Kinetics and Mechanism of Atmospheric Reactions of Partially Fluorinated Alcohols

E. S. Vasil'ev[a], I. I. Morozov[a], W. Hack[b], K.-H. Hoyermann[b], and M. Hold[b]

[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*
[b] *Institut für Physikalische Chemie der Universität Göttingen, Germany*
e-mail: vasiliev@center.chph.ras.ru
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Abstract—Gas-phase reactions typical of the Earth's atmosphere have been studied for a number of partially fluorinated alcohols (PFAs). The rate constants of the reactions of CF_3CH_2OH, CH_2FCH_2OH, and CHF_2CH_2OH with fluorine atoms have been determined by the relative measurement method. The rate constant for CF_3CH_2OH has been measured in the temperature range 258–358 K ($k = (3.4 \pm 2.0) \times 10^{13}\exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(1.5 \pm 1.3)$ kJ/mol). The rate constants for CH_2FCH_2OH and CHF_2CH_2OH have been determined at room temperature to be $(8.3 \pm 2.9) \times 10^{13}$ ($T = 295$ K) and $(6.4 \pm 0.6) \times 10^{13}$ ($T = 296$ K) cm^3 mol^{-1} s^{-1}, respectively. The rate constants of the reactions between dioxygen and primary radicals resulting from PFA + F reactions have been determined by the relative measurement method. The reaction between O_2 and the radicals of the general formula $C_2H_2F_3O$ ($CF_3CH_2\dot{O}$ and $CF_3\dot{C}HOH$) have been investigated in the temperature range 258–358 K to obtain $k = (3.8 \pm 2.0) \times 10^{8}\exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(10.2 \pm 1.5)$ kJ/mol. For the reaction between O_2 and the radicals of the general formula C_2H_4FO ($\dot{C}HFCH_2O$, $CH_2F\dot{C}HOH$, and $CH_2FCH_2\dot{O}$) at $T = 258$–358 K, $k = (1.3 \pm 0.6) \times 10^{11}\exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(5.3 \pm 1.4)$ kJ/mol. The rate constant of the reaction between O_2 and the radicals with the general formula $C_2H_3F_2O$ ($\dot{C}F_2CH_2O$, $CHF_2\dot{C}HOH$, and $CHF_2CH_2\dot{O}$) at $T = 300$ K is $k = 1.32 \times 10^{11}$ cm^3 mol^{-1} s^{-1}. For the reaction between NO and the primary radicals with the general formula $C_2H_2F_3O$ ($CF_3CH_2\dot{O}$ and $CF_3\dot{C}HOH$), which result from the reaction $CF_3CH_2OH + F$, the rate constant at 298 K is $k = 9.7 \times 10^{9}$ cm^3 mol^{-1} s^{-1}. The experiments were carried out in a flow reactor, and the reaction mixture was analyzed mass-spectrometrically. A mechanism based on the results of our studies and on the literature data has been suggested for the atmospheric degradation of PFAs.
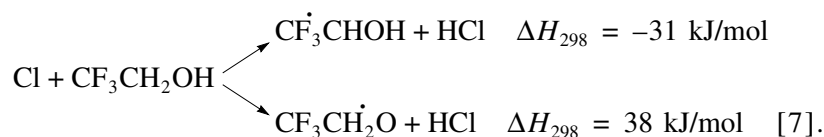
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Freons are considered to be potential destroyers of the Earth's ozone layer. Moreover, accumulating in the troposphere, they add to the greenhouse effect. In view of this, various kinds of Freon substitutes have been suggested [1–3]. Possible Freon substitutes are partially fluorinated alcohols (PFAs). They appear as a real alternative to Freons in the EUROTRAC projects. PFAs are free of chlorine and bromine, the elements that are primarily responsible for ozone depletion. A candidate Freon substitute must meet a variety of physicochemical criteria. First of all, it must be more reactive toward species present in the troposphere, lest it accumulate to enhance the greenhouse effect. If this is the case, its lifetime will be short, ruling out the formation of extra photolysis products on its entry into the stratosphere. Before switching to new Freon substitutes, it is necessary to study their physical and chemical properties in detail. From the chemical standpoint, it is very important to investigate their reactions with main atmospheric reagents, including $\dot{O}H$ and $\dot{N}O_3$ radicals and

halogen atoms. There have already been studies on reactions between $\dot{O}H$ and PFAs [4, 5]. The most abundant tropospheric oxidizer in the daytime is the hydroxyl radical $\dot{O}H$. The mechanism of oxidation in the presence of atmospheric radicals includes the formation of primary radicals, which are oxidized into ultimate products via a multistep process. The secondary reactions of primary radicals with the main atmospheric oxidizers—O_2, NO_2, and NO—are of special interest.

