ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 95 (1996) 197–202

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

F_2 laser (158 nm) photolysis of CO_2 and hydrofluorocarbon systems

Masanobu Kojima [a,*,1], Yuichi Ojima [b], Nobuaki Nakashima [b,*], Yasukazu Izawa [b],
Chiyoe Yamanaka [c], Tohoru Akano [d]

[a] *Faculty of Liberal Arts, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390, Japan*
[b] *Institute of Laser Engineering, Osaka University, 2-6 Yamada-Oka, Suita, Osaka 565, Japan*
[c] *Institute for Laser Technology, 2-6 Yamada-Oka, Suita, Osaka 565, Japan*
[d] *Kansai Electric Power Co., Nakoji, Amagasaki, Hyogo 676, Japan*

Received 17 March 1995; accepted 20 October 1995

Abstract

F_2 laser (158 nm) photolysis of gas mixtures of CO_2 and hydrofluorocarbons (HFCs) gives the corresponding alcohols and ketones. The initial step of photolysis is a bond breaking reaction to give CO and an electronically excited oxygen atom $O(^1D)$. The excited atom is partially inserted into the HFC C–H bonds and is partially quenched to the triplet atom $O(^3P)$. The dependence of the yields of the alcohols on the gas pressure and the size of the HFC can be explained in terms of the formation of hot alcohols and collisional relaxation. The insertion rate constant of $O(^1D)$ has been estimated to be $(1.5 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for $CF_3CF_2CH_3$ based on the quantum yield of $CF_3CF_2CH_2OH$ production.

Keywords: F_2 laser photolysis; CO_2–hydrofluorocarbon systems; Bond breaking reaction; Collisional relaxation

1. Introduction

The kinetics of the reaction between $O(^1D)$ and hydrofluorocarbons (HFCs) has been studied in relation to the depletion of the ozone layer in the stratosphere [1]. The basic reaction mechanism between $O(^1D)$ and hydrocarbons has been studied in detail in Ref. [2]. In the case of CH_4, two processes co-exist: the insertion of $O(^1D)$ into the C–H bonds and the stripping of H to form CH_3 and OH radicals [3–11]. Similar processes presumably explain the reactions of hydrocarbons and HFCs with $O(^1D)$. One of the initial steps is the insertion of $O(^1D)$ into the C–H bonds and the formation of hot alcohols. The product distribution depends on the collisional relaxation and lifetimes of the hot molecules. In the case of HFCs, $O(^1D)$ produces hot alcohols and is quenched. The branching ratio depends on the molecular structures of the HFCs. Warren et al. [12] have measured the removal rate constants of HFCs by $O(^1D)$, generated by O_3 photolysis using a 193 nm laser. The quenching rate constants of $O(^1D)$ were determined directly by measuring the $O(^3P)$ concentrations using the technique of time-resolved vacuum UV atomic fluorescence.

The reactions and quenching rates between $O(^1D)$ and HFCs have been analysed in this study on the basis of specific reaction products: alcohols. In a previous investigation [13], product analysis indicated that an $O(^1D)$ atom is inserted into the C–H bonds of CH_4, CF_3H and CF_3CH_3 molecules, and the product distribution can be explained in terms of the collisional relaxation of the initial products of hot alcohols.

$O(^1D)$ can be generated from many sources by UV–vacuum UV photolysis of simple molecules: O_3, O_2, N_2O and CO_2. CO_2 in particular is a good source, because the molar extinction coefficient (ϵ) in the vacuum UV region is not too low and one of the products, CO, is inactive. Direct vacuum UV photolysis of CO_2 has recently been carried out [14]. At the 158 nm laser line (where the HFC molecules treated show practically no absorption), the quantum yield of $O(^1D)$ formation is 0.94 and the remainder (0.06) is $O(^3P)$.

The photon number at the 158 nm laser line was measured by chemical actinometry and compared with a commercial laser power meter.

2. Experimental details

2.1. Materials and laser

Trifluoromethane (CHF_3; stated purity, 98% minimum), 1,1,1-trifluoroethane (CF_3CH_3; 99% minimum) and

---

* Corresponding authors.

