The Arrhenius Parameters for the Reactions of O Atoms with Ethene and Five Fluoroethenes

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The rate constants for the reactions of ground-state oxygen atoms with ethene and five fluoroethenes have been measured over the temperature range of 240—450 K, using a pulse radiolysis-resonance absorption technique. The rate constants were well expressed by the following Arrhenius expressions: $k(O+C_2H_4)=8.4\times10^6\exp(-712/T)$; $k(O+C_2H_3F)=3.1\times10^6\exp(-622/T)$; $k(O+CH_2=CF_2)=2.4\times10^6\exp(-638/T)$; $k(O+cis\text{-}CHF=CHF)=1.9\times10^6\exp(-500/T)$; $k(O+C_2HF_3)=3.0\times10^6\exp(-544/T)$; $k(O+C_2F_4)=8.1\times10^6\exp(-634/T)$, in units of $m^3mol^{-1}s^{-1}$. The change in the preexponential factors with the degree of fluorination is discussed in terms of the conventional transition-state theory.

The temperature dependence of the rate constant for the reactions of ground-state oxygen atoms with simple olefins has been widely investigated over the last two decades.[1] Especially, the rate constants for ethene have been measured extensively.[2-10] On the other hand, only a limited number of data are available for the reactions of O(^{3}P) with fluoroethenes.[11-19] The room-temperature rate constants for the reactions of O(^{3}P) with fluoroethenes have been measured by several groups, including the members of our laboratory.[12-19] It has been found that the rate constants do not change monotonously with the number of the substituted fluorine atoms.[12,14] Ethene and tetrafluoroethene are more reactive than the others, while difluoroethene has the lowest reactivity. According to the competitive experiments by Jones and Moss,[12] this change in reaction rate is due to the change in activation energies. However, their conclusion is based only on the rate measurements at two temperatures, 298 and 423 K. It is hard, we believe, to estimate the Arrhenius parameters from only two points of data. In order to make it clear if the change in the room-temperature rate constants is due to the change in the preexponential factors or to that in the activation energies, we measured the temperature dependence of the rate constants for the reactions of O(^{3}P) with ethene and five fluoroethenes.

Experimental

The experimental apparatus and the procedure were similar to those described previously.[20-22] Briefly, a mixture of CO_2 (70—140 Pa) and ethene or fluoroethenes (7—31 Pa) diluted with excess Ar (90 kPa) was irradiated with an electron pulse generated by a Febetron 706 (Hewlett Packard Co.). Oxygen molecules were not used as the O-atom source, since O_2 molecules are reactive to O atoms and disturb the estimation of the rate constants.[21] After the pulse, the concentration of the ground-state oxygen atoms was monitored by the light absorption of resonance triplet lines around 130 nm. As the source of the resonance radiation of oxygen atoms, a microwave-powered lamp with a flow of He and a trace amount of O_2 was used. Ar (Jonan Kyodo Sanso), He (Japan Helium Center), and O_2 (Nihon Sanso) were used from cylinders without further purification. The sources of the other materials were: Takachiho Kako: CO_2 and C_2H_4, Daikin Co.: C_2H_3F and C_2HF_3, Japan Halon Co.: $CH_2=CF_2$, and PCR: *cis*-CHF=CHF. The C_2F_4 was prepared by the thermal decomposition of Teflon. These gases were used after purification through several freeze-thaw cycles. The purity of the C_2H_4, C_2H_3F, and C_2HF_3 has been checked in a previous work.[14] The purity of the $CH_2=CF_2$, *cis*-CHF=CHF, and C_2F_4 was checked mass-spectroscopically. There was no detectable impurity, except that C_2F_4 contained about 1% of C_3F_6, which is much less reactive than C_2F_4.[11]