The purpose of our work was to study the kinetics of the reactions between dioxygen and the radicals resulting from the primary oxidation of PFAs, namely, CF_3CH_2OH, CH_2FCH_2OH, and CHF_2CH_2OH. For this study, it was necessary to find an appropriate source of primary radicals. It was reported that the reaction between chlorine atoms and ethanol proceeds, with a probability of >95%, via the abstraction of an H atom from the $\dot{C}H_2$ group [6]. By analogy, it can be assumed that the main reaction channel in the interaction between Cl and a PFA (e.g., 2,2,2-trifluoroethanol) is

$Cl + CF_3CH_2OH \longrightarrow CF_3\dot{C}HOH + HCl$. The bond dissociation energies calculated for the CF_3CH_2OH molecule indicate that the channel involving abstraction from the CH_2 group is exothermic:

$$Cl + CF_3CH_2OH \begin{cases} \nearrow CF_3\dot{C}HOH + HCl & \Delta H_{298} = -31 \text{ kJ/mol} \\ \searrow CF_3CH_2\dot{O} + HCl & \Delta H_{298} = 38 \text{ kJ/mol} \quad [7]. \end{cases}$$

The rate constant of this reaction at room temperature is $k = 5.6 \times 10^{11}$ cm^3 mol^{-1} s^{-1} [8]. However, the reaction between Cl and PFA is not quite a convenient source of radicals, because it is difficult to obtain a sufficiently high Cl concentration. As a consequence, the free-radical products of this reaction will form in low yield and will be difficult to detect experimentally. By contrast, passing difluorine through a radio-frequency discharge produces high concentrations of F atoms. In order to determine the formation of free radicals, we studied the kinetics of gas-phase reactions between some PFAs and fluorine atoms. 2-Fluoroethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol are typical PFAs. It was found that their reactions with F atoms are appropriate laboratory-scale sources of primary free radicals. The rate constants of these reactions have not been reported; therefore, any information concerning these rate constants would be of interest and of independent significance.
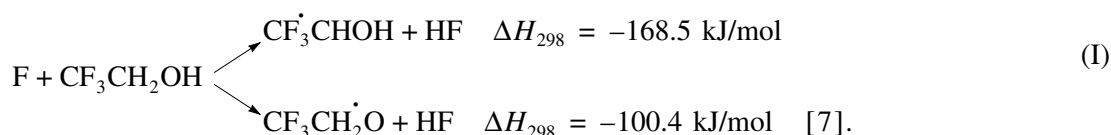
EXPERIMENTAL

Experimental setups and kinetic measurements were detailed in an earlier paper [1]. Experiments were carried out using a mass spectrometer with a modulated molecular beam. A cylindrical Pyrex flow reactor with a length of 50 cm and an inner diameter of 2.3 cm was attached to the mass spectrometer. The reactor had a mobile axial injector 0.9 cm in diameter and a jacket temperature-controlled with a circulating liquid. The temperature of this liquid determined the reactor temperature, which could be varied between 253 and 373 K and was maintained with an accuracy of ±2 K. Several replica runs were carried at several-week-long intervals in order to rule out the effect of data fluctuation. The carrier gas was helium. The typical gas velocity in the reactor was 6 m/s, and the total gas pressure in the reactor was 0.8–1.3 Torr. Fluorine atoms were produced in a radio-frequency discharge generated in a CF$_4$–He or F$_2$–He mixture (He was in >90% excess). The quartz discharge tube was positioned at a distance of 40 cm from the entrance hole of the mass spectrometer. A synthetic sapphire (Al$_2$O$_3$) ceramic insert was placed into the discharge tube in order to diminish the formation of oxygen atoms by the reaction between fluorine atoms and the tube material. PFA was introduced into the reaction zone through the axial injector. The gas flow rate was controlled and stabilized with a gas flow controller (Mass Flow Controller Series 1100, Type 1160 B). The gas pressure in the reactor was measured with an MKS Baratron (Type 122A) diaphragm pressure gauge. Stable reagents, atoms, and free radicals were admitted into the mass spectrometer as molecular beams. The beam formation system consisted of a nozzle and a separator. It was pumped using an oil vapor pump. The molecular beam was modulated in the chamber between the separator and the ion source of the quadrupole mass spectrometer. Electron-impact ionization was used. The electron energy ranged between 12 and 100 eV. The electron current was varied between 0 and 2 mA. After mass separation, ion currents were recorded using a secondary electron multiplier. The ion detection system included a synchronous detector (Princeton Applied Research, Model 124A) and an IBM PC. The lower PFA detection limit was ~10^{-14} mol/cm for a signal accumulation time of 300 s. The contact time in the reaction was varied by moving the injector some distance up to 30 cm. In the investigation of dioxygen–free radical reactions, dioxygen was injected into the reaction zone together with PFA.

The following chemicals were used: 99.996% helium (Messer Griesheim), oxygen gas (99.995%, Messer–Griesheim), 99% 2,2,2-trifluoroethanol (Lancaster), 95% 2,2-difluoroethanol (Fluorochem Ltd.), 95% 2-fluoroethanol (Aldrich), and 98.9% fluorine as 5% F$_2$ in He (Merck AG).