[1] Present address: Faculty of Agriculture, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390, Japan.

1010-6030/96/$15.00
SSDI 1010-6030(95)04257-1

1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$; 97% minimum) were purchased from PCR, and CO_2 (99.995% minimum) was obtained from Sumitomo Seiki Co. The vacuum UV spectra of the gases used in this experiment were measured with an Acton Research Corporation VUVMS-502 spectrometer. The HFC molecules have practically no absorption at 158 nm; therefore CO_2 ($\epsilon = 63$ M^{-1} cm^{-1}) is selectively excited by light under the conditions described [15].

The excitation light source was an F_2 laser (Lambda Physik LPF205). The typical output was 60 mJ per pulse (after correction factor of 1.48 ± 0.08 for a Gentec ED500 power meter) with a pulse width of 20 ns full width at half-maximum (FWHM) and a repetition rate of 10 Hz.

2.2. *Photolysis of gas mixture of CO_2 and HFC*

The mixtures of CO_2 (100 Torr unless stated otherwise; 1 Torr = 133.322 Pa) and HFC (30–900 Torr) were photolysed at room temperature for 50 s, i.e. by 500 irradiation shots through an MgF_2 window. The sample cell had an inner diameter of 2 cm and was 8 cm in length. It was calculated that more than 99.8% of the incident laser energy was absorbed. The products were analysed using a Shimadzu GC-14A gas chromatograph equipped with a G-950 capillary column (40 m × 1.2 mm, Chemical Inspection & Testing Institute) and an FID to determine the concentration of alcohols. The concentration of CO was measured using a gas chromatograph with a WG-100 column (2 m, GL Science) and a TCD.

3. Results and discussion

3.1. *Photoproducts and their pressure dependence*

3.1.1. *CHF_3*

Irradiation of CO_2/CHF_3 (100 Torr/100 Torr) mixtures in the sample cell with a 158 nm laser gave carbonyl fluoride (COF_2) exclusively; trifluoromethanol (CF_3OH) and the dimeric product hexafluoroethane (CF_3CF_3) were not observed. This is in agreement with the work of Aker et al. [16a] and Burks and Lin [16b,c], in which only HF was observed in the reaction of CHF_3 with $O(^1D)$, generated by the UV photolysis of ozone, suggesting the formation of COF_2. (Recently, it has been reported that COF_2 is the dominant product in the reactions of $O(^1D)$ with $CBrF_3$ and $CBrF_2CBrF_2$ [16d].) The formation of COF_2 indicates that the initial product is CF_3OH, which is known to decompose rapidly to COF_2 and HF at room temperature [17]. However, it is interesting to note that the elimination of HF from thermalized CF_3OH is endothermic. Thus there is still an argument for the fragmentation process [18].

3.1.2. *CF_3CH_3*

Similar photolysis of CO_2/CF_3CH_3 mixtures produced 2,2,2-trifluoroethanol selectively, the yield of which increased linearly depending on the initial pressure of CF_3CH_3 (100–900 Torr) as shown in Fig. 1(a). In relation to this reaction, a study concerning the mechanism of HF formation from hot CF_3CH_2OH has been reported [16c]. Although a variety of minor products were detected by gas chromatography in the present reaction, it was not possible to identify them because, in most cases, authentic samples could not be obtained.

