PHOTOCHEMICAL MODULATION SPECTROSCOPY OF OXYGEN ATOM REACTIONS WITH OLEFINS*

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Summary

We used photochemical modulation spectroscopy to study the primary radical products of oxygen atom—olefin reactions by their optical absorption. In contrast with earlier work done by mass spectrometric sampling we found that the "vinoxy" radical CH_2CHO is an important primary product with ethylene and monosubstituted ethylenes. We characterized two electronic transitions of this radical with origins at 347.7 and 1249 nm and estimated the yields of CH_2CHO and HCO in the oxygen atom reactions by comparison with reference reactions of unit quantum yield. Two sources of CH_2CHO formation were identified: a pressure-independent pathway and a pressure-dependent mechanism which complements the stabilization of epoxides and aldehydes. Mercury-photosensitized decomposition of the corresponding epoxides also produces large yields of CH_2CHO. Our observations of pressure-independent fragmentation forming CH_2CHO link together early observations of a similar mechanism by Cvetanovic and recent low pressure flow and molecular beam experiments by several groups. A mechanism which accounts for the different characteristics of the pressure-independent and pressure-dependent pathways is discussed.

1. Introduction

In this paper we are concerned primarily with a quantitative evaluation of the reaction pathways leading to the primary products of oxygen atom—olefin reactions, in particular to the fragment CH_2CHO, at intermediate pressures (0.05 - 1 atm). The subject of oxygen atom reactions with olefins has been extensively studied and reviewed repeatedly [1 - 3], but it now appears that it is not as well understood as previously believed. The pioneering work in this field has been done by Cvetanovic [1]. For the purpose of later discussion we shall summarize part of his findings as follows. There are two dominant reaction types: (a) the formation, via a diradical addition complex, of hot epoxides, aldehydes and ketones which are stabilized or decompose depending on the pressure and molecular size; (b) pressure-independent fragmentation where the oxygen atom

appears to displace one substituent from the end of the double bond to which it adds:

$$O + C_2H_4 \rightarrow CH_3 + HCO \tag{1a}$$

$$\rightarrow H + CH_2CHO \tag{1b}$$

$$\rightarrow H_2 + CH_2CO \tag{1c}$$

Type (b) was observed only for alkyl substituents in non-terminal olefins, although for ethylene Cvetanovic postulated the analogous reaction (1b) [4]. Type (a) reaction gives only traces of stabilized products with ethylene at 1 atm, while the decomposition products CH_3 and HCO were estimated to account for 75% of the overall process. A third minor pathway, reaction (1c), was also noted.

While Cvetanovic used final product analysis, the primary reaction products were later directly observed by mass spectrometry sampling techniques [5, 6]. The results were essentially interpreted in terms of type (a) processes, and no unequivocal evidence for Cvetanovic's pressure-independent fragmentation pathway was found. For ethylene in particular, reaction (1b) was claimed to be absent, reaction (1c) was measured to contribute 5% and the remaining 95% was ascribed to reaction (1a). However, at the same time MacFadden and Currie [7] were unable to detect CH_2CHO with a mass spectrometer in an unrelated photolysis reaction where the radical was known to be formed. In retrospect the mass spectrometry sampling experiments suffered from two other drawbacks: the inability to distinguish isomers and the lack of systematic pressure variations.
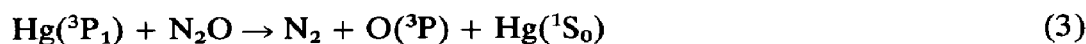
The fact that there was something wrong with the picture derived from the sampling experiments was first discovered by Lee and coworkers [8]. Under true molecular beam conditions they found only CH_2CHO formed in the $O + C_2H_4$ reaction. The parent ion of this product, CH_2CHO^+, was detected as well as the ions HCO^+, CH_3^+ and CH_2CO^+ which were shown to result from fragmentation of CH_2CHO^+. Products of type (a) reactions were absent. The formation of CH_2CHO in the $O + C_2H_4$ reaction was subsequently also reported by Inoue and Akimoto [9] who detected its presence under fast flow conditions by laser-induced fluorescence. The same detection method was recently used by Luntz and Kleinermans [10] in a crossed molecular beam experiment. They found CH_2CHO formed in the oxygen atom reactions of ethylene, propene and 1-butene, and they examined its vibrational excitation. Energy partitioning was found to be non-statistical, indicating that no long-lived complex intermediate is involved. The kinetic energy thresholds for CH_2CHO formation were determined to be 1 kcal mol^{-1} for all three olefins. This does not parallel the activation energies of the overall reaction which are 1 kcal mol^{-1} for ethylene but 0 kcal mol^{-1} for propene and 1-butene [11].