RESULTS AND DISCUSSION

Reaction (I): F + CF₃CH₂OH ⟶ Products

$$F + CF_3CH_2OH \begin{cases} \nearrow CF_3\dot{C}HOH + HF & \Delta H_{298} = -168.5 \text{ kJ/mol} \\ \searrow CF_3CH_2\dot{O} + HF & \Delta H_{298} = -100.4 \text{ kJ/mol} \quad [7]. \end{cases} \qquad \text{(I)}$$

The rate constant of this reaction was determined using the reaction

$$F + CH_4 \longrightarrow \dot{C}H_3 + HF \qquad (RI)$$
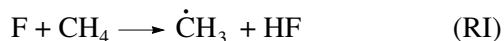
as the reference. The rate constant ratio for reactions (I) and (RI) was measured in the temperature range $258\ K < T < 358\ K$ at a helium pressure of 1.3 Torr. PFA and methane were fed simultaneously into the reactor. It can be demonstrated that the following relationship is valid under our experimental conditions:

$$\ln([CF_3CH_2OH]_{-F}/[CF_3CH_2OH]_{+F}) \\ = k_1/k_{r1}\ln([CH_4]_{-F}/[CH_4]_{+F}), \qquad (1)$$

where k_1 and k_{r1} are the rate constants, $[CF_3CH_2OH]_{-F}$ and $[CH_4]_{-F}$ are the concentrations of PFA and the reference reactant (CF_3CH_2OH and CH_4) before the reaction, and $[CF_3CH_2OH]_{+F}$ and $[CH_4]_{+F}$ are the same concentrations in the course of the reaction with fluorine atoms. The k_1/k_{r1} ratio was determined using relationship (1). The CF_3CH_2OH consumption varied, and its maximum value at room temperature was ~23%. CF_3CH_2OH and CH_4 were determined as their molecular peaks in mass spectra (m/e 100 and 16, respectively). Because the CF_3CH_2OH intensity was very low, low-energy (29.5-eV) electrons were used in ionization. This enabled us to diminish dissociative ionization and thereby increase the relative intensity of the molecular peak. The mass spectrum of CF_3CH_2OH indicated no fragments with m/e 16, facilitating the independent detection of either reactant. Note that, when PFA is consumed to an insignificant extent, the contribution from the fragment ions of the products or reaction (I) to the mass spectrum can be neglected. Data processing in terms of

Eq. (1) has demonstrated that $k_1/k_{r1} = 1.36$ at 300 K. Substituting $k_{r1} = 4.77 \times 10^{13}$ cm^3 mol^{-1} s^{-1} [9] into this ratio, we obtain $k_1 = (6.5 \pm 1.6) \times 10^{13}$ cm^3 mol^{-1} s^{-1}.
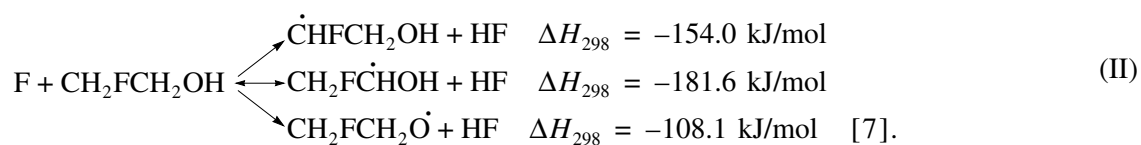
The plot of Eq. (1) for 258 K, which allows the rate constant of reaction (I) to be determined, is shown in Fig. 1. IUPAC recommends that the rate constants of bimolecular reactions at $T = 200$–300 K should be represented as $k = A\exp(-E/RT)$ [9].

Figure 2 displays the Arrhenius plot of k_1 at $T = 258$–358 K. The least squares analysis of the experimental data leads to $k_1 = (3.4 \pm 2.0) \times 10^{13}\exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(1.5 \pm 1.3)$ kJ/mol. Note the small value of the exponent. Hence, only the "effective" value of the activation energy can be considered.

The reaction mechanism was elucidated by mass spectrometric analysis of the reaction products. Figure 3 shows a portion of the mass spectrum of 2,2,2-trifluoroethanol and the reaction products. The light columns represent the mass spectrum of CF_3CH_2OH, and the dark columns represent the same portion of the spectrum during the reaction between 2,2,2-trifluoroethanol and fluorine atoms. The spectrum of the products exhibits strong peaks at m/e 20, 29, 30, 32, 50, 69, 83, 98, 99, and 129. The growth of the peak at m/e 99 is due to the formation of $CF_3CH_2\dot{O}$ and $CF_3\dot{C}HOH$ ($C_2H_2F_3O$) radicals. The peak at m/e 20 is assignable to the stable reaction product HF. The peaks at m/e 29, 30, 32, 50, 69, 83, and 98 are assignable to fragment ions of reaction products, such as CF_3CH_2O. The peak at m/e 129 is possibly due to a product of secondary reactions.