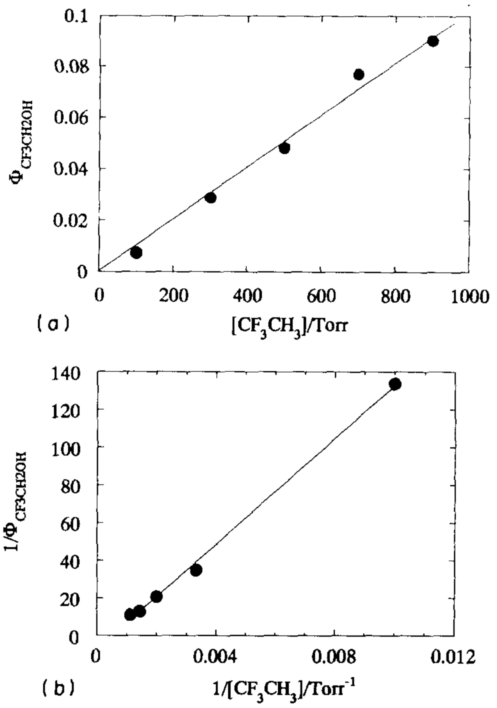

Fig. 1. (a) Effect of initial pressure of CF_3CH_3 on the quantum yield of production of CF_3CH_2OH during the photolysis of CO_2/CF_3CH_3 mixtures in the presence of 100 Torr of CO_2. (b) Plots of $1/\Phi_{CF_3CH_2OH}$ vs. $1/[CF_3CH_3]$.

3.1.3. *$CF_3CF_2CH_3$*

In the case of $CF_3CF_2CH_3$, the yield of 2,2,3,3,3-pentafluoropropanol ($CF_3CF_2CH_2OH$) increased almost linearly with an increase in the initial pressure of $CF_3CF_2CH_3$ up to 200 Torr. However, the yield became almost constant when the initial pressure was greater than approximately 500 Torr (Fig. 2(a)). Similar to the case of CF_3CH_3, several minor unknown products were observed by gas chromatography.

3.2. *Laser energy measurement and chemical actinometry*

Commercial power meters were compared with chemical actinometers at 193 and 248 nm [19] and at the excimer laser lines [20] and reasonable agreement was found between them. However, to date, no calibration of the 158 nm laser line has been made. The laser power evaluated in this paper was 1.48 ± 0.08 times the value indicated by a Gentec ED500 Joulemeter, as calibrated against results obtained by CO_2 chemical actinometry. The power meter gave a correct value at 193 nm.

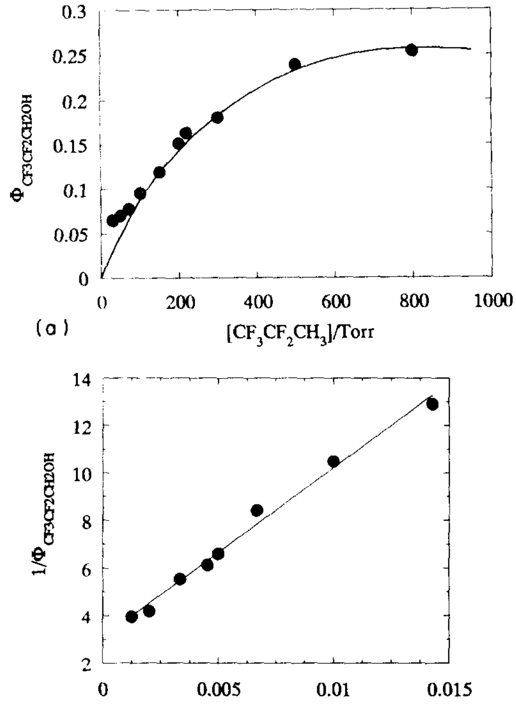

Fig. 2. (a) Effect of initial pressure of $CF_3CF_2CH_3$ on the quantum yield of production of $CF_3CF_2CH_2OH$ during the photolysis of $CO_2/CF_3CF_2CH_3$ mixtures in the presence of 100 Torr of CO_2. (b) Plots of $1/\Phi_{CF_3CF_2CH_2OH}$ vs. $1/[CF_3CF_2CH_3]$.

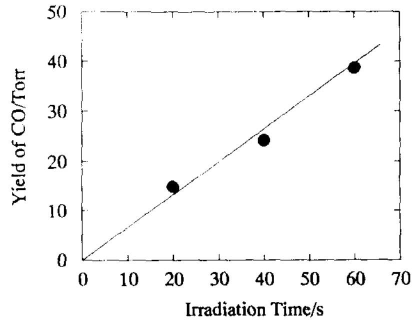

Fig. 3. Yield of CO produced during the photolysis of CO_2/CF_3CH_3 (300 Torr/300 Torr) mixtures vs. irradiation time.