Results

The first-order rate constants were determined by a procedure similar to that described in previous papers.[21,22] Although the room-temperature rate constant for O+C_2H_4 did not change systematically with the partial pressure of C_2H_4 over 15 Pa, it did increase with the decrease in the partial pressure of ethene below 12 Pa. Similar results have also been reported by Sugawara *et al.*[21] This increase in the apparent rate constant has been considered to be the result of secondary processes, such as reactions between O atoms and the CH_3 radicals formed in the reaction of O and C_2H_4.[21] Such secondary reactions seem less important in the cases of O+fluoroethenes. For example, in the case of C_2HF_3, no increase in the apparent rate constants could be observed at pressures higher than 7 Pa at 295 K. In general, secondary reactions are considered to become more important at low temperatures. Therefore, at low temperatures, more attention was paid and the experiments were performed with partial pressures of over 21 Pa. Although the scatter of the data was more severe at low temperatures, no systematic partial pressure dependence of the rate constants could be observed. The rate constants at each temperature are summarized in Table 1 and plotted in Fig. 1 in the form of Arrhenius plots. All the data are well characterized by Arrhenius equations. The Arrhenius parameters, as determined by the least-squares method, are listed in Table 2.

Discussion

Comparison with Literature Values. A number of measurements have been performed on the temperature dependence for the reaction of atomic oxygen with

TABLE 1. RATE CONSTANTS OF O-ATOM ADDITION TO ETHENE AND FLUOROETHENES. UNCERTAINTIES ARE STANDARD DEVIATIONS

Reactant	T/K	$k_r \times 10^{-6}$/m^3 mol^{-1} s^{-1}
C_2H_4	454	1.68±0.28
	375	1.29±0.12
	330	0.99±0.11
	296	0.70±0.11
	270	0.54±0.13
	239	0.46±0.09
C_2H_3F	452	0.76±0.10
	369	0.58±0.05
	325	0.44±0.04
	297	0.39±0.04
	266	0.30±0.05
	240	0.23±0.04
$CH_2=CF_2$	446	0.59±0.03
	375	0.43±0.01
	322	0.31±0.02
	293	0.26±0.03
	268	0.22±0.01
	241	0.17±0.01
cis-CHF=CHF	448	0.64±0.06
	376	0.54±0.06
	333	0.41±0.03
	297	0.37±0.07
	273	0.31±0.03
	243	0.26±0.04
C_2HF_3	454	0.91±0.09
	387	0.73±0.12
	322	0.57±0.09
	295	0.46±0.07
	266	0.38±0.04
	241	0.32±0.03
C_2F_4	446	1.91±0.18
	375	1.52±0.12
	325	1.16±0.02
	296	0.91±0.10
	265	0.70±0.09
	243	0.63±0.10

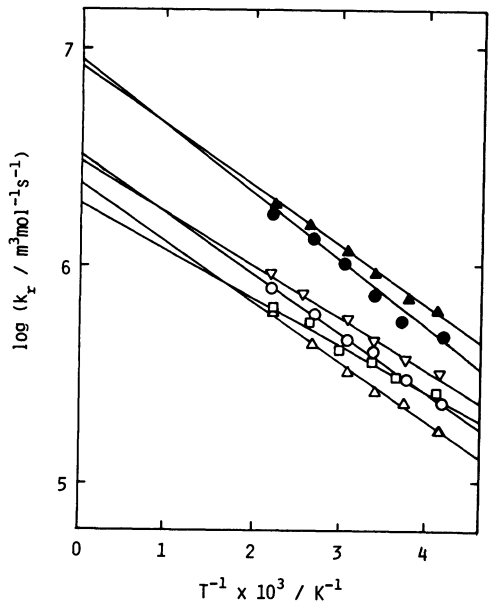

Fig. 1. Arrhenius plots for O+C_2H_4 (●), O+C_2H_3F (○), O+$CH_2=CF_2$ (△), O+*cis*-CHF=CHF (□), O+C_2HF_3 (▽), and O+C_2H_4 (▲).

