Photocatalytic Oxidative Decomposition of Fluoroalkenes by Titanium Dioxide

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Photoirradiation (>200 nm) of anatase TiO_2 induces decomposition of fluoroalkenes [hexafluoropropene (6FP), tetrafluoroethylene (4FE), 3,3,3-trifluoropropene (3FP), 1,1-difluoroethylene (2FE) and fluoroethylene (1FE)] as well as ethylene (0FE) in air at room temperature. The decomposition requires the coexistence of photoirradiation, air, TiO_2 and water on the catalyst, suggesting that TiO_2-photosensitized oxygenation is operative. Formation of carbon dioxide and hydrogen fluoride was commonly observed. The order of reactivity of the fluoroalkenes is 6FP > 4FE ≫ 2FE > 0FE > 3FP = 1FE. The major reaction path of 6FP gave equimolar trifluoroacetic acid and CO_2 as products via oxidative cleavage of the carbon–carbon double bond, while 4FE yielded CO_2 predominantly. The most probable intermediate in these reactions is a dioxetane products via direct addition of superoxide anion radical ($O_2^{·-}$) and/or addition of molecular oxygen following electron injection into the fluoroalkene.

Many papers have proposed the practical application of photocatalytic reactions by semiconductor particles such as titanium dioxide: e.g. organic synthesis,[1] decomposition of waste materials,[2] deposition of metal from solution[3] and deactivation of microorganisms.[4] Alkenes are suitable substrates for the photocatalytic organic synthesis, and undergo epoxidation or oxidative cleavage to give carbonyl derivatives in the presence of molecular oxygen.[5] Fox and co-workers suggested a mechanism involving the cation radical of the alkenes together with superoxide anion radical ($O_2^{·-}$) in the solid–liquid phase photocatalytic reaction of alkene substituents of aromatic compounds.[6] This paper describes the solid–gas phase photocatalytic reaction of fluoroalkenes, especially perfluoroalkenes such as hexafluoropropene (6FE) and tetrafluoroethylene (4FE), on TiO_2.

Thermal and/or photochemical oxidative decompositon of chlorinated and/or brominated fluoroalkenes has been extensively reported,[7] and partly used in industrial processes.[8] The perfluoroalkenes are, however, rather stable and their reactivity remains ambiguous. In this paper, the TiO_2-photosensitized decompositon of fluoroalkenes is reported and the reaction mechanism discussed.

Experimental

Materials.—Anatase TiO_2 powder (Merck) was used without further activation. The fluorine-containing compounds, except 3,3,3-trifluoropropene (3FP, SCM Chemicals), were obtained from Daikin Industries Ltd. Ethylene was supplied by Takachiho Chemicals. The water used was passed through an ion-exchange resin and distilled.

Apparatus.—An 8 W low-pressure mercury arc (20 mm diameter, 140 mm long) was used as a light source, which was incorporated in a cylindrical Pyrex cell (50 mm in diameter, 210 mm long, 390 cm^3 vol.) equipped with ground joints and valves (Fig. 1). Gaseous products liberated during the irradiation were measured with a Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector and He carrier.
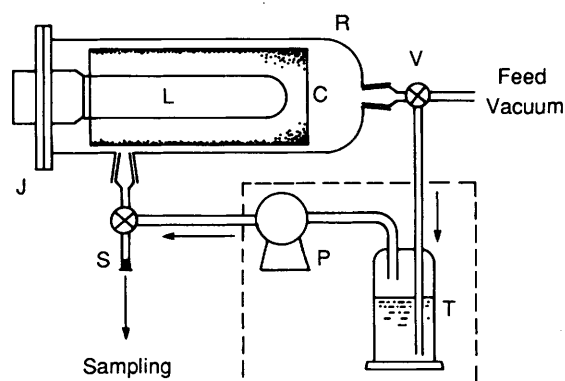

Fig. 1. Schematic representation of photocatalytic reaction system: R, reaction cell; V, Pyrex three-way valve; L, low-pressure mercury arc; C, Pyrex tube, the inner surface of which was covered with TiO_2 catalyst; J, ground Pyrex–Teflon joint; P, circulation pump; S, silicone-rubber septum for gas sampling; T, trap with or without a sodium hydroxide solution. The part surrounded by the dashed line was used as necessary.