3.2.1. CO_2 photolysis

The photochemistry of CO_2 at 158 nm was expected to correspond to Eq. (1) (see Section 3.3) [14]. When gas mixtures of CO_2/CF_3CH_3 (300 Torr/300 Torr) were photolysed for 20, 40 and 60 s, the CO pressure increased in proportion to the irradiation time as shown in Fig. 3. Although many different values for the quantum yield of formation of CO have been reported, we employed unity as the most reliable value, following the results reported by Slanger and Black [21], who explained that the CO deficiencies observed in earlier work on CO_2 photolysis were probably caused by heterogeneous processes. In the case of 50 s irradiation, the observed amount of CO was 32.5 Torr. Therefore the absorbed photon number was calculated to be 5.3×10^{17} photons s^{-1}, in other words 5.3×10^{16} photons per pulse (66.5 mJ per pulse) against the cell volume. A power meter (Gentec ED500) indicated 45 mJ per pulse after the light had passed through the MgF_2 window. The correction factor was 1.48 times the value indicated by the power meter.

3.3. Mechanism

The reaction mechanism between $O(^1D)$ and hydrocarbons has been established [2]. Although the same elemental processes are present in the reaction between $O(^1D)$ and HFCs, there are several distinctive features. $O(^1D)$ is quenched by HFC, the efficiency depending on the number of F atoms and the structure of the molecule [12,16a,22,23]. The intermediate state hot molecule will have a longer lifetime than that of the corresponding alcohols based on hydrocarbons. The bond dissociation energies of the C–C and C–F bonds for HFCs are higher than those of the corresponding alcohols. HF elimination will be one of the major fragmentation processes. Therefore the hot molecule probably undergoes a different pattern of fragmentation.

The following mechanism can be proposed

$$CO_2 \xrightarrow{158\ \text{nm}} CO + O(^1D\text{: }0.94,\ ^3P\text{: }0.06) \qquad (1)$$

$$O(^1D) \xrightarrow{k_q[RCH_3] + k_{q'}[CO_2]} O(^3P) \qquad (2)$$

$$RCH_3 + O(^1D) \xrightarrow{k_i} RCH_2OH^* \qquad (3)$$

$$RCH_3 + O(^1D) \xrightarrow{k_a} RCH_2 + OH \qquad (4)$$

$$RCH_2OH^* \xrightarrow{k_f} \text{Fragmentation} \qquad (5)$$

$$RCH_2OH^* + M \xrightarrow{k_{ROH}} RCH_2OH + M \qquad (6)$$

$$O(^3P) + O(^3P) \longrightarrow O_2 \qquad (7)$$

Photolysis of CO_2 with the 158 nm laser gives CO and $O(^1D)$ with quantum yields of unity and 0.94 respectively (Eq. (1)). In Eq. (2), $O(^1D)$ is quenched to give $O(^3P)$ by collision with HFC (quenching rate constant k_q) and CO_2 (quenching rate constant $k_{q'}$). In Eq. (3), $O(^1D)$ undergoes insertion into the C–H bonds of HFC (insertion rate constant k_i) to give the corresponding hot alcohol (RCH_2OH^*). In Eq. (4), $O(^1D)$ abstracts a hydrogen atom from HFC to generate alkyl and hydroxyl radical pairs (hydrogen abstraction rate constant k_a). In Eq. (5), the hot alcohol decomposes to give several products (fragmentation rate constant k_f), and in Eq. (6) finally collapses to relaxed (cold) alcohols, losing the excess vibrational energy gained in collision with the added gases (deactivation rate constant of ROH^* in collision with added gases k_{ROH}). As shown in Eqs. (1) and (2), the present system includes $O(^3P)$; however, it does not undergo insertion into the C–H bonds of HFC to give RCH_2OH^* because of the triplet spin. Most of the $O(^3P)$ atoms probably collapse to give triplet oxygen molecules through combination with other $O(^3P)$ atoms (Eq. (7)) [24].