Reaction (II): F + CH$_2$FCH$_2$OH $\longrightarrow$ Products

$$F + CH_2FCH_2OH \begin{cases} \dot{C}HFCH_2OH + HF & \Delta H_{298} = -154.0 \text{ kJ/mol} \\ CH_2F\dot{C}HOH + HF & \Delta H_{298} = -181.6 \text{ kJ/mol} \\ CH_2FCH_2\dot{O} + HF & \Delta H_{298} = -108.1 \text{ kJ/mol} \quad [7]. \end{cases} \qquad (II)$$

The rate constant of this reaction was determined using two reference reactions, namely, reaction (RI) and

$$F + cyclohexane \longrightarrow products. \qquad (RII)$$
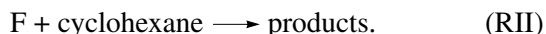
The ratio of the rate constants of reactions (II) and (RI) was measured at a pressure of 1.2 Torr and 278 K < T < 358 K, and the ratio of the rate constants of reactions (II) and (RII) was measured at 295 K. CH_2FCH_2OH, cyclo-C_6H_{12}, and CH_4 were determined as their molecular peaks at m/e 64, 84, and 16, respectively. Because the molecular peak due to CH_2FCH_2OH was rather intense, 70-eV electrons were used in ionization. The mass spectrum of 2-fluoroethanol for this
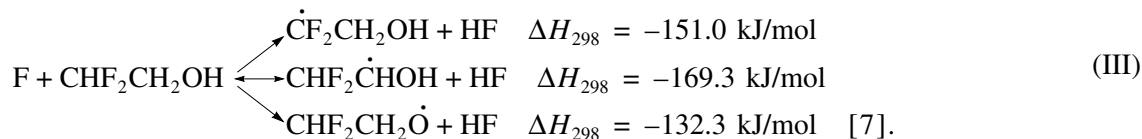
electron energy is known from the literature. It shows only a slight, if any, fragment peak at m/e 16. The mass spectrum of cyclohexane exhibits no fragment peak at m/e 64. Therefore, reactions (RI) and (RII) can be used as reference reactions and it is possible to independently monitor the concentrations of the reference reactants and CH_2FCH_2OH. Note that the contribution from the fragment ions of the products of reactions (II) and (RII) can be neglected because of the low consumption of CH_2FCH_2OH and cyclo-C_6H_{12}. The following rate constant ratios were obtained at room temperature: $k_2/k_{r1} = 2.37$ and $k_2/k_{r2} = 0.69$. Figure 4 shows how the CH_2FCH_2OH concentration is related to changes in the cyclohexane concentration. Using the k and k_{r2} values

reported in the literature, we found that the mean rate constant of reaction (II) at 295 K is $k_2 = (8.3 \pm 2.9) \times 10^{13}$ cm^3 mol^{-1} s^{-1}. By comparing the experimental k_2/k_{r1} data with the k_{r1} data known from the literature for $T = 258$–358 K, we estimated the activation energy of reaction (II) at $E_a = -0.5$ kJ/mol.

Reaction (III): F + CHF$_2$CH$_2$OH $\longrightarrow$ Products

$$F + CHF_2CH_2OH \left\langle \begin{array}{ll} \dot{C}F_2CH_2OH + HF & \Delta H_{298} = -151.0 \text{ kJ/mol} \\ CHF_2\dot{C}HOH + HF & \Delta H_{298} = -169.3 \text{ kJ/mol} \\ CHF_2CH_2\dot{O} + HF & \Delta H_{298} = -132.3 \text{ kJ/mol} \quad [7]. \end{array} \right. \tag{III}$$

The rate constant of this reaction was determined using two reference reactions, namely, reaction (RI) and

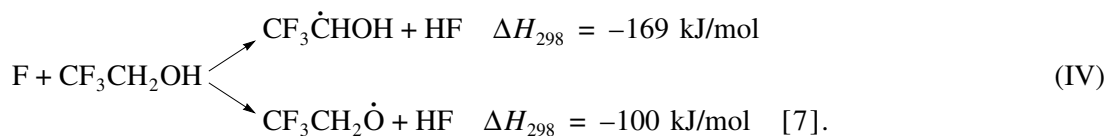$$\text{F + cyclopentane} \longrightarrow \text{products.} \tag{RIII}$$
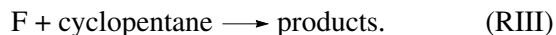
We chose reaction (RIII) for the reason that k_3 and k_{r3} are similar and it is necessary to independently monitor, by mass spectrometry, the CHF$_2$CH$_2$OH and cyclo-C$_5$H$_{10}$ concentrations as peaks at m/e 82 and 70, respectively. The mass spectrum of 2,2-difluoroethanol recorded at the ionizing electron energy of 70 eV exhibited no fragment peak at m/e 16, and it was, therefore, possible to detect CHF$_2$CH$_2$OH and CH$_4$ independently. Measurements were taken at room temperature and a helium pressure of 1.0 Torr. The maximum CHF$_2$CH$_2$OH consumption was ~12%. This low PFA conversion made it possible to avoid, to a large extent, the reactions between secondary radicals and fluorine atoms. The following rate constant ratios were measured at room temperature: $k_3/k_{r1} = 1.46$ and $k_3/k_{r3} = 0.34$. Hence, the mean rate constant of reaction (III) at 296 K is $k_3 = (6.4 \pm 0.6) \times 10^{13}$ cm^3 mol^{-1} s^{-1}.