Conditions of the GC analyses were as follows: for O_2, a molecular sieve 5A column (3 mm in diameter, 3 m long) at 323 K; for 6FP, a Chromosorb 101 column (3 mm; 3 m) at 353 K; for the other compounds, a Porapak Q (3 mm in diameter, 4 m long) column at 353 K. ^{19}F NMR spectra were obtained with a JEOL EX90 (84 MHz) instrument. Typical conditions for the NMR measurements were as follows: spectral width 20 kHz; data points, 16 384; pulse width, 13 × 10^{-6} s; pulse interval 3.0 s; number of transients, 16. Atomic absorption spectroscopy was performed on a Shimadzu AA780.

Procedure.—A paste-like mixture of TiO_2 (1.8–8.2 g) with distilled water (ca. 4 cm^3), with or without additives (see the Results and Discussion section), was applied onto the inner surface of a Pyrex tube and dried overnight at 353 K in air. Just before the experiment, distilled water (1.5–2.5 cm^3) was sprayed uniformly onto the catalyst. The catalyst tube thus prepared

Table 1. Photocatalytic decomposition of fluoroalkenes, ethylene and fluoroalkanes.[a]

		Condition				Result	
Run	Substrate[b]	Feed/mmol	TiO$_2$/g	H$_2$O/g	Irrad./h	Consumption (%)	CO$_2$/mmol
1	6FP	1.9	3.8	1.6	0.8	100	3.0
2	4FE	2.0	4.9	2.6	2.5	89	3.1
3	3FP	2.4	4.9	3.1	4.0	16	0.4
4	2FE	2.0	5.2	2.9	4.0	36	0.6
5	1FE	2.1	3.7	2.3	4.0	16	0.3
6	0FE	1.7	4.5	3.0	4.0	22	0.5
7	4FM	1.9	6.5	3.5	4.0	11	0.1
8	3FM	2.0	6.0	2.6	4.0	3	0.2
9	6FE	2.0	5.9	3.3	4.0	13	0.1

[a] Gaseous mixture of substrates and air was irradiated under atmospheric pressure at room temperature by an 8 W low-pressure mercury arc in the presence of moistened TiO$_2$ catalyst. [b] See text for definition of abbreviations.

was placed in the reaction cell and evacuated with a rotary pump for 5 min. After the evacuation, 50–60% of the sprayed water remained on the catalyst surface. Fluoroalkene (1.9–2.4 mmol) and air dried by silica gel were introduced into the cell and irradiated at atmospheric pressure and at ambient temperature. In some cases, the gaseous reaction mixture was circulated with an external diaphragm pump (2.5 dm^3 min^{-1}) connected to the cell. A small portion of gaseous sample was withdrawn and analysed by GC at appropriate intervals during irradiation.

After the irradiation, sodium hydroxide solution (2.5 mol dm^{-3}, 50–100 cm^3) was injected into the cell, and the reaction cell was allowed to stand for 1 h with occasional shaking to dissolve products such as hydrogen fluoride and trifluoroacetic acid (TFAOH). TiO$_2$ particles in the washing were removed by centrifugation and the supernatant solution was diluted appropriately with distilled water. Fluoride anion was measured by colorimetry with Alfusone reagent (Dojindo Chemicals, Japan) calibrated with standard sodium fluoride solutions. Thus, HF was measured in the form of F$^-$ in the present experiments.

The diluted washings (0.5 cm^3) from the reaction mixture of 6FP and 4FE were analysed by ^{19}F NMR spectroscopy. To the sample solution was added deuterium dioxide (0.5 cm^3, CEA) for the magnetic field lock and 1,1,1,3,3,3-hexafluoropropan-2-ol (4 mm^3, Nacalai Tesque) as an internal standard. The chemical shift of the standard was appointed as −77.0 and −77.1 ppm downfield from trichlorofluoromethane. The molar amounts of TFAO$^-$ and F$^-$ obtained from 6FP were calculated by comparison of the integrated peak area with the standard. The amount of F$^-$ thus obtained was equal to that from the colorimetric measurement within experimental error (ca. 3%).