These new results indicate that with ethylene and terminal olefins a process occurs which is analogous to Cvetanovic's pressure-independent fragmentation and should persist to high pressures since it is a direct reaction. The question thus arises whether this process is a major or a minor process. It might be expected to be a minor process since Cvetanovic observed no type (b) reaction with terminal olefins [12]. We therefore investigated the contributions of CH_2CHO-forming processes up to pressures of 1 atm, using optical absorption spectroscopy

of CH_2CHO and a reference reaction which produces a known yield of this species. Similar measurements were made for some related reactions and for the product radical HCO. This work also led to new information on the electronic states of CH_2CHO which is useful for discussing the dynamics of the pressure-dependent and pressure-independent pathways.

2. Experimental details

The decomposition of N_2O photosensitized by mercury vapor offers a convenient way to modulate the rate of oxygen atom reactions by modulating the 253.7 nm excitation. With a large excess of N_2O only the following reactions are important:

$$Hg(^1S_0) \xrightarrow{\text{253.7 nm}} Hg(^3P_1) \tag{2}$$

$$Hg(^3P_1) + N_2O \rightarrow N_2 + O(^3P) + Hg(^1S_0) \tag{3}$$

$$O(^3P) + \text{olefin} \rightarrow \text{products} \tag{4}$$

This method was introduced by Cvetanovic [13] who first used it to study the final products [14] and later to measure oxygen atom reaction rates by a modulated chemiluminescence technique [15]. We employed the same scheme for measuring the modulated optical absorption of the primary radical products by phase-sensitive detection. Our apparatus has been described in detail previously [16]. It is capable of detecting absorption amplitudes of 10^{-6} in the UV and 10^{-7} in the near IR. In the present experiments we used a modulation frequency of 270 Hz and an average photolysis intensity of about 10^{-5} einsteins l^{-1} s^{-1}. Reactant partial pressures were chosen to be high enough to avoid effects of product build-up in the flow reactor; this is particularly important in the mercury-photosensitized reaction of ethylene oxide. Nitrogen was used as a carrier gas except in the low pressure N_2O runs. Under the conditions employed the radical formation rate follows the photolysis intensity, while the decay occurs by radical–radical reactions and is sufficiently slow to produce a phase shift of $45°$ - $60°$ in the product radical concentrations. This phase shift was taken into account when we calculated radical formation rates from absorption amplitudes.

3. Electronic spectra of CH_2CHO

We initially observed the UV absorption spectrum shown in Fig. 1 in the $O + C_2H_4$ reaction. The phase shift was consistent with a primary free-radical product. By producing the same transient spectrum in the reaction

$$Hg(^3P_1) + CH_3-OC_2H_3 \rightarrow CH_2CHO + CH_3 + Hg(^1S_0) \tag{5}$$
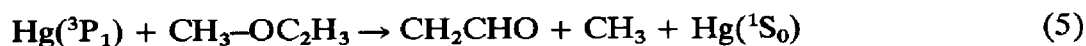
which is known to generate CH_2CHO radicals with unit quantum yield [17], as well as in analogous mercury-photosensitized reactions of $C_2H_5-OC_2H_3$ [18] and $CH_3CO-OC_2H_3$, we convinced ourselves that the product observed is the CH_2CHO radical. Reaction (5) gave the strongest signal, as expected.

