is no strong thermodynamic preference for the breaking of either bond. There does not seem to be any structural reason to break one bond rather than the other.

There is, however, another possible scenario. As the chain is lengthened, there is an ever more rapid delocalization of the energy. The unimolecular decomposition is allowed full scope and a 3,2 H atom shift may become the dominant process because so much more energy is released in that channel. This is because the products are two stable molecules rather than two unstable radicals. As shown in Table 2, the exothermicity of the reaction producing the next shorter alkene and formaldehyde increases with increasing chain length. We assume that a large exothermicity will be accompanied by a lowering of a barrier and a greatly increased density of states.

HCO in Flames. Cheskis and Scherer have each detected CHO by absorption in a methane−oxygen flame.[15,16] This raises the question of the origin of the HCO. What chemical reactions produce the HCO? We have verified that the reaction O + CH$_3$ does not produce HCO. The reaction

$$\text{O} + \text{CH}_2 \rightarrow \text{HCO} + \text{H} \tag{4}$$

releases so much energy, 379 kJ/mol, that it is most unlikely that the weak C−H bond of HCO (59 kJ/mol) could survive. We have done some preliminary experiments to see how rapidly H atoms could collide with CO molecules in the presence of a third body and produce HCO.

$$\text{H} + \text{CO} + \text{M} \rightarrow \text{HCO} + \text{M} \tag{5}$$

An H atom precursor was irradiated in the presence of a large excess (several hundred Torr) of CO. A broad red absorption was found in the same region as HCO but it was structureless. This absorption had the same appearance whether the H atom precursor was acetylene or H$_2$S. Our tentative conclusion is that the red absorption is due to HCO in an excited vibrational state and that the red light takes this system to the Ã state but to such a high level that dissociation is extremely fast. We conclude that the O + C$_2$H$_4$ reaction is a more likely source of the structured HCO absorption seen in methane−oxygen flames. Another possible source is an abstraction of an H atom from H$_2$CO by an H or O atom.

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References and Notes

(1) Quandt, R.; Min, Z.; Wang, X.; Bersohn, R. *J. Phys. Chem.* **1998**, *102*, 60.
(2) Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115.
(3) NIST Chemical Kinetics Database 17-2Q98, NIST Standard Reference Data, Gaithersburg, MD, 1993.
(4) Schmoltner, A. M.; Chu, M.; Brudzynski, R. J.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 6926.
(5) Hunziker, H. E.; Kneppe, H.; Wendt, H. R. *J. Photochem.* **1981**, *17*, 377.
(6) Bley, U.; Dransfeld, P.; Himme, B.; Koch, M.; Temps, F.; Wagner, H. G. *Symp. (Int.) Combust. (Proc.)* **1988**, No. 22, 997.
(7) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1975.
(8) Lee, S.-H.; Chen, I.-C.; Adamson, G. W.; Field, R. W. *J. Mol. Spectrosc.* **1997**, *182*, 385.
(9) Bernstein, J. S.; Song, X. M.; Cool, T. A. *Chem. Phys. Lett.* **1988**, *145*, 188.
(10) Stone, B. M.; Noble, M.; Lee, E. K. C. *Chem. Phys. Lett.* **1985**, *118*, 83.
(11) O'Keefe, A.; Deacon, D. A. G. *Rev. Sci. Instrum.* **1988**, *59*, 2544.
(12) Byrd, Edward, F. C. Private communication.
(13) *Handbook of Chemistry and Physics;* Lide, D., Ed.; CRC Press: Boca Raton, FL, 1997.
(14) *Thermodynamic Data of Organic Compounds;* Ridley, J. B., Naylor, R. P., Kirby, S. P., Eds.; Chapman and Hall: London, 1986.
(15) Cheskis, S. *J. Chem. Phys.* **1995**, *102*, 1851.
(16) Scherer, J. J.; Rakestraw, D. J. *Chem. Phys. Lett.* **1997**, 265, 169.