A catalyst containing Ag$^+$ (TiO$_2$–Ag$^+$) was prepared from the mixture of TiO$_2$ with aqueous Ag$_2$SO$_4$ solution. After irradiation, the catalyst was scraped off, rinsed several times with distilled water to remove unchanged Ag$^+$, dried overnight at 343 K and treated with concentrated nitric acid. Ag$^+$ dissolved in this solution was measured by atomic absorption spectroscopy after appropriate dilution.

The quantum yield was determined as a ratio of the reaction rate of 6FP decrease and photon flux. The flux was estimated on the assumption of complete energy conversion in the mercury arc from electricity into light at 254 nm. Therefore, the yield so obtained refers to the minimum value.

Molecular orbital *ab initio* calculation was performed by means of the GAUSSIAN-86 (6-31+G* base set).

Results and Discussion

Photocatalytic Decomposition of Fluoroalkenes.—Several fluoroalkenes and ethylene, as well as some fluoroalkanes, were photoirradiated in the presence of moistened TiO$_2$ under aerated conditions (Table 1). The fluoroalkanes tetrafluoromethane (4FM), trifluoromethane (3FM) and hexafluoroethane (6FE) were less reactive under these reaction conditions. Kutsuna and co-workers[9] have demonstrated the TiO$_2$-photo-induced decomposition of trichlorofluoromethane, a compound suspected of destroying the stratospheric ozone layer.[10] In the present study, fluorinated hydrocarbons without any other halogen atom were used. Since substitution of fluorine with chlorine or bromine may extend the photoabsorption to longer wavelength[11] and, furthermore, photocatalytic decomposition of trihalogenomethanes in aqueous TiO$_2$ suspension has been reported,[12] the present results suggest that the photoinduced reaction in the presence of TiO$_2$ can be applied to the decomposition of chlorinated or brominated fluorocarbons.

Among the fluoroalkenes and ethylene (0FE), perfluoroalkenes 6FP and 4FE were decomposed most readily. The order of reactivity was 6FP > 4FE ≫ 2FE > 0FE > 3FP = 1FE, suggesting the effectiveness of perfluorination for the photocatalytic decomposition. These alkenes commonly yielded CO$_2$ and HF.

Photocatalytic Decomposition of 6FP.—Table 2 summarizes the results of photocatalytic decomposition of 6FP under several reaction conditions. 6FP was not decomposed in the dark or in the absence of TiO$_2$. Further, oxygen (O$_2$) was indispensable: 6FP decrease was negligible under a nitrogen atmosphere. SiO$_2$ powder showed almost no activity, even under photoirradiation in the presence of O$_2$ and water. These facts show that the decomposition proceeds through photoexcitation of TiO$_2$ by low-pressure mercury arc (emitting predominantly at 254 nm) irradiation, but not by direct photoexcitation of 6FP. The 6FP decomposition was also induced by irradiation with a 400 W high-pressure mercury arc (emitting mostly at 365 nm) outside the cell (the cell wall is transparent at >290 nm). This result confirms the reaction mechanism involving TiO$_2$ photoexcitation, because the anatase-type TiO$_2$ absorbs light of wavelength <390 nm.[13]

Another interesting phenomenon is that the decomposition required the presence of water on the catalyst. Water sprayed on the inside wall of the reaction cell, not on the catalyst, was ineffective. The TiO$_2$ catalyst prepared with an aqueous solution of sodium chloride, potassium chloride or sodium hydroxide photosensitized the 6FP decomposition even in the absence of sprayed water. Such inorganic water-soluble compounds may result in a small amount of water remaining on the catalyst as a concentrated aqueous solution. The participation of water in the reaction mechanism will be described elsewhere.