3.4. Determination of the rate constants

On the basis of the above mechanism, the quantum yields of the alcohols can be expressed by

$$\Phi_{ROH} = \Phi_{O(^1D)} \times \frac{k_i[RCH_3]}{(k_q + k_i + k_a)[RCH_3] + k_{q'}[CO_2]} \times \frac{k_{ROH}[M]}{k_f + k_{ROH}[M]} \qquad (8)$$

Under high pressure conditions, the last term, $k_{ROH}[M]/(k_f + k_{ROH}[M])$, will be close to unity, because k_f is much smaller than $k_{ROH}[M]$. Then the inverse of Φ_{ROH} can be given by

$$1/\Phi_{ROH} = 1/\Phi_{O(^1D)} \times \left[\left(1 + \frac{k_q + k_a}{k_i}\right) + \frac{k_{q'}[CO_2]}{k_i[RCH_3]}\right] \qquad (9)$$

The slope of the plot of $1/\Phi_{ROH}$ vs. $1/[RCH_3]$ is $1/\Phi_{O(^1D)} \times k_{q'}[CO_2]/k_i$, and the intercept is $1/\Phi_{O(^1D)} \times [1 + (k_q + k_a)/k_i]$. For CF_3CH_3, the plot is apparently linear (Fig. 1(b)), but the intercept gives a negative value (−3.9). This is probably because the assumption of $k_f \ll k_{ROH}[M]$ does not occur at the initial pressure of the CF_3CH_3 employed (100–900 Torr); therefore, Eq. (9) is not suitable in this case. Related to this work, Green and Wayne [25] have measured the sum of k_a and k_i for the reaction of $O(^1D)$ with CF_3CH_3 in a static, competitive, experiment to be $(1.0 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, relative to the rate constant for the reaction of $O(^1D)$ with N_2O, but did not analyse the alcohol produced. For $CF_3CF_2CH_3$, the linear plot of $1/\Phi_{CF3CF2CH2OH}$ vs. $1/[CF_3CF_2CH_3]$ gives 710 as the slope and 3.1 as the intercept (Fig. 2(b)). The ratios of $k_{q'}/k_i$ and $(k_q + k_a)/k_i$ were calculated to be 6.7 and 1.9 respectively. As $k_{q'}$ has been measured to be $(1.2 \pm 0.09) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [26], k_i is estimated to be $(1.5 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Two measurements have been made of the total rate constant for $O(^1D)$ removal in the reaction of $O(^1D)$ with CHF_3: 8.4×10^{-12} cm^3 molecule^{-1} s^{-1} based on an analysis of the $O(^3P)$ concentration [22a], and 4.0×10^{-11} cm^3 molecule^{-1} s^{-1} based on $O(^1D)$ concentration measurements [23]. In Ref. [23], it was also reported that the hydrogen abstraction rate is about 8% of the total reaction with CHF_3, i.e. k_a with CHF_3 is expected to be 0.3×10^{-11} to 0.07×10^{-11} cm^3 molecule^{-1} s^{-1}. However, in the present product analysis, no formation of CF_3CF_3, as a dimeric product from CF_3 radicals, was observed by gas chromatography for the reaction of $O(^1D)$ with CHF_3 [13]. In addition, the yields of the unknown products were negligible due to the high pressure of CF_3CH_3 and $CF_3CF_2CH_3$. Therefore if k_a with $CF_3CF_2CH_3$ is approximately 0.3×10^{-11} cm^3 molecule^{-1} s^{-1}, k_q can tentatively be estimated at $(2.5 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and the branching ratio for quenching, $k_q/(k_q + k_i + k_a)$, at approximately 0.58. It has been reported that the branching ratio depends on the number of F atoms; for example, 0 for CH_4, 0.25 for CH_3F, 0.77 for CHF_3 and 0.54 for CH_3CHF_2 [12,16a,22,23]. Compared with these values, the estimate calculated here is considered to be reasonable.