TABLE 2. ARRHENIUS PARAMETERS FOR THE REACTIONS OF O ATOMS WITH ETHENE AND FLUOROETHENES. UNCERTAINTIES ARE STANDARD DEVIATIONS

Reactants	$A \times 10^{-6}$/m^3 mol^{-1} s^{-1}	E/kJ mol^{-1}
C_2H_4	8.40±1.25	5.92±0.41
C_2H_3F	3.06±0.23	5.17±0.21
$CH_2=CF_2$	2.36±0.14	5.30±0.17
cis-CHF=CHF	1.92±0.25	4.15±0.35
C_2HF_3	3.00±0.15	4.53±0.12
C_2F_4	8.13±0.67	5.27±0.24

C_2H_4. The Arrhenius parameters previously obtained for this reaction are summarized in Table 3. The agreement among the activation energies is rather good. However, the agreement among the preexponential factors is rather poor. The present value of the preexponential factor seems to be a little large, but this discrepancy is not considered to be serious, since these values were all obtained by extrapolation.

The room-temperature rate constants for ethene and fluoroethenes are listed in Table 4. Unfortunately, for $CH_2=CF_2$ and C_2F_4 there is some disagreement between the present values and those of Sugawara *et al.*, who used the same technique and the same apparatus.[14] The only difference is that they used a He/O_2 mixture as the O atom source, while we used Ar/CO_2. Since O atoms react with O_2, Sugawara *et al.* had to correct their data to estimate the reaction rates. The rate for the O+O_2 reaction under the conditions of Sugawara *et al.* was comparable to or larger than the rates for the O+fluoroethenes reactions. This may be the cause of the discrepancy. Apart from the values of Sugawara *et al.*, the present values seem to be a little larger than those obtained with different techniques. This cannot be accounted for by secondary reactions, as has been discussed in detail in a previous paper, since no partial-pressure dependence could be observed.[21] Figure 2 compares the Arrhenius plot obtained by Atkinson and Pitts for C_2H_3F[13] and the present one. The rate constants obtained in this work are larger than those of Atkinson and Pitts by a factor of 2. The cause of this discrepancy is not certain. Figure 2 also shows the results of the competitive work by Jones and Moss.[12] Since their values are relative ones, they were placed on an absolute basis using the rate constants for ethene determined in the present work.

Effect of the Substitution by F Atoms on the Arrhenius Parameters. As is shown in Table 2, the activation energies do not change greatly with the number of substituted fluorine atoms. This is not unexpected since the ionization potentials of ethene and fluoroethenes are not very different.[23] It is now well established that there is a good correlation between the activation energies and the ionization potentials in the reactions of O(^{3}P) with alkenes and alkynes.[24] On the other hand, the preexponential factors change by a factor of 4. It should also be noted that this factor first decreases upon fluorine substitution, and then increases again, so that the values for ethene and tetrafluoro-

TABLE 3. ARRHENIUS PARAMETERS FOR THE REACTION OF O WITH C_2H_4

Author(Ref.)	Method[a]	T/K	$A\times10^{-6}$/m^3 mol^{-1} s^{-1}	E/kJ mol^{-1}
Elias(2)	DF-CL	223—465	10.8±3.6	6.7±0.8
Elias(3)	DF-CL	223—613	8.4	6.7
Westenberg(4)	DF-ESR	195—715	5.0	6.3[b]
Davis(5)	FP-RF	232—500	3.3±0.2	4.7±0.1
Atkinson(6)	HgS-CL-PS	301—392	3.4	5.3±0.8
Singleton(7)	HgS-CL-PS	298—486	7.0±0.9	7.0±0.4
Atkinson(8)	FP-CL	298—439	5.6	6.2±0.8
Nicovich(9)	FP-RF	298—944	7.3±3.7	7.2±1.6[c]
Perry(10)	LP-CL	294—820	6.5±0.3	6.5±0.1[d]
This work	PR-RA	239—454	8.4±1.2	5.9±0.4