Fig. 2 shows the time course of 6FP decomposition in the

Table 2. Photocatalytic decomposition of 6FP under various conditions.

| | Condition | | | | | | | Result | |
| | | Catalyst | | | Additive[a] | | | | |
Run	Feed/mmol		Wt./g	Atmosphere		Wt./g	Irrad./h	Consumption (%)	CO_2/mmol
1	2.1	TiO_2	4.0	Air	—	0.0	1.5	3	0.1
2	2.1	TiO_2	7.6	Air	aq. NaOH		1.0	98	3.6
3	2.1	TiO_2	8.2	Air	aq. KCl		1.0	94	3.0
4	1.9	TiO_2	3.8	Air	H_2O	1.6	0.8	100	3.0
5	2.1	—	0.0	Air	H_2O	1.0	1.0	0	0.0
6	2.1	TiO_2	5.0	Air	H_2O	1.0[b]	1.0	0	0.0
7	2.0	SiO_2	4.8	Air	H_2O	1.0	1.0	0	0.0
8	1.8	TiO_2	3.8	Air	H_2O	1.9	0.0	0	0.0
9	1.6	TiO_2	1.8	Air	H_2O	1.1	2.0[c]	100	2.7
10	2.2	TiO_2	3.0	N_2	H_2O	1.8	1.0	0	0.0

[a] Additives except water were mixed with the TiO_2 slurry before application onto the catalyst tube. [b] Water was sprayed onto the inner surface of the reaction vessel, not onto the catalyst. [c] Irradiation was performed by a 400 W high-pressure mercury arc outside the reaction vessel (see the text).
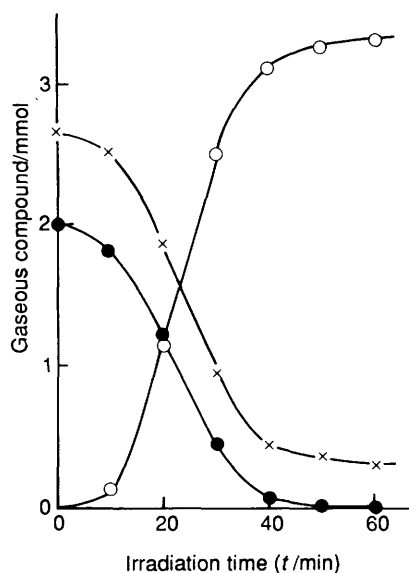

Fig. 2. Time course of the photocatalytic decompositon of 6FP (●), accompanied by O_2 consumption (×) and CO_2 liberation (○).

reaction vessel equipped with a circulation pump. The decomposition was slow in the initial stage, but accelerated to give a maximum rate of 0.15 mmol min⁻¹. The maximum rate corresponds to a quantum yield of 0.14 on the assumption that one photon induces the decomposition of one molecule of 6FP. The yield is markedly higher than the liquid–solid phase photocatalytic reaction of propan-2-ol,[13] and similar to that observed in water photolysis by TiO_2.[14] Note the fact that the quantum yield should be a minimum (see the Experimental section); further, a one-photon process was presumed as above). Since the yield was less than unity, it cannot be evidence for a chain mechanism.

The 6FP decrease was stopped by shutdown of light from the mercury arc, showing the absence of long-lived intermediates, and started again by re-irradiation without significant loss of reaction rate. The sigmoidal time course curve may indicate that activation of catalyst and/or compilation of active species on the catalyst are involved in the reaction. In a control experiment,

* Difficulty in uniform spreading of concentrated HF on the catalyst caused the poor reproducibility of the results.

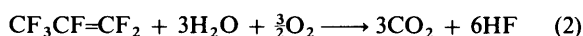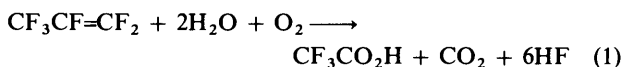the presence of HF on the TiO_2 catalyst (without extra addition of water) before irradiation reduced the induction period observed in the photocatalytic reaction.* The reason for the induction period could be that the product HF accumulated as the reaction proceeds accelerates the reaction: one possibility is that dissolution of fluorinated hydrocarbons in the concentrated HF layer on the catalyst enhances the photocatalytic reaction. Water sprayed on the catalyst may act as an absorbent of the photocatalytically liberated HF.

Products and Stoichiometry of Decomposition of 6FP and 4FE.—In the photocatalytic reaction of 6FP, GC analyses detected CO_2 as one of the carbon-containing products. Although a previous report[15] has shown that carbonyl fluoride (COF_2) was decomposed in the GC column and detected as CO_2, and the intermediacy of COF_2 may be presumed as discussed afterwards, the gaseous product here should be CO_2 under the reaction conditions in which the amount of water present on the catalyst was enough to hydrolyse COF_2 to CO_2.