Table 1
Quantum yields of production of alcohols (Φ_{ROH}) and lifetimes of hot alcohols (τ_{ROH^*})

HFC →	ROH	Φ_{ROH}[a]	τ_{ROH^*} (ps)	
			Obsd.	Calcd.[b]
CH_4	CH_3OH	0.012 ± 0.001	0.8	0.4[c]
CH_3CH_3	CH_3CH_2OH	0.013 ± 0.001	>4	12[c]
CF_3CH_3	CF_3CH_2OH	0.066 ± 0.001	–	[d]
$CF_3CF_2CH_3$	$CF_3CF_2CH_2OH$	0.19 ± 0.02	–	[d]

[a] Determined with the gas mixture CO_2/HFC (300 Torr/300 Torr); F_2 laser; power, 60 mJ per pulse (10 Hz); irradiation time, 50 s.
[b] Calculated estimated lifetime.
[c] Ref. [27].
[d] See text.

3.5. Lifetime and yield of hot alcohol

Table 1 shows the lifetimes of the hot alcohols (τ_{ROH}*), calculated using k_f in the fragmentation processes from hot alcohols, together with the quantum yields of the alcohols (Φ_{ROH}) produced by the photolysis of gas mixtures of CO_2/HFC and CO_2/hydrocarbons (300 Torr/300 Torr).

The lifetimes of the hot molecules (τ) are defined here as the inverse of the sum of the dissociation rate constants (k_f) of the hot molecules at a fixed internal energy. Each k_f denotes a specific rate constant and can be estimated using unimolecular reaction theory [28]. At a fixed energy, τ ($= 1/k_f$) corresponds to $h\rho^*/W$, where h is Planck's constant, ρ^* is the state density and W is the sum of the reaction routes.

The introduction of C–F bonds is expected to make the lifetimes of the hot molecules longer than those of the corresponding hydrocarbons because of several factors. Firstly, ρ^* increases considerably more than W due to the effect of the low vibration modes of the C–F bonds (C–F stretching mode, approximately 1140 cm^{-1}). Indeed, it has been demonstrated that the lifetime of hot fluorotoluene ($CH_3C_6F_5$, $\tau_F = 1300$ ns) is 2.6 times longer than that of hot toluene ($\tau_H \approx 500$ ns) with an internal energy of approximately 630 kJ mol^{-1} [29]. This is consistent with the fact that the vibrational frequency of the C–F bond is lower than that of the C–H bond (C–H stretching mode, approximately 2900 cm^{-1}). Secondly, the major fragmentation process will be the HF elimination process instead of OH dissociation as in the case of hydrocarbons. The lowest activation energy has been estimated for the HF elimination process as shown in Table 2. The elimination rate constant has been discussed for CF_3CH_3 on the RRKM basis [30], and the constant is 10^9 s^{-1} with an energy of 450 kJ mol^{-1}. Therefore the corresponding constant for $CF_3CH_2OH^*$ with an energy value of 565.5 kJ mol^{-1} may be of the order of 10^{10} s^{-1}. The constant for the large sized molecule $CF_3CF_2CH_2OH^*$ is estimated to be several times smaller than that of $CF_3CH_2OH^*$. The lifetime of

Table 2
Fragmentation processes from hot alcohols and calculated dissociation rate constants

Fragmentation process		E_d [a] (kJ mol^{-1})	k_f [b,c] (10^9 s^{-1})
$CH_3CH_2OH^* \rightarrow$	$CH_3CH_2 + OH$	382	55
	$CH_3 + CH_2OH$	343	26
	$C_2H_4 + H_2O$	298	2.5
	$H_2 + CH_3CHO$	469	<1
	$H + CH_2CH_2OH$	394	0.4
	$H + CH_3CHOH$	389	0.6
$CF_3CH_2OH^* \rightarrow$	$CF_3CH_2 + OH$	394	0.5
	$CF_3 + CH_2OH$	423	<0.1
	$CF_2CH_2 + HOF$	–	–
	$HF + CHF_2CHO$	297 [d]	[e]
	$F + CF_2CH_2OH$	545	<0.1
	$H + CF_3CHOH$	425 [d]	<0.1

[a] Dissociation energy at 300 K [27,30,31].

[b] Ref. [27] for CH_3CH_3 and this work for CF_3CH_3 with vibrational frequencies reported in Ref. [32].

[c] Dissociation rate constant.

[d] Dissociation energy based on the data for CF_3CH_3 [31].

[e] See text.