The PFAs were recently put forward as a new generation of chlorofluorocarbon substitutes. The degradation of PFAs in the troposphere is most likely due to reactions involving the $\dot{O}H$ radical. For this reason, our study was focused on these reactions. It is possible to compare the above rate constants of PFA–fluorine atom reactions with the rate constants of PFA–$\dot{O}H$ reactions available from the literature [4]. The rate constants of the reactions of CH$_2$FCH$_2$OH, CHF$_2$CH$_2$OH, and CF$_3$CH$_2$OH with fluorine atoms are related as 8.3 : 6.4 : 6.5 (10^{13} cm^3 mol^{-1} s^{-1}). The rate constants of the reactions of these compounds with $\dot{O}H$ are related as 6.5 : 2.11 : 0.66 (10^{11} cm^3 mol^{-1} s^{-1}). It is assumed that the reactivity of CX$_3$CH$_2$OH (X = H, F) toward $\dot{O}H$ decreases as the number of fluorine atoms in the CX$_3$ group is increased and this is primarily due to the inductive effect of the fluorine atoms on the electron density in the transition complex. The fluorine atoms in the CX$_3$ group decrease the electron density on the H atom being abstracted from the CH$_2$ group and destabilize the transition state. In the reactions between a PFA and a fluorine atom, the abstraction of an H atom from the CH$_2$ group is thermodynamically the most favorable process and, at the same time, the effect of the CX$_3$ group on the transition complex seems to be negligible. The slight increase in reactivity observed in going from CF$_3$ to CH$_2$F is likely to be merely due to the increase in the number of H atoms in the PFA molecule.


Reaction (IV): O$_2$ + C$_2$H$_2$F$_3$O $\longrightarrow$ Products

The reaction between fluorine atoms and 2,2,2-trifluoroethanol was used as the source of CF$_3$$\dot{C}$HOH and CF$_3CH_2$$\dot{O}$ radicals (with the general formula C$_2$H$_2$F$_3$O):

$$F + CF_3CH_2OH \left\langle \begin{array}{ll} CF_3\dot{C}HOH + HF & \Delta H_{298} = -169 \text{ kJ/mol} \\ CF_3CH_2\dot{O} + HF & \Delta H_{298} = -100 \text{ kJ/mol} \quad [7]. \end{array} \right. \tag{IV}$$

Both reaction channels are exothermic, and, therefore, the formation of two free-radical products would be expected. It is very difficult to predict the channel via which the reaction will proceed. It is of interest to evaluate the rate of disappearance of both free-radical products in their reactions with dioxygen. Obviously, the radicals that form via these channels react with dioxygen at different rates. Therefore, it is possible to experimentally determine only the total rate constant of the disappearance of CF$_3$$\dot{O}$HOH and CF$_3CH_2$$\dot{O}$ (C$_2$H$_2$F$_3$O) in their reactions with dioxygen (k_4).

$\ln([CF_3CH_2OH]_{-F}/CF_3CH_2OH_{+F})$
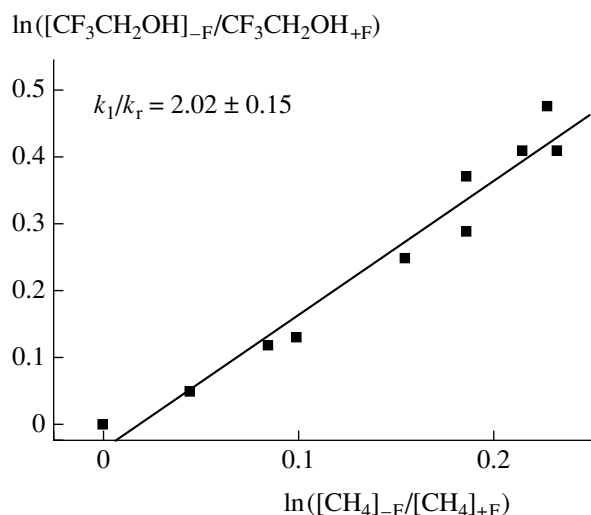
Fig. 1. Relationship between the consumption of CF_3CH_2OH and CH_4 in the reactions of these compounds with fluorine atoms at 258 K.

Reaction (IV) was investigated at $T = 258–358$ K by the relative measurement method. The oxygen partial pressure in the reactor was varied between 0.08 and 0.1 Torr.

Preliminary experiments have demonstrated that reaction (IV) is rather slow and its grate constant is $\sim 2 \times 10^{10}$ cm^3 mol^{-1} s^{-1}. For this reason, the trimolecular reaction

$$\dot{C}HCl_2 + O_2 + He \longrightarrow products \qquad (RIV)$$
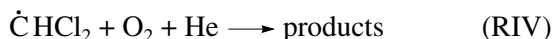
was used as the reference. Its rate is similar to the rate of reaction (RIV) under the experimental conditions examined. The source of $\dot{C}HCl_2$ radicals was the reaction

$$F + CH_2Cl_2 \longrightarrow \dot{C}HCl_2 + HF. \qquad (RV)$$

The reaction between dichloromethyl and dioxygen (reaction (RIV)) was studied earlier in a wide temperature range in a flow reactor using photoionization mass spectrometry [10]. The low-pressure limit was determined for the rate constant of this reaction ($k_{r4(0)}$).