In a ¹⁹F NMR spectrum of the diluted washing obtained by 6FP decomposition, peaks appearing at -76.2, -121.9 and -151.2 ppm were assigned to the fluorine-containing products trifluoroacetate (TFAO⁻), F⁻ and BF_4^-, respectively. Fluoride and borofluoride also appeared in the spectrum resulting from 4FE decomposition. Fig. 3 shows the molar amount of products and consumption of O_2 as a function of 6FP consumption. A fairly linear relation was observed for each product. The molar amounts of carbon (CO_2 + 2 × TFAO⁻) and fluorine (F⁻ + 3 × TFAO⁻ + 4 × BF_4^-) atoms observed in the products were almost proportional to the 6FP consumption. The slope of the linear relationship for carbon (3.0) indicates the quantitative detection of carbon-containing products, while 73% of fluorine was detected. In a large-scale experiment, 13.0 mmol of 6FP was converted into 5.6 mmol of TFAOH (isolation yield 43%) by TiO_2 (8.2 g) with water (6.0 g).

The formation of BF_4^- is attributed to corrosion of the inner surfaces of the glassware by liberated HF: it was observed that the weight of catalyst tube decreased and the inner surface of the reaction cell was whitened slightly by the photocatalytic reaction. The Pyrex glassware used in this study contains silicon oxide (SiO_2, 81 wt%), boron oxide (B_2O_3, 13 wt%), aluminium oxide (Al_2O_3, 2 wt%) and sodium oxide (Na_2O, 4 wt%).[16] Control experiments showed that treatment of the tube with hydrofluoric acid resulted in the formation of BF_4^- as the sole product appearing in the ¹⁹F NMR spectrum; fluorosilicate anion could not be detected. The molar amount of BF_4^- was 77% of that calculated from the weight decrease and composition
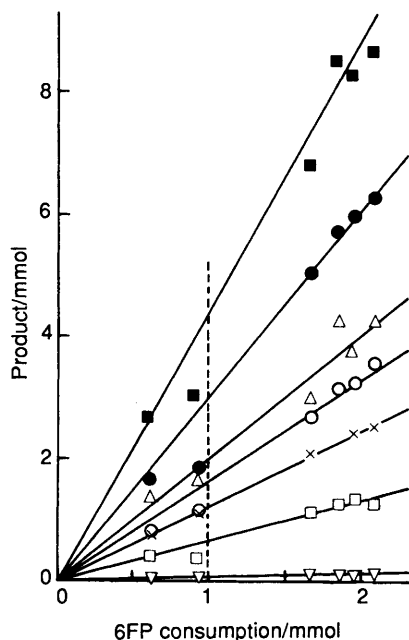
Fig. 3. Relationship between 6FP consumption and product yields: △, F⁻; ○, CO_2; ×, O_2 consumption; ☐, TFAO⁻; ▽, BF_4^-: ■, sum of fluorine-containing products (F⁻ + 3 × TFAO⁻ + 4 × BF_4^-); ●, sum of carbon-containing products (CO_2 + 2 × TFAO⁻).

of the glassware on the assumption of homogeneous corrosion.*

Fig. 4 shows the linear relation between the consumption of 6FP and the amount of glass corrosion in the several photocatalytic reactions. This correlation suggests that part of the HF liberated during the photocatalytic reaction attacks the glassware and is detected as F⁻ and BF_4^- by the subsequent NaOH treatment. The relatively larger deviations in the plot between 6FP consumption and F⁻ formation (Fig. 3) showed that the significant experimental error in the detection of F⁻ could not be excluded, presumably because of adsorption of F⁻ onto the TiO_2 surface and undissolved SiF_4 and BF_3 in the gas phase.