a) DF: discharge flow; CL: chemiluminescence; ESR: electron-spin resonance; FP: flash photolysis; RF: resonance fluorescence; HgS: Hg-photosensitization; PS: phase-shift; LP: laser photolysis; PR: pulse radiolysis; RA: resonance absorption. b) Deduced from the data between 226 K and 381 K, because of the nonlinearity in the Arrhenius plot at high temperatures. c) Deduced from the data between 298 K and 438 K. d) Deduced from the data between 294 K and 445 K.

TABLE 4. ROOM-TEMPERATURE RATE CONSTANTS FOR THE REACTIONS OF O ATOMS WITH ETHENE AND FLUOROETHENES IN UNITS OF 10^5 m^3 mol^{-1} s^{-1}

Author(Ref.)	Method[a]	C_2H_4	C_2H_3F	CH_2=CF_2	*cis*-CHF=CHF	C_2HF_3	C_2F_4
Jones(12)[b]	PA	(1.00)	(0.41)	(0.22)	(0.31)	(0.57)	(1.70)
Huie(15)	DF-MS	5.1[c]	2.6	2.2			
Atkinson(16)	HgS-CL-PS	4.0[d]	1.6				
Atkinson(13)	FP-CL	4.6[e]	1.6				
Gutman(17)	DF-MS	4.8[f]	2.1[f]	1.9	2.2	5.0	
Koda(19)	HgS-CL	4.3				1.9	4.3
Sugawara(14)	PR-RA	6.0	3.1	1.2		3.8	4.9
this work	PR-RA	7.0	3.9	2.6	3.7	4.6	9.1
this work[b]		(1.00)	(0.56)	(0.37)	(0.53)	(0.66)	(1.30)

a) PA: product analysis; MS: mass spectroscopy; for other abbreviations, see Table 3. b) Relative values. c) Ref. 5. d) Ref. 6. e) Ref. 8. f) Ref. 18.

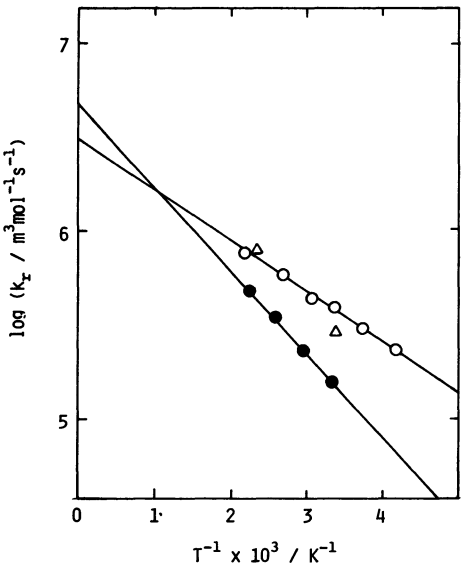

Fig. 2. Arrhenius plot for O+C_2HF_3 reaction; ●: Atikinson and Pitts, △: Jones and Moss, and ○: this work. Values of Jones and Moss were placed on an absolute basis using the present results for ethene.

ethene are nearly the same. Sugawara *et al.* tried to interpret the change in the room-temperature rate constants in terms of "approachability," the reactivity index calculated by the INDO method.[14] However, approachability is a conception correlated to the activation energy and cannot be employed to explain the change in the preexponential factors. Any correlation between the approachability and the room-temperature rate constants must be fortuitous.