The UV spectrum starts with a prominent 0–0 band at 347.7 nm (3.57 eV), which agrees with a band head observed by Currie and Ramsay at 347.3 nm under higher resolution [19]. This band and the first three vibronic bands also appear in the fluorescence excitation spectrum of Inoue and Akimoto [9]. All remaining bands can be interpreted as combinations of these three vibronic fundamentals. Below 330 nm the spectrum is probably predissociated since no laser-induced fluorescence has been observed [9]. Integration of the entire spectrum, including the continuum, gives an oscillator strength $f = (1.8 \pm 0.4) \times 10^{-3}$, corresponding to a radiative lifetime of $(0.8 \pm 0.2) \times 10^{-6}$ s. Since this agrees with the observed fluorescence lifetime, the emission yield must be close to 1.0 for the lowest vibronic states.

In the near IR we detected a second region of CH_2CHO electronic absorption from 1000 to 1250 nm. The spectra observed in the $O + C_2H_4$ reaction and in reaction (5) were again identical and are shown in Fig. 2. The prominent 0–0 band of this electronic transition is located at 1249 nm (0.99 eV). We have not yet determined the oscillator strength of this transition but it is certainly much smaller than that of the UV system.

On the basis of recent *ab initio* calculations carried out by Dupuis [20] the UV and near-IR spectra can be assigned to the $B,2\ ^2A''–X,1\ ^2A''$ and $A,1\ ^2A'–X,1\ ^2A''$ transitions respectively of the CH_2CHO radical. The three states are essentially derived from the three allylic resonance structures of CH_2CHO as indicated in Fig. 3. While the X and B states are hybrids of the two structures of species a'', the A state represents the a' structure and may thus properly be called the "vinoxy" radical. This becomes evident when the calculated C–C and C–O bond lengths are compared with those of acetaldehyde and vinyl alcohol which are also represented in Fig. 3.
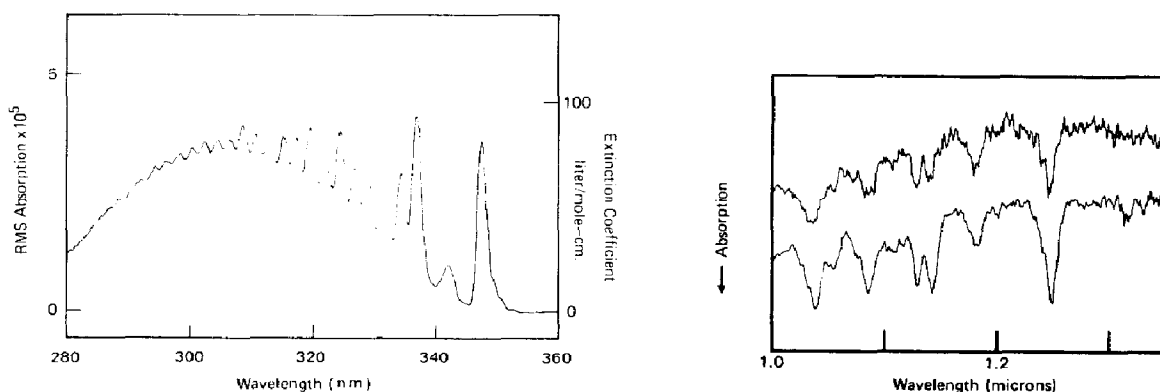

Fig. 1. The transient UV absorption spectrum of CH_2CHO generated from the mercury-photosensitized decomposition of $CH_3OC_2H_3$ in 1 atm of nitrogen (spectral slit width, 1.6 nm). The same spectrum was observed in the oxygen atom reactions of ethylene, propene and 1-butene.