On the basis of these results, the stoichiometries of 6FP decomposition shown in eqns. (1) and (2) were presumed. The

$$CF_3CF{=}CF_2 + 2H_2O + O_2 \longrightarrow$$
$$CF_3CO_2H + CO_2 + 6HF \quad (1)$$

$$CF_3CF{=}CF_2 + 3H_2O + \tfrac{3}{2}O_2 \longrightarrow 3CO_2 + 6HF \quad (2)$$

molar ratio of detected TFAOH to CO_2 indicates that 63% and 37% of 6FP was decomposed through eqns. (1) and (2), respectively. The calculated molar ratio of O_2 and 6FP consumed through these reactions is 1.2, which is close to the observed ratio of 1.25 (see Fig. 3).

Similarly, the stoichiometry of 4FE decomposition was obtained from the relations shown in Fig. 5 as eqn. (3). Almost

$$CF_2{=}CF_2 + 2H_2O + O_2 \longrightarrow 2CO_2 + 4HF \quad (3)$$
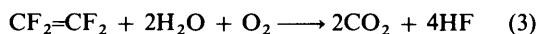
90% of fluorine and carbon atoms were detected in the forms of F⁻ with BF_4^- and CO_2, respectively. A small amount of

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* The following glass corrosion reactions can be assumed.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$
$$B_2O_3 + 8HF \longrightarrow 2HBF_4 + 3H_2O$$
$$SiF_4 + 2H_2O \longrightarrow 4HF + SiO_2 \text{ (in the aqueous NaOH solution)}$$
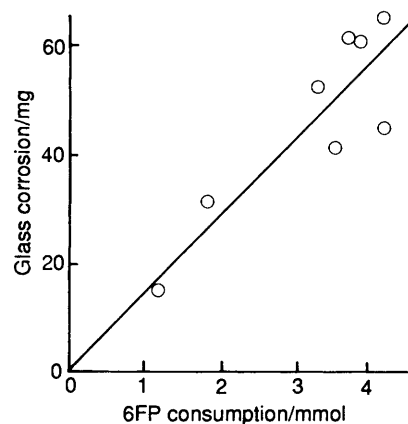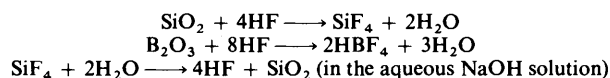

Fig. 4. Relationship between 6FP consumption and amount of corroded glass tube.
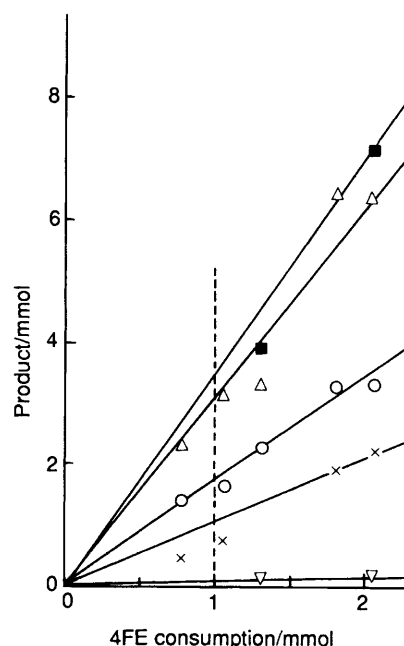

Fig. 5. Relationship between 4FE consumption and product yields: for legend see Fig. 3.

undetected product(s) produced by the photocatalytic reaction remains to be identified.

Effect of Silver Ion on TiO_2.—Fig. 6 shows the time course of the photocatalytic reaction in the presence of Ag^+. The rate of 6FP consumption was markedly decreased, while the surface of TiO_2 was turned grey by photoirradiation owing to the deposition of silver metal. Photoirradiation of TiO_2 suspended in silver salt solution led to Ag deposition along with O_2 liberation.[3c] As the deposition proceeded, light flux absorbed by TiO_2 might be decreased because of the deposited Ag. In a separate experiment, Ag-deposited TiO_2 catalyst with negligible Ag^+ was prepared by prolonged irradiation and used for the 6FP decomposition (also shown in Fig. 6). The photocatalytic activity of TiO_2–Ag was lower than bare TiO_2, but higher than TiO_2 with Ag^+. These facts indicate that the decrease of TiO_2 activity by the addition of Ag^+ is accounted for not by the inner filter effect of deposited Ag but by the inhibition of reduction by the photogenerated electron [eqns. (4) and (5), where e⁻ and