The temperature dependence of the rate constant for the O+C_2H_4 reaction, including the nonlinearity in the Arrhenius plot at high temperatures, has been successfully explained by the conventional transition-state theory.[7,10] According to this theory, the rate constant is expressed by:

$$k_r = \kappa L \frac{kT}{h} \frac{F_t^{\dagger}}{F_t^{O} F_t^{R}} \frac{f_r^{\dagger}}{f_r^{R}} \frac{f_v^{\dagger}}{f_v^{R}} \frac{f_e^{\dagger}}{f_e^{O}} \exp(-E/kT). \quad (1)$$

Here, the symbols have their ordinary meanings; κ is the transmission coefficient, L is the path degeneracy, and F_t, f_r, f_v, and f_e are the translational, rotational, vibrational, and electronic partition functions respectively. Symmetry numbers are not included in the rotational partition functions. The superscripts, O, R, and †, are used to designate O atoms, reactant molecules (ethene or fluoroethene), and the transition states respectively. If we restrict the present discussion to the relative values of the rate constants, the common terms for all reactions of O+ethene or fluoroethenes, such as the partition functions for O atoms, may not be taken into account. The electronic states of the transition states are correlated to the spin-orbit states of the O(^3P_J) atoms. Since the spin-orbit splittings of the O(^3P_J) atoms are small, 1.89 and 0.82 kJ/mol, it can be assum-

ed that the energy separations of the electronic states of the transition states are small and that the electronic partition functions, $f_e^{\ddagger}$, are almost the same. Singleton and Cvetanović have postulated that, in the reaction of $O(^3P)$ with aliphatic olefins, the two new vibrations of the bending mode of the transition state are harmonic and have equal frequencies, ν, and that the partition functions for all the other vibrations in the transition state and the reactant cancel each other out.[7] If we employ this assumption, the temperature-dependent preexponential term in Eq. 1, A_T according to the notation of Singleton and Cvetanović,[7] can be written as:

$$A_T = C\kappa L\left[\frac{m^{\ddagger}}{m^{R}}\right]^{3/2}\left[\frac{I^{\ddagger}}{I^{R}}\right]^{1/2} T^{-1/2}\{1-\exp(-h\nu/kT)\}^{-2}. \quad (2)$$

Here, C is a constant independent of the nature of the reactant or the temperature, while m and I stand for the masses and the products of the three principal moments of inertia of the reactant or the transition state. The superscripts have the same meanings as in Eq. 1. The value of ν in Eq. 2 for ethene has been estimated by Singleton and Cvetanović[7] and by Perry[10] to be between 100 and 300 cm^{-1}, judging from the curvature in the Arrhenius plot. Substituting these values, it can easily be shown that the temperature dependence of the preexponential factor cannot be ignored compared to that of the exponential term. Since the experimentally obtained A factors listed in Table 2 are deduced under the assumption that the rate constants can be characterized by a simple Arrhenius equation, $k_r=A\exp(-E/kT)$, it is not fair to compare the values in Table 2 with those calculated by Eq. 2 at a certain temperature. Therefore, we re-analyzed the present results using the following equation:

$$k_r = A'T^{-1/2}\{1-\exp(-h\nu/kT)\}^{-2}\exp(-E/kT). \quad (3)$$

Here, A' is the temperature independent part of the preexponential factor:

$$A' = C\kappa L\left[\frac{m^{\ddagger}}{m^{R}}\right]^{3/2}\left[\frac{I^{\ddagger}}{I^{R}}\right]^{1/2}. \quad (4)$$