The rate constant ratio for reactions (IV) and (RIV) was derived from the expression

$$\ln([C_2H_2F3O]_{-O_2}/[C_2H_2F_3O]_{+O_2})$$
$$= k_4/k_{r4}\ln([CHCl_2]_{-O_2}/[CHCl]_{+O_2}), \qquad (2)$$

where k_4 and k_{r4} are the rate constants of reactions (IV) and (RIV), $[C_2H_2F_3O]_{-O_2}$ and $[CHCl_2]_{-O_2}$ are the initial concentrations of $C_2H_2F_3\dot{O}$ and $\dot{C}HCl_2$, and $[C_2H_2F_3O]_{+O_2}$ and $[CHCl_2]_{+O_2}$ are the concentrations of these species during their reactions with dioxygen molecules. The concentrations of radicals with the general formula $C_2H_2F_3\dot{O}$ and of $\dot{C}HCl_2$ radicals were monitored as $C_2H_2F_3O^+$ and $CH^{35}Cl^{37}Cl^+$ ion intensities at m/e 99 and 85 under the conditions of reactions (I) and (RV), respectively. The decrease in the 2,2,2-trifluoroetanol and dichloromethane concentrations during these reactions and the corresponding decrease in the fragment ion intensities at m/e 99 and 85 were taken into account. Note that the mass spectrum of the products of reaction (I) (Fig. 3) exhibited no peak at m/e 85. Therefore, it was possible to detect independently the radicals with the general formula $C_2H_2F_3\dot{O}$ and the $\dot{C}HCl_2$ radical. Figure 5 presents the plot of relationship (2), illustrating the variation of the consumption of $C_2H_2F_3\dot{O}$ and $\dot{C}HCl_2$ radicals during their reactions with dioxygen at 298 K.

In the calculation of the trimolecular rate constant k_{r4} for our experimental conditions, we used the Troe equation [11] in the following form:

$$\log k_{r4} = \log\{k_{r4(0)}[He]/(1 + k_{r4(0)}[He]/k_{r4(\infty)}\}$$
$$+ (\log F_c)/(1 + [(1/N_c)\log\{k_{r4(0)}[He]/k_{r4(\infty)}\}]^2),$$

with $F_c = \exp(-T/C)$ and $N_c = 0.75 - 1.27\log F_c$, where C is a constant. Note that, in the Troe equation, the rate constant at low pressures depends only slightly on the parameters F_c and $k_{(\infty)}$. For this reason, the constant C was set to be 255, the value recommended for the reaction between $\dot{C}Cl_3$ and dioxygen [12]. The high-pressure limit of the rate constant was calculated using the familiar formula $k_{r4(\infty)} = 1.69 \times 10^{12} (T/298)^{-1.4}$ cm^3 mol^{-1} s^{-1} [12], which was set up for the case of nitrogen as the carrier gas. The low-pressure limit of the rate constant for helium at the carrier gas is $k_{r4(0)} = 1.56 \times 10^{17}(T/298)^{-6.7}$ cm^6 mol^{-2} s^{-1}.

Table 1. Temperature-dependent rate constant data for reactions (IV) and (RIV)

Rate constant	T, K				
	258	278	298	328	358
$k_4 \times 10^{-10}$, cm^3 mol^{-1} s^{-1}	4.31	3.50	1.84	1.55	1.22
$k_{r4} \times 10^{-10}$, cm^3 mol^{-1} s^{-1}	2.30	1.31	0.62	0.43	0.23
k_4/k_{r4}	1.87	2.68	2.95	3.60	5.41
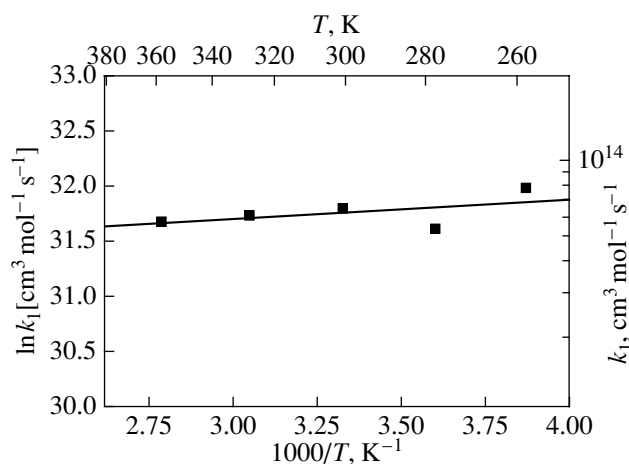
Fig. 2. Arrhenius plot of the rate constant of the reaction between 2,2,2-trifluoroethanol and fluorine atoms.

Fig. 3. Portions of the mass spectra of CF_3CH_2OH and of the products of its reaction with fluorine atoms.

Table 1 lists k_4 data, calculated rate constants of the reference reaction (k_{r4}), and k_4/k_{r4} ratios determined experimentally at various temperatures. An analysis of these temperature-dependent data led to $k_4 = (3.8 \pm 2.0) \times 10^8 \exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(10.2 \pm 1.5)$ kJ/mol. Here, the exponent is small, so only the "effective" value of the activation energy can be considered.