$$TiO_2 \longrightarrow e^- + h^+ \text{ (photoexcitation)} \quad (4)$$

Table 3. Calculated HOMO and LUMO levels and charge density of fluoroalkenes, ethylene and fluoroalkanes, and their reactivity in TiO_2 photocatalytic reaction.
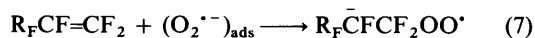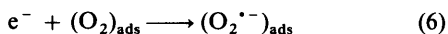
Entry	Structure	Energy level/a.u.		Charge density			% Consumption per hour
		HOMO	LUMO	C(1)	C(2)	C(3)	
6FP	$C(1)F_2=C(2)F–C(3)F_3$	−0.39	0.07	0.81	0.24	1.15	≈100
4FE	$C(1)F_2=C(2)F_2$	−0.38	0.08	0.65	0.65		36
3FP	$C(1)H_2=C(2)H–C(3)F_3$	−0.40	0.07	−0.30	−0.24	1.10	4
2FE	$C(1)F_2=C(2)H_2$	−0.39	0.08	0.75	−0.49		9
1FE	$C(1)FH=C(2)H_2$	−0.39	0.09	0.22	−0.52		4
0FE	$C(1)H_2=C(2)H_2$	−0.38	0.09	−0.39	−0.39		6
4FM	$C(1)F_4$	−0.69	0.08	1.67			3
3FM	$C(1)F_3H$	−0.60	0.08	0.97			1
6FE	$C(1)F_3–C(2)F_3$	−0.60	0.12	1.08	1.08		3
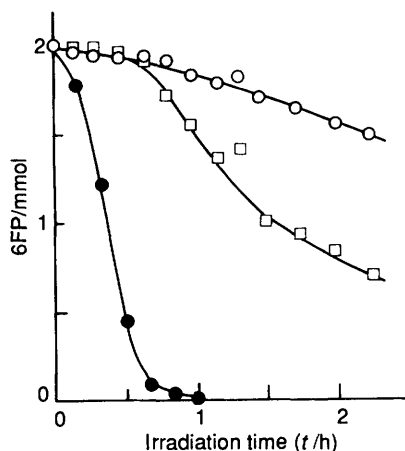
Fig. 6. Time course of the photocatalytic decomposition of 6FP by Ag^+-loaded TiO_2 (O) and Ag-loaded TiO_2 (□). The time course by TiO_2 alone in Fig. 2 (●) is shown for comparison.

$$Ag^+ + e^- \longrightarrow Ag \text{ (deposition)} \quad (5)$$

h^+ refer to the photogenerated electron and positive hole, respectively].

Mechanism of Photocatalytic Reaction of Perfluoroalkenes.—The results shown in Table 1 suggest that perfluoroalkenes such as 6FP and 4FE were decomposed more readily than the partly fluorinated alkenes or ethylene. This suggests that the first chemical step involved in the photocatalytic decomposition of fluoroalkenes is nucleophilic attack on the double bond, which is made possible because of the electron-withdrawing effect of the fluorine and/or perfluoroalkyl group.*

In the present system, superoxide anion radical ($O_2^{•-}$) is the most likely nucleophilic intermediate. $O_2^{•-}$ may be generated from surface-adsorbed O_2 by the photochemical reaction shown in eqn. (6), with the nucleophilic addition of $O_2^{•-}$ perfluoroalkenes leading to the anion radical [eqn. (7), where
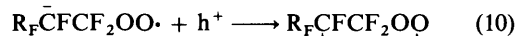
$$e^- + (O_2)_{ads} \longrightarrow (O_2^{•-})_{ads} \quad (6)$$

$$R_FCF=CF_2 + (O_2^{•-})_{ads} \longrightarrow R_F\bar{C}FCF_2OO^• \quad (7)$$

$R_F = CF_3$ or F]. From the charge density distribution for 6FP estimated by *ab initio* calculation (Table 3), addition at the C(1) position was assumed. Perfluoroalkenes are liable to undergo nucleophilic addition compared with partly fluorinated

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* The effect of the perfluoroalkyl group may be small, as suggested by an *ab initio* calculation of 3FP (see Table 3).