Fig. 2. The transient near-IR absorption spectrum of CH_2CHO generated from $O + C_2H_4$ (upper trace) and $Hg(^3P_1) + CH_3OC_2H_3$ (lower trace) at the same photolysis intensity and total pressure (1 atm). The sensitivity in the upper trace is twice that of the lower trace (spectral slit width, 4.8 nm).
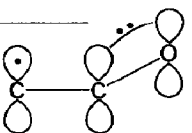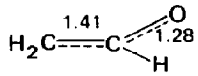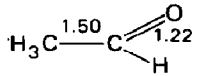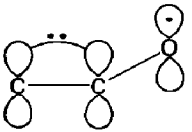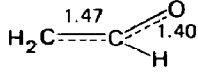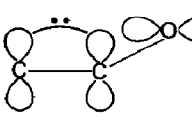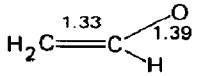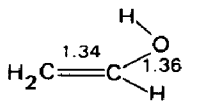
Resonance Structures	M. Dupuis, MCHF Calculations (Ref. 20). Bond lengths in Å. All states are planar.	
a''	$H_2C\overset{1.41}{=\!=\!=}C\overset{O}{\underset{H}{\diagup}}{}^{1.28}$ X,1^2A'' 0 eV	$H_3C\overset{1.50}{-\!-\!-}C\overset{O}{\underset{H}{\diagup}}{}^{1.22}$ Acetaldehyde (Ref. 21)
a''	$H_2C\overset{1.47}{=\!=\!=}C\overset{O}{\underset{H}{\diagup}}{}^{1.40}$ B,2^2A'' 3.2 eV (exp. 3.57 eV)	
a'	$H_2C\overset{1.33}{=\!=\!=}C\overset{O}{\underset{H}{\diagup}}{}^{1.39}$ A,1^2A' 0.5 eV (exp. 0.99 eV)	$H_2C\overset{1.34}{=\!=\!=}C\overset{H\diagdown O}{\underset{H}{\diagup}}{}^{1.36}$ Vinyl Alcohol (Ref. 22)

Fig. 3. Resonance structures and the lowest three electronic states of the CH_2CHO radical. Bond lengths for the related molecules acetaldehyde and vinyl alcohol are shown for comparison.

4. CH₂CHO yields

The term "yield" is used here to designate the number of CH_2CHO molecules formed per oxygen or excited mercury atom, *i.e.* the fractional contribution of all reaction paths forming CH_2CHO to the overall reaction. For the oxygen atom—olefin reactions this was measured by comparing the CH_2CHO absorption signal at 347.7 nm with the signal obtained from reaction (5) under identical conditions of modulated photolysis. Yields are based on that of reaction (5) being 1.0 [17]. Corrections were made for some quenching of $Hg(^3P_1)$ by the olefin. The results are summarized in Fig. 4. With ethylene and 1-butene the yields were 0.36 ± 0.04 and 0.17 ± 0.02 respectively, independent of pressure in the 40 - 760 Torr pressure range. With propene the yield increased with decreasing pressure, starting near the 1-butene value at 760 Torr and approaching the value for ethylene at 40 Torr.

In a similar manner we measured CH_2CHO yields for the mercury-photosensitized reaction of ethylene oxide, which is related to the O + C_2H_4 reaction [4]. The measurements were made at 1249 nm to circumvent the interference of some HgH absorption at 347.7 nm. A CH_2CHO yield of 0.7 ± 0.1, independent of total pressure from 80 to 760 Torr, was observed. Only a small fraction of this yield, if any, is contributed by the abstraction reaction path forming HgH. We noted another minor channel in the mercury-photosensitized reaction of ethylene oxide: excited complex emission, which we observed in the wavelength region where it is known to occur for ethers and alcohols [23].

CH_2CHO was also observed at 347.7 nm in the mercury-photosensitized reaction of propene oxide, and its yield was roughly estimated to be 0.2 - 0.3. A
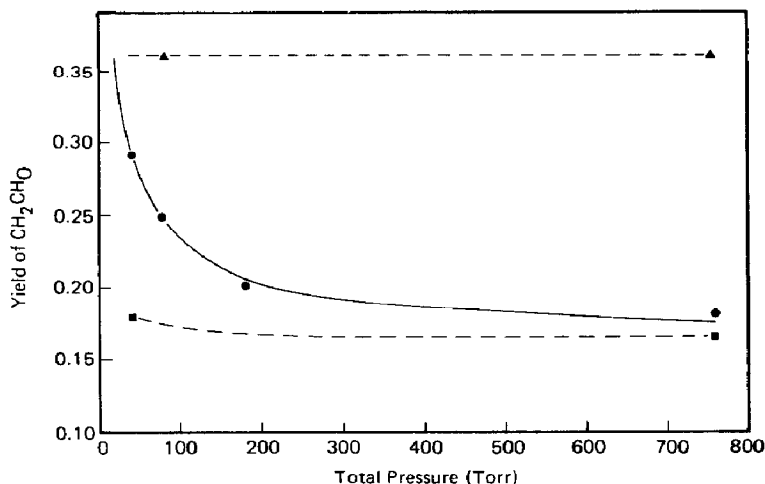
Fig. 4. The yield of CH_2CHO per oxygen atom as a function of total pressure for the oxygen atom reactions of ethylene, propene and 1-butene: ——, calculated with rate parameters which fit the propene oxide stabilization data in ref. 12; ▲, $O + C_2H_4$; ●, $O + C_3H_6$; ■, $O + C_4H_8$.