$CF_3CH_2OH^*$ is probably of the order of 100 ps and that of $CF_3CF_2CH_2OH^*$ is probably of the order of 500 ps. Thirdly, the dissociation energies of the C–O, C–C and C–H bonds increase as shown in Table 2. The process of C–C bond cleavage ($E_d = 343$ kJ mol^{-1}), for instance from $CH_3CH_2OH^*$, contributes about one-third of the total fragmentation process, whereas this process for $CF_3CH_2OH^*$ ($E_d = 423$ kJ mol^{-1}) will be negligible. Finally, hot alcohols with C–F bonds have an internal energy value lower than those without C–F bonds as shown below.

$$O(^1D) + CH_3CH_3 \longrightarrow CH_3CH_2OH^* \quad (+589.8 \text{ kJ mol}^{-1})$$

$$O(^1D) + CF_3CH_3 \longrightarrow CF_3CH_2OH^* \quad (+565.5 \text{ kJ mol}^{-1})$$

The introduction of C–F bonds causes an increase in Φ_{ROH} as shown in Table 1: for example, $\Phi_{CF3CH2OH}$ is 5.5 times greater than $\Phi_{CH3CH2OH}$. There is no doubt that the result correlates with the increase in lifetime of the hot alcohols caused by the introduction of C–F bonds: in this study, the lifetime of $CF_3CF_2CH_2OH^*$ is estimated to be about 1000 times longer than that of CH_3OH^*.

4. Conclusions

The deactivation process of $O(^1D)$ to $O(^3P)$ by HFCs and hydrochlorofluorocarbons (HCFCs) has been investigated by several researchers. However, there has been no kinetic study of the insertion process of $O(^1D)$ into the HFC C–H bonds based on an analysis of the corresponding alcohols produced, although several studies have dealt with the fragmentation products from the alcohols. In this investigation, the insertion rate was determined to be $(1.5 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} by measuring the quantum yield of alcohol produced in the case of $CF_3CF_2CH_3$, using $O(^1D)$ generated by vacuum UV (158 nm) laser photolysis of CO_2. A laser power meter (Gentec ED500) was calibrated at 158 nm by comparison with a CO_2 chemical actinometer, and the correction factor was estimated to be 1.48 ± 0.08.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (No. 06640563). The research was also conducted as a project of the Research Society for CO_2 Fixation sponsored by the Institute for Laser Technology under the commission of the Kansai Electric Power Company, Inc.

References

[1] (a) A.R. Ravishankara and E.R. Lovejoy, *J. Chem. Soc., Faraday Trans.*, *90* (1994) 2159; (b) F.S. Rowland and M.J. Molina, *Rev. Geophys. Space Phys.*, *13* (1975) 1; (c) R. Stokarski and R.J. Cicerone, *Can. J. Chem.*, *52* (1974) 1610; (d) R.J. Cvetanovic', *Can. J. Chem.*, *52* (1974) 1452.

[2] (a) H. Yamazaki and R.J. Cvetanovic', *J. Chem. Phys.*, *41* (1964) 3703; (b) G. Paraskevopoulos and R.J. Cvetanovic', *J. Chem. Phys.*, *50* (1969) 590; (c) G. Paraskevopoulos and R.J. Cvetanovic', *J. Am. Chem. Soc.*, *91* (1969) 7572; (d) G. Paraskevopoulos and R.J. Cvetanovic', *J. Chem. Phys.*, *52* (1970) 5821; (e) L.M. Quick and R.J. Cvetanovic', *Can. J. Chem.*, *49* (1971) 2193; (f) P. Michaud and R.J. Cvetanovic', *J. Phys. Chem.*, *76* (1972) 1375; (g) A.J. Colussi and R.J. Cvetanovic', *J. Phys. Chem.*, *79* (1975) 1891.

[3] W.B. DeMore and O.F. Raper, *J. Chem. Phys.*, *46* (1967) 2500.

[4] R.I. Greenberg and J. Heicklen, *Int. J. Chem. Kinet.*, *4* (1972) 417.

[5] C.-L. Lin and W.B. DeMore, *J. Phys. Chem.*, *77* (1973) 863.