alkenes.[19] In the absence of fluoroalkenes, accumulation of $(O_2^{•-})_{ads}$ leads to the recombination of electron–hole pairs. Therefore, negligible decrease of O_2 could be observed in the absence of fluoroalkenes. The injection of e^- into the alkene moiety activated by the perfluoroalkyl group followed by addition of O_2 in the ground state [eqns. (8) and (9)] would lead to the same reaction intermediate shown in eqn. (7): there are no experimental data to distinguish the alternative mechanism.

$$R_FCF=CF_2 + e^- \longrightarrow R_F\bar{C}F\dot{C}F_2 \quad (8)$$

$$R_F\bar{C}F\dot{C}F_2 + O_2 \longrightarrow R_F\bar{C}FCF_2OO^• \quad (9)$$
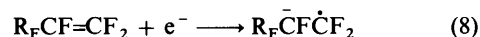
In Table 3 are listed the calculated HOMO and LUMO levels of fluoroalkenes. The decrease in LUMO level tends to enhance the reactivity in the present photocatalytic system. However, the reactivity of fluoroalkenes predominantly depends on the charge density in C=C bonds: highly reactive 6FP and 4FE have positive charge at both the C(1) and C(2) position. The relatively lower activity of 3FP, despite a LUMO energy comparable to 6FP and 4FE could be attributed to relatively lower charge density at the C=C bond and the electron withdrawing effect of F atoms inducing the marked decrease in electron density at the CF_3 carbon. These findings are consistent with the mechanism involving nucleophilic attack of the reaction intermediate—superoxide anion radical—directly on the fluoroalkenes and/or electron injection into the C=C moiety as a preceding reaction. The HOMO level, corresponding to the ability of these compounds to undergo one-electron oxidation, seems to be independent of their relative reactivity.

The reaction sequence shown in eqns. (10)–(13) could lead to the observed products *via* a dioxetane intermediate.

$$R_F\bar{C}FCF_2OO^• + h^+ \longrightarrow R_F\underline{CFCF_2OO} \quad (10)$$

$$R_F\underline{CFCF_2OO} \longrightarrow R_FCOF + FCFO \quad (11)$$

If $R_F = CF_3$ (6FP):

$$CF_3COF + H_2O \longrightarrow CF_3CO_2H + HF \quad (12)$$

$$FCFO + H_2O \longrightarrow CO_2 + 2HF \quad (13)$$

Heicklen and co-workers have reported the reaction of 6FP[17] and 4FE[18] with the oxygen atom generated by the mercury-sensitized decomposition of N_2O in the absence of water. The main products from 6FP and 4FE were COF_2 and trifluoroacetyl fluoride (TFAF), and COF_2, respectively. The ratio of COF_2 to TFAF from 6FP was almost unity in the absence of O_2, but was > 1 under higher O_2 pressure. Since in

the presence of water COF_2 and TFAF could be readily hydrolysed to CO_2 and TFAOH, respectively,[19,20] the product distributions by the oxygen-atom-induced reaction are quite similar to those obtained in the present experiments. The reaction shown as eqn. (14) leading to oxygen atom adsorbed on

$$(O_2{}^{\cdot-})_{ads} + h^+ \longrightarrow 2(O:)_{ads} \qquad (14)$$
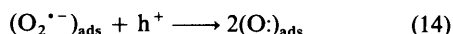
the TiO_2 catalyst has been reported.[21] However, the decomposition via oxygen atom seems unlikely not only because the presumed epoxide [eqn. (15)] and/or its degradation products*

$$R_F CF{=}CF_2 + O: \longrightarrow R_F \underline{CFCF_2O} \qquad (15)$$
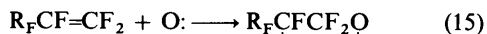
could not be detected but also because there is so much difference in reactivity among several fluoroalkenes (see Table 1).

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* In the case of 6FP, hydrolysis of the epoxide to 2,2-dihydroxy-3,3,3-trifluoropropanoic acid, a hydrated form of trifluoropyruvic acid, has been reported.[22] Neither of these, however, was detected in the reaction mixture from 6FP under the present reaction conditions.

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