survey of the mercury-photosensitized reactions of acetaldehyde and propionaldehyde showed no formation of CH_2CHO, as expected.

5. HCO yields

In the $O + C_2H_4$ reaction we measured the yield of HCO in order to assess independently the importance of reaction path (1a). For this purpose the mercury-photosensitized decomposition of acetaldehyde

$$Hg(^3P_1) + CH_3CHO \rightarrow CH_3 + HCO + Hg(^1S_0) \tag{6}$$
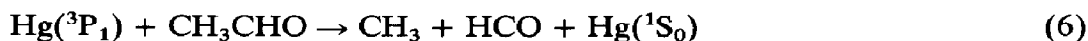
was used as a unit yield reference reaction for HCO [24], whose absorption was measured at 563.2 nm (2_0^{11} band). By comparing the absorption from the oxygen atom and reference reactions, the yields were determined to be 0.58 and 0.52 ± 0.06 at 80 Torr and 760 Torr total pressure respectively. These values can be checked in the following way. If we accept the 0.05 yield for path (1c), as determined by mass spectrometry [5, 6], and allow for a yield of 0.1 or less of stabilized CH_3CHO in path (1a) at 760 Torr [25], the fractional yields of paths (1a), (1b) and (1c) add up to unity at both pressures within the limits of error.

6. Discussion

6.1. Final product distribution

For the reaction $O + C_2H_4$ we can make a rough estimate of the final products expected from the radicals formed in the major reaction paths (1a) and (1b). We assume the relation $k_{ij} = (k_{ii}k_{jj})^{1/2}$ for the rate constant of radical i reacting

with radical j, and for each such reaction we account only for the major products, those of either recombination or disproportionation. The product yields are then given by

$$Y_{ij} = \frac{y_i \nu_j}{1 + \delta_{ij}} \sum_{n=1}^{4} y_n$$

regardless of the values of the k_{ii}. The y_i are the yields of radicals CH_3, HCO, C_2H_5 and CH_2CHO. Hydrogen atoms are immediately converted to C_2H_5 by reaction with C_2H_4. The final product yields thus derived are compared in Table 1 with Cvetanovic's observations [14]. Agreement is good, considering the approximations used. The extra consumption of C_2H_4 is seen to be due to hydrogen atoms produced in reaction path (1b) and not to hydrogen atoms coming from the decomposition of HCO.

Our results for the oxygen atom reactions of propene and 1-butene show that two of Cvetanovic's rules [1] must be modified. First, pressure-independent fragmentation does occur with terminal olefins and amounts to 15% - 20% in the intermediate pressure range for the olefins investigated here. This includes only loss of the alkyl group; loss of a hydrogen atom may also take place but was not measured in our experiments. Secondly, attack of the more substituted carbon does occur, but in view of the final products observed [12] it appears to lead predominantly to pressure-independent fragmentation.