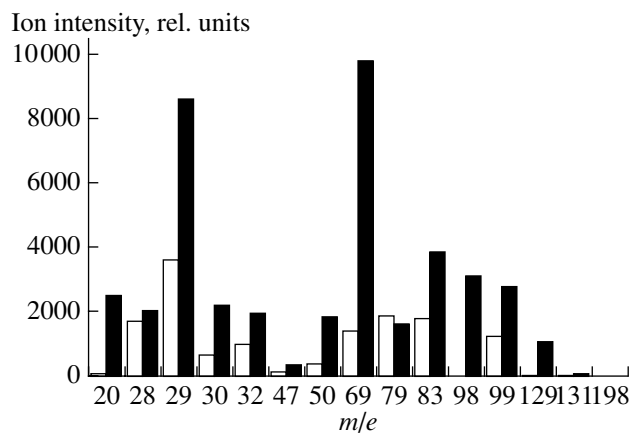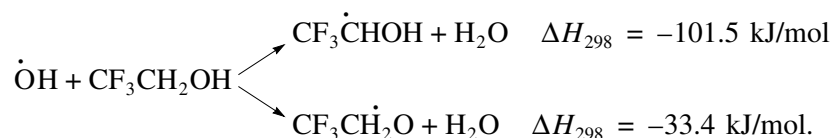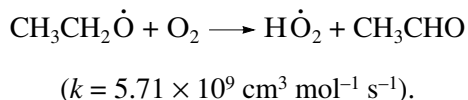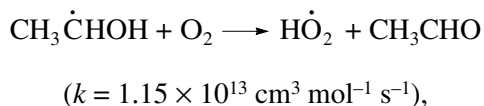As is mentioned above, the dominant oxidizer in the troposphere in the daytime is the hydroxyl radical $\dot{O}H$. Both channels of the reaction between 2,2,2-trifluoroethanol and $\dot{O}H$ are exothermic, and it can be assumed that the reaction yields the isomeric radicals $CF_3\dot{C}HOH$ and $CF_3CH_2\dot{O}$:

$$\dot{O}H + CF_3CH_2OH \begin{cases} CF_3\dot{C}HOH + H_2O \quad \Delta H_{298} = -101.5 \text{ kJ/mol} \\ CF_3C\dot{H}_2O + H_2O \quad \Delta H_{298} = -33.4 \text{ kJ/mol.} \end{cases}$$

In the Earth's atmosphere, the resulting radicals react with dioxygen. No data concerning these reactions have been reported in the literature. However, reactions of the isomeric radicals CH_3CHOH and $CH_3CH_2\dot{O}$ with dioxygen are known, which can be regarded as analogues of reaction (IV):

$$CH_3\dot{C}HOH + O_2 \longrightarrow H\dot{O}_2 + CH_3CHO$$

$$(k = 1.15 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}),$$

$$CH_3CH_2\dot{O} + O_2 \longrightarrow H\dot{O}_2 + CH_3CHO$$

$$(k = 5.71 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}).$$

These reactions yield the same products. Based on this analogy, it can be assumed that $CF_3\dot{C}HOH$ will react with O_2 more rapidly than $CF_3CH_2\dot{O}$. Furthermore, it is likely that the secondary reactions of these radicals yield the same products:

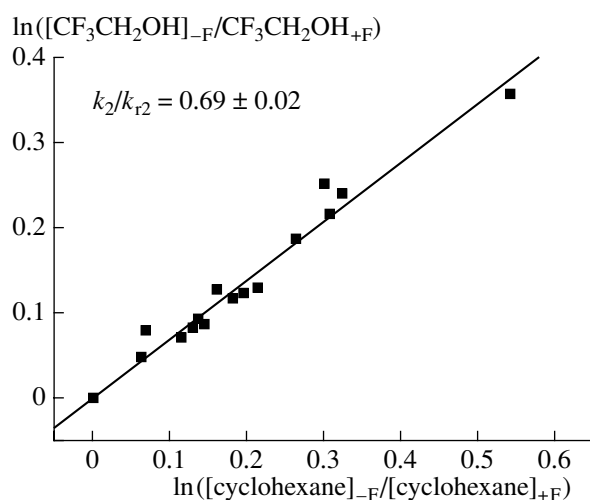$$CF_3\dot{C}HOH + O_2 \longrightarrow H\dot{O}_2 + CF_3CHO,$$

$$CF_3CH_2\dot{O} + O_2 \longrightarrow H\dot{O}_2 + CF_3CHO.$$
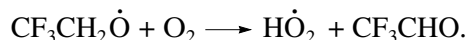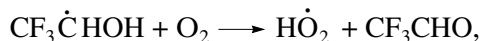
The observed height of the peak at m/e 98 confirms that reaction (IV) yields the stable product $CF_3C(O)H$, which undergoes further conversion in the atmosphere. The atmospheric fate of the $H\dot{O}_2$ radical, the other product of the reactions, is well known and has been widely discussed [18].