[6] P. Casavecchia, R.J. Buss, S.J. Sibener and Y. Lee, *J. Chem. Phys.*, *73* (1980) 6351.

[7] P.M. Aker, J.J.A. O'Brien and J.J. Sloan, *J. Chem. Phys.*, *84* (1986) 745.

[8] Y. Oshima, M. Saito, S. Koda and H. Tominaga, *Chem. Lett.*, (1988) 203.

[9] S.G. Cheskis, A.A. Iogansen, P.V. Kulakov, I.Yu. Razuvaev, O.M. Sarkisov and A.A. Titov, *Chem. Phys. Lett.*, *155* (1989) 37.

[10] T. Suzuki and E. Hirota, *J. Chem. Phys.*, *98* (1993) 2397.

[11] H. Arai, S. Sato and S. Koda, *J. Phys. Chem.*, *98* (1994) 12.

[12] R. Warren, T. Gierczak and A.R. Ravishankara, *Chem. Phys. Lett.*, *183* (1991) 403.

[13] M. Kojima, Y. Ojima, N. Nakashima, Y. Izawa, T. Akano and C. Yamanaka, *Chem. Lett.*, (1992) 1309.

[14] (a) Y.F. Zhu and R.J. Gordon, *J. Chem. Phys.*, *92* (1990) 2897; (b) A. Stolow and Y.T. Lee, *J. Chem. Phys.*, *98* (1993) 2066.

[15] J.W. Rabalaic, J.M. McDonald, V. Scherr and S.P. McGlynn, *Chem. Rev.*, *71* (1971) 73.

[16] (a) P.M. Aker, B.I. Niefer and J.J. Sloan, *J. Chem. Phys.*, *87* (1987) 203; (b) T.L. Burks and M.C. Lin, *Chem. Phys.*, *33* (1978) 327; (c) T.L. Burks and M.C. Lin, *Int. J. Chem. Kinet.*, *13* (1981) 977; (d) H. Lorenzen-Schmidt, R. Weller, O. Schrems and C. Nielsen, *Proc. SPIE-Int. Soc. Opt. Eng.*, *2089* (1993) 286.

[17] G. Klöter and K. Seppelt, *J. Am. Chem. Soc.*, *101* (1979) 347.

[18] J.S. Francisco, *Chem. Phys. Lett.*, *218* (1994) 401.

[19] (a) N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, *77* (1982) 6040; (b) N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, *79* (1983) 2727.

[20] Y. Izumi, K. Ema, T. Yamamoto, S. Kawasaki, Y. Shimizu, S. Sugimoto and N. Suzuki, *Rev. Laser Eng., 19* (1991) 247.

[21] T.G. Slanger and G. Black, *J. Chem. Phys., 68* (1978) 1844.

[22] (a) A.P. Force and J.R. Wiesenfeld, *J. Phys. Chem., 85* (1981) 782; (b) C.R. Park and J.R. Wiesenfeld, *Chem. Phys. Lett., 186* (1991) 170.

[23] I.S. Fletcher and D. Husain, *J. Phys. Chem., 80* (1976) 1837.

[24] H. Okabe, *Photochemistry of Small Molecules*, Wiley, 1978.

[25] R.G. Green and R.P. Wayne, *J. Photochem., 6* (1976/77) 371.

[26] J.A. Davidson, C.M. Sadowski, H.I. Schiff, G.E. Streit, C.J. Howard, D.A. Jennings and A.L. Schmeltekopf, *J. Chem. Phys., 64* (1976) 57.

[27] W. Tsang, *Int. J. Chem. Kinet., 8* (1976) 193.

[28] P.J. Robinson and K.A. Holbrook, *Unimolecular Reaction*, Wiley, London, 1972.

[29] N. Nakashima and K. Yoshihara, *J. Phys. Chem., 93* (1989) 7763.

[30] D.F. McMillen and D.M. Golden, *Annu. Rev. Phys. Chem., 33* (1982) 493.

[31] A.S. Rodgers and W.G.F. Ford, *Int. J. Chem. Kinet., 5* (1973) 965.

[32] V.F. Kalasinsky and H.V. Anjaria, *J. Phys. Chem., 84* (1980) 1940.