6.2. Pressure dependence

From the results of Lee and coworkers [8] and those of Luntz and Kleinermans [10], it appears that the addition complex mechanism is pressure induced, but our experiments did not cover the low pressure range where this would become evident. Instead we observed the decomposition or the stabilization of the complexes which were formed with the aid of collisions. In this respect the results shown in Fig. 4 are complementary to Cvetanovic's observations for the stabilization of epoxides and aldehydes in the same pressure range (no stabilization with ethylene, complete stabilization with 1-butene and intermediate be-

TABLE 1

The final product yields for the $O + C_2H_4$ reaction, calculated from the yields of primary radicals determined in this work and compared with those actually observed

Reactants consumed							
$O(^3P)$	C_2H_4						
1.0	1.38	Ref. 14					
1.0	1.36	This work					
Products formed							
CO	CH_4	C_2H_6	C_3H_8	CH_3CHO	C_2H_5CHO	C_3H_7CHO	
0.50	0.11	0.17	0.17	0.15	0.20	0.05	Ref. 14
0.49	0.18	0.20	0.11	0.11	0.11	0.06	This work

Yields are expressed relative to the amount of $O(^3P)$ consumed.

havior, *i.e.* pronounced pressure dependence, for propene) [12]. It thus appears that there are two reaction paths forming CH_2CHO: a pressure-independent component which is responsible for the asymptotic high pressure yields of 0.17 and 0.19 with 1-butene and propene and a pressure-dependent component which is evident for propene and may also be present with ethylene. Since aldehydes do not decompose to give CH_2CHO, the precursor for CH_2CHO must be a biradical or a hot epoxide molecule.

To test this hypothesis, the two-step decomposition–stabilization mechanism for propene oxide established by Cvetanovic [12] was used to calculate the CH_2CHO yields, assuming that CH_2CHO is the decomposition product of the first step. It was found that, with decomposition-to-stabilization ratios k_d/k_s of 27 Torr for the first step and 85 Torr for the second step, both Cvetanovic's propene oxide stabilization data [12] and the pressure-dependent part of the CH_2CHO yield could be fitted simultaneously. The latter fit is represented by the full curve in Fig. 4. The decomposition product of the second step is probably acetaldehyde.

Another indication that biradicals or hot epoxides are a source of CH_2CHO is provided by the CH_2CHO yields observed in the mercury-photosensitized decomposition of ethylene oxide and propene oxide. The former process has been noted to resemble the $O + C_2H_4$ reaction in its final product distribution [4]. Presumably this is due to the fact that in both reactions the CH_2–CH_2–O diradical is an initial intermediate, albeit with different energy content. The high CH_2CHO yield observed in the sensitized ethylene oxide decomposition suggests, by analogy with the propene case, that part of the CH_2CHO we observed in the $O + C_2H_4$ reaction may be formed via an addition complex mechanism which is collision induced.

6.3. Mechanism

From the observations known to date a picture emerges which is consistent with Cvetanovic's scheme [1] to the extent outlined in Section 1. His pressure-independent fragmentation process corresponds to a direct reaction which operates in the absence of collisions and persists, without pressure effects, to at least 1 atm. The addition complex mechanism, which leads to epoxides, aldehydes, ketones and their fragments, is collision induced but saturates already at low pressures (below the 40 Torr lower limit of our experiments). This strikingly different behavior of the two reaction types is hard to reconcile with Cvetanovic's proposal that the same diradical is the primary intermediate in both cases. A possible solution of this problem has been independently suggested by Dupuis [20] and Luntz [26] and can be substantiated with our spectroscopy results for CH_2CHO. It takes into account that there are two different types of electronic states of the initial triplet diradical which cannot be interconverted by internal rotation around the original C=C bond. (For a discussion of diradical states see ref. 27. The (σ,σ) and (σ,π) states are easily converted to the states discussed here by internal rotation.) In Fig. 5 these states are shown for CH_2–CH_2–O in a geometry which is close to the transition state for loss of a hydrogen atom [20]. If the hydrogen atom is expelled, the CH_2CHO fragment is left in the X,1 $^2A''$ state when formed from

the (π,π) diradical but in the first excited A,1 ^{2}A' state when formed from the (π,σ) diradical.