In order to estimate the magnitude of A' from the experimental results, it is necessary to know the value of ν. It was impossible, however, to determine the three parameters, A', ν, and E, uniquely from the present data alone. For the first step, we assumed that ν is independent of the degree of fluorination; we used the value for ethene determined by Singleton and Cvetanović and by Perry, between 100 and 300 cm^{-1}. The present experimental results could also be well characterized by Eq. 3 under such assumptions, and it was found that the relative values of A' are essentially the same as those of A listed in Table 2. The value of $(m^{\ddagger}/m^{R})^{3/2}$, can easily be calculated. The results are shown in Table 5. In order to calculate the ratio of the rotational partition functions, $(I^{\ddagger}/I^{R})^{1/2}$, it is necessary to know the geometry of the reactant molecule and the transition state. The structural parameters for the ground-state fluoroethene molecules have been determined experimentally by Carlos *et al.*[25] The geometry of the transition state of the C_2H_4O complex has been theoretically calculated,[26] but those of the fluoroethenes are not known. Therefore, for the first step, we assumed that the geometry of the intermediate complexes for all the fluoroethenes is analogous to that for ethene; *i.e.*, the C–O internuclear distance and the C–C–O angles are the same. The results are shown in Table 5. Both $(m^{\ddagger}/m^{R})^{3/2}$ and $(I^{\ddagger}/I^{R})^{1/2}$ decrease with the number of the substituted F atoms. As for C_2H_3F and $C_2H_2F_2$, the relative values of the products of $(m^{\ddagger}/m^{R})^{3/2}$ and $(I^{\ddagger}/I^{R})^{1/2}$ are comparable to the relative preexponential factors, A and A'. Therefore, the decrease in the preexponential factors from C_2H_4 to $C_2H_2F_2$ can be explained by assuming that the geometry of the transition states and the frequencies of the newly formed vibrations are similar for these reactants. However, it is difficult to explain the increase in the preexponential factors from $C_2H_2F_2$ to C_2F_4. In other words, it is hard to interpret why the preexponential factors for ethene and tetrafluoroethene are nearly the same under the assumptions that: 1) the geometries of the transition states are similar; 2) the newly formed vibrational frequencies of the transition states are the same, and 3) the transmission coefficients are the same. The identity of the A factors for C_2H_4 and C_2F_4 can not be accounted for by the change in the geometry of the transition states alone. For example, even if we assume

Table 5. Comparison of the relative A factors and the products of $(m^{\ddagger}/m^{R})^{3/2}$ and $(I^{\ddagger}/I^{R})^{1/2}$

Reactants	A or A'[a] (experimental)	$\left[\frac{m^{\ddagger}}{m^{R}}\right]^{3/2}$	$\left[\frac{I^{\ddagger}}{I^{R}}\right]^{1/2}$	$\left[\frac{m^{\ddagger}}{m^{R}}\right]^{3/2}\times\left[\frac{I^{\ddagger}}{I^{R}}\right]^{1/2}$[a]
C_2H_4	1.00	1.97	7.29	1.00
C_2H_3F	0.36	1.56	4.36	0.48
$CH_2{=}CF_2$	0.28	1.40	2.50	0.24
cis-CHF=CHF	0.23	1.40	2.59	0.25
C_2HF_3	0.36	1.31	1.94	0.18
C_2F_4	0.97	1.25	1.59	0.14
			2.98[b]	
			3.14[c]	

a) Values relative to that for ethene; the differences between A and A' are less than 5% when ν is a certain value between 100 and 300 cm^{-1}. b) Calculated by assuming that r(C–O) is twice as long as that for the transition state of C_2H_4O. c) Calculated by assuming that r(C–C) is twice as long as that for the transition state of C_2H_4O.

that the C–O or C–C internuclear distance of the transition state for C_2F_4 is twice as long as that for C_2H_4, the value of $(I^{\dagger}/I^{R})^{1/2}$ changes only by a factor of 2, as is shown in Table 5. The path degeneracy, L, must be 4 in both cases. Therefore, there remain only two possibilities. One is a change in κ; the other, one in ν. The present results for C_2H_4 and C_2F_4 can be explained if we assume that the degenerate vibrational frequencies of the bending mode of the transition states are 300 cm^{-1} and 110 cm^{-1} respectively. However, in this interpretation, it is necessary to assume that the vibrational frequencies of the transition states suddenly change from $C_2H_2F_2$ to C_2HF_3, which sounds unrealistic. The next problem is, then, to see if it is reasonable to assume that the values of κ for C_2HF_3 and C_2F_4 are larger than those for ethene or the other fluoroethenes. This will be discussed in the next section.