The consequences of this are illustrated in Fig. 6 in a schematic potential energy diagram for the H + C_2H_4 reaction. It can be seen that the triplet diradical of configuration (π,σ) is trapped, since the A–X electronic energy difference in CH_2CHO is 23 kcal mol^{-1} and the shift of a hydrogen atom to give triplet acetaldehyde requires a high activation energy which Dupuis [20] has estimated to be 50 kcal mol^{-1}. In the absence of collisions this diradical will thus redissociate
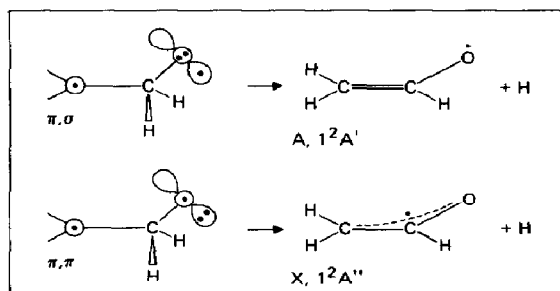

Fig. 5. Adiabatic dissociation pathways for the (π,σ) and (π,π) configurations of the CH_2–CH_2–O diradical. The structure of the diradical is drawn to represent approximately the transition state.
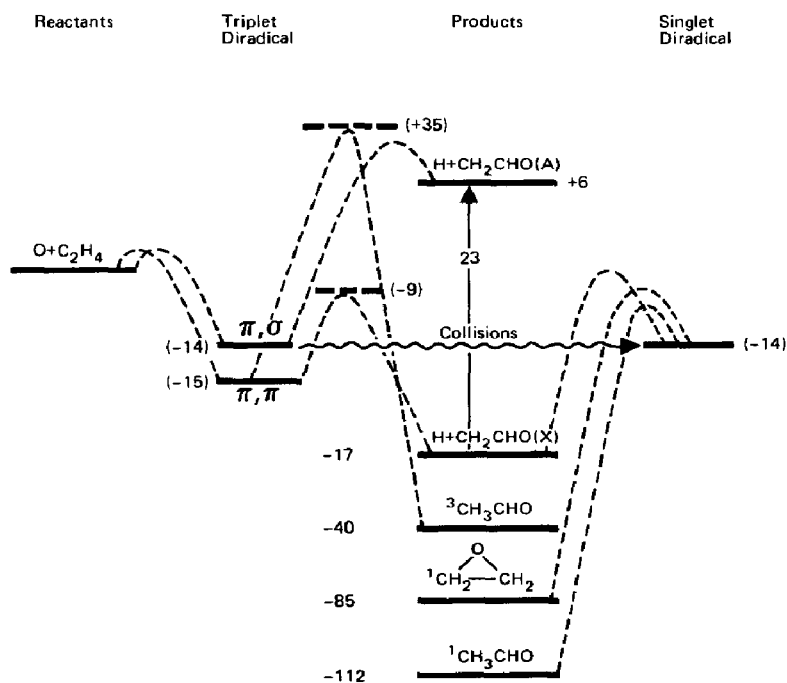

Fig. 6. A schematic potential energy diagram (not to scale) for the O + C_2H_4 reaction. Energy levels, in kilocalories per mole, are given relative to O + C_2H_4. Values in parentheses have been obtained by *ab initio* MCSCF calculations [20].

to O + C_2H_4. With collisions it can be converted into an isoenergetic singlet diradical which now has low activation energy pathways available to give hot ground state epoxide and aldehyde as well as H + $CH_2CHO(X,1\ ^2A'')$. The trapped diradical must have a relatively long unimolecular lifetime for this mechanism to be consistent with experiment. For the (π,π) triplet diradical, one pathway is open in the absence of collisions, *i.e.* fragmentation into H + CH_2CHO. This is the reaction channel observed in the molecular beam experiments.

Among the predictions which can be made on the basis of this mechanism is an increase in pressure-independent fragmentation with temperature or reactant kinetic energy. Such an effect has actually been noted by Cvetanovic [1]. It would be interesting to test whether the activated process forms $CH_2CHO(A,1\ ^2A')$ with ethylene, as anticipated. The mechanism also permits somewhat different energy thresholds for the direct fragmentation and addition processes, as observed by Luntz and Kleinermans [10]. Another point which needs to be investigated is the fall-off with decreasing pressure of the collision-induced addition process. In several early studies no marked pressure variation of the total rate of the O + C_2H_4 reaction in the 0.25 - 20 Torr pressure range was found [28]. However, from what is known now the fall-off must occur somewhere between the conditions at 40 Torr and the collision-free conditions of the molecular beam experiments.