Detailed Mechanism of the Reaction. With regard to the change in κ, tunneling effects cannot be expected in the present cases, but the contribution of the reverse reaction from the intermediate diradical to its initial components may be expected. In the reaction of oxygen atoms with ethene, it is known that there are two main exit channels: the fragmentation into CH_2CHO+H and that into CH_3+HCO.[1,27] Under the beam conditions, only the CH_2CHO fragment could be detected,[28] while both could be detected in comparable yields under the bulk conditions.[27] In order to explain these experimental results, the following reaction mechanism was considered; it is similar to that proposed by Hunziker *et al.*:[27]

$$O + C_2H_4 \longrightarrow {}^3C_2H_4O^*, \quad (5)$$

$$O + C_2H_4 \rightleftarrows {}^3C_2H_4O^{**}, \quad (6)$$

$${}^3C_2H_4O^* \longrightarrow CH_2CHO + H, \quad (7)$$

$${}^3C_2H_4O^{**} + M \rightleftarrows {}^1C_2H_4O^* + M, \quad (8)$$

$${}^1C_2H_4O^* \longrightarrow CH_3 + HCO, \quad (9)$$

$${}^1C_2H_4O^* + M \longrightarrow C_2H_4O + M. \quad (10)$$

Here, ${}^3C_2H_4O^*$ and ${}^3C_2H_4O^{**}$ represent two different types of electronic states of the initial triplet diradicals, the (π,π) and (π,σ) states, following the nomenclature of Yamaguchi *et al.*[29] ${}^1C_2H_4O^*$ stands for the singlet-state diradical, which is isoenergetic to ${}^3C_2H_4O^{**}$. Although Hunziker *et al.* mention nothing about the precursor of CH_3 and HCO, this singlet state may be the precursor.[18] Now, if the rate for the reverse reaction of Reaction 6 is large enough compared to the rates for Reactions 9 and 10, the apparent value of κ will be less than unity. It is necessary to assume an equilibrium between the singlet and the triplet diradicals, Reaction 8, in order to explain the constancy of the yields of HCO at high pressures.[27] It should also be noted that the precursor of CH_3 and HCO may not necessarily be the singlet diradical. The important point in this discussion is that there must be a reverse reaction to reproduce atomic oxygen, even at high pressures. Gutman and his co-workers have studied the reactive routes for the O+fluoroethenes reactions by using mass-spectrometric detection.[17,18] They have found that the reactions for C_2H_4 and C_2H_3F do not proceed by C–C bond breakage, while those for C_2F_4 and C_2HF_3 appear to proceed exclusively by this route. This conclusion for C_2F_4 is consistent with the finding of other experimental work that the only exit channel is the decomposition to CF_2 and CF_2O:[19,30]

$$O + C_2F_4 \longrightarrow {}^3C_2F_4O^*, \quad (11)$$

$${}^3C_2F_4O^* \longrightarrow CF_2 + CF_2O. \quad (12)$$

Gorry *et al.* have shown that the triplet diradical, ${}^3C_2F_4O^*$, is very short-lived because of its great exoergicity and that it decomposes to $CF_2({}^3B_1)$ and CF_2O.[30] If the reverse reaction of Reaction 11 is minor, then the value of κ should be larger than that for the O+ethene reaction. The situation for C_2HF_3 must be similar to that for C_2F_4, while that for C_2H_3F must be similar to that for C_2H_4. As for the reactions of O+difluoroethenes, many reactive routes, including the C–C bond rupture, are possible, although the production of CH_2O and CF_2 from $O+CH_2=CF_2$ seems minor.[17] The present results imply that the values of κ for the reactions of O+difluoroethenes are similar to that for ethene. Therefore, if C–C bond rupture occurs in these cases, that process must be slow. Further experimental studies to determine the initial products of these reactions, as well as their yields, are to be desired.

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