Acknowledgments

References

1 R.J. Cvetanovic, *Adv. Photochem.*, *1* (1963) 115.
2 R.E. Huie and J.T. Herron, in R.K. Jennings and R.B. Cundall (eds.), *Progress in Reaction Kinetics*, Vol. 8, Pergamon, Oxford, 1978 p. 1.
3 M.C. Lin, in K.P. Lawley (ed.), *Potential Energy Surfaces*, Wiley, New York, 1980, p. 136.
4 R.J. Cvetanovic, *Can. J. Chem.*, *33* (1955) 1684.
5 J.R. Kanofsky and D. Gutman, *Chem. Phys. Lett.*, *15* (1972) 236.
   J.R. Kanofsky, D. Lucas and D. Gutman, *Proc. 14th Int. Symp. on Combustion, 1972*, Combustion Institute, 1973, p. 285.
   F.J. Pruss, I.R. Slagle and D. Gutman, *J. Phys. Chem.*, *78* (1974) 663.
6 B. Blumenberg, K. Hoyerman and R. Sievert, *Proc. 16th Int. Symp. on Combustion, 1976*, Combustion Institute, 1977, p. 841.
7 K.O. MacFadden and C.L. Currie, *J. Chem. Phys.*, *58* (1973) 1213.
8 Y.T. Lee, *14th Informal Conf. on Photochemistry, Newport Beach, CA, April 1980*.
   R.J. Buss, R.J. Baseman, G. He and Y.T. Lee, *J. Photochem.*, *17* (1981) 389.
9 G. Inoue and H. Akimoto, *J. Chem. Phys.*, *74* (1981) 425.
10 A. Luntz and K. Kleinermans, *J. Phys. Chem.*, *85* (1981) 1966.
11 J.T. Herron and R.F. Huie, *J. Phys. Chem. Ref. Data*, *2* (1973) 467.
12 R.J. Cvetanovic, *Can. J. Chem.*, *36* (1958) 623.

13 R.J. Cvetanovic, *J. Chem. Phys., 23* (1955) 1203.
14 R.J. Cvetanovic, *J. Chem. Phys., 23* (1955) 1375.
15 R. Atkinson and R.J. Cvetanovic, *J. Chem. Phys., 55* (1971) 659.
16 H.E. Hunziker, *IBM J. Res. Dev., 15* (1971) 10.
17 R.V. Morris and S.V. Filseth, *Can. J. Chem., 48* (1970) 924.
18 E. Murad, *J. Am. Chem. Soc., 83* (1961) 1327.
19 Unpublished result cited by J.M. Brown, *J. Mol. Spectrosc., 31* (1969) 118.
20 M. Dupuis, NRCC, Lawrence Radiation Laboratory, University of California, Berkeley, CA, personal communication.
21 G. Herzberg, *Molecular Spectra and Molecular Structure,* Vol. 3, Van Nostrand, New York, 1966, p. 643.
22 W.J. Bouma and L. Radom, *J. Mol. Struct., 43* (1978) 267.
23 O.P. Strausz, J.M. Campbell, S. De Paoli, H.S. Sandhu and H.E. Gunning, *J. Am. Chem. Soc., 95* (1973) 732.
24 F.P. Lossing, *Can. J. Chem., 35* (1957) 305.
25 M. Eusuf and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem., 76* (1972) 437.
26 A. Luntz, IBM Research Laboratory, San Jose, CA, personal communication.
27 K. Yamaguchi, S. Yabushita, T. Fueno, S. Kato and K. Morokuma, *Chem. Phys. Lett., 70* (1980) 27.
28 L. Elias and H.I. Schiff, *Can. J. Chem., 38* (1960) 1657.
    J.M. Brown and B.A. Thrush, *Trans. Faraday Soc., 63* (1967) 630.
    F. Stuhl and H. Niki, *J. Chem. Phys., 57* (1972) 5403.