Reaction (V): $O_2 + C_2H_4FO \longrightarrow$ Products

The formation of the isomeric radicals $\dot{C}HFCH_2OH$, $CH_2F\dot{C}HOH$, and $CH_2FCH_2\dot{O}$ (with the general formula C_2H_4FO) is thermodynamically possible in the reaction between fluorine atoms and CH_2FCH_2OH. Note that the different radicals resulting from reaction (II) may react with O_2 at different rates. In our experiments, we measured the total disappearance rate of the radicals with the general formula

$\ln([CF_3CH_2OH]_{-F}/CF_3CH_2OH_{+F})$

$k_2/k_{r2} = 0.69 \pm 0.02$

$\ln([\text{cyclohexane}]_{-F}/[\text{cyclohexane}]_{+F})$

Fig. 4. Relationship between the consumptions of CH_2FCH_2OH and cyclohexane in the reactions of these compounds with fluorine atoms at 295 K.

$\ln([C_2H_2F_3O]_{-O_2}/[C_2H_2F_3O]_{+O_2})$

$k_4/k_{r4} = 2.95 \pm 0.26$

$\ln([CHCl_2]_{-O_2}/[CHCl_2]_{+O_2})$
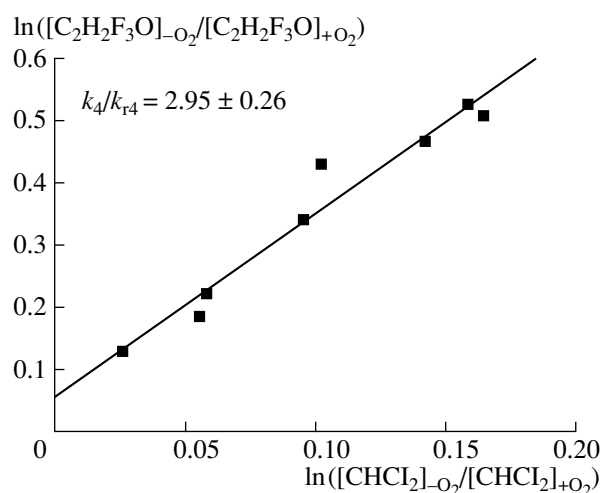
Fig. 5. Relationship between the consumption of the radicals with the general formula $C_2H_2F_3\dot{O}$ and the consumption of $\dot{C}HCl_2$ in the reactions of these radicals with dioxygen at 298 K.

C_2H_4FO. The reaction between C_2H_4FO and dioxygen was studied by the relative measurement method between 258 and 358 K. The reference was the bimolecular reaction

$$1,4\text{-dioxanyl} + O_2 \longrightarrow \text{products}, \qquad (RVI)$$
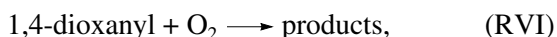
whose rate constant at room temperature is $k_{r6} \approx 10^{12}$ cm^3 mol^{-1} s^{-1}. In the temperature range examined, $k_{r6} = 2.5 \times 10^{11}\exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(3.9 \pm 1.2)$ kJ/mol [13]. The concentrations of radicals in reactions (V) and (RVI) were monitored as mass spectrometric peaks at m/e 63 (for $C_2H_4FO^+$) and 87 (for $C_4H_7O_2^+$). The ratio of the rate constants of reaction (V) and the reference reaction, k_5/k_{r6}, was determined using a relationship similar to Eq. (2). Next, knowing k_{r6}, we calculated k_5. Figure 6 illustrates, in a coordinate system allowing the k_5/k_{r6} ratio to be determined, the consumption of C_2H_4FO and 1,4-dioxanyl radicals in their reactions with dioxygen at 298 K. The temperature-dependent k_5 data thus obtained are listed in Table 2.

In the narrow temperature range of 258–358 K, k_5 obeys the Arrhenius equation with a constant preexponential factor (Fig. 7): $k_5 = (1.3 \pm 0.6) \times 10^{11} \times \exp(-E/RT)$ cm^3 mol^{-1} s^{-1}, where $E = -(5.3 \pm 1.4)$ kJ/mol. This temperature dependence provides information concerning only the "effective" value of the activation energy.

The stable products of reaction (V) were identified. The products forming in the flow reactor were frozen in a liquid-nitrogen trap. The gas mixture was analyzed by FTIR spectroscopy while gradually warming the trap to room temperature. The IR spectra of HCHO, HCFO, and CH_2FCHO were recorded. Using this technique, we identified the following stable products: $HFC=C(OH)H$, HCHO, HCFO, and CH_2FCHO.

Figure 8 depicts the evolution of the mass spectrum during the reaction in the flow reactor. The most pronounced growth was observed for the peaks at m/e 28, 29, 30, 44, 47, 48, 60, 61, and 62. The changes in the peak intensities at m/e 30 ($HCHO^+$), as well as at m/e 29 and 28 (fragment ions), are due to the formation of formaldehyde (HCHO). The growth of the peaks at m/e 48 ($HCFO^+$) and 47 is likely due to the formation of

Table 2. Temperature-dependent rate constant data for the reaction $O_2 + C_2H_4FO \longrightarrow$ products

| Rate constant	T, K				
	258	278	298	328	358
$k_5 \times 10^{-12}$, cm^3 mol^{-1} s^{-1}	1.63	1.20	1.23	0.91	0.79
$k_{r6} \times 10^{-12}$, cm^3 mol^{-1} s^{-1} [13]	1.54	1.35	1.21	1.05	0.93
k_5/k_{r6}	1.06	0.89	1.02	0.87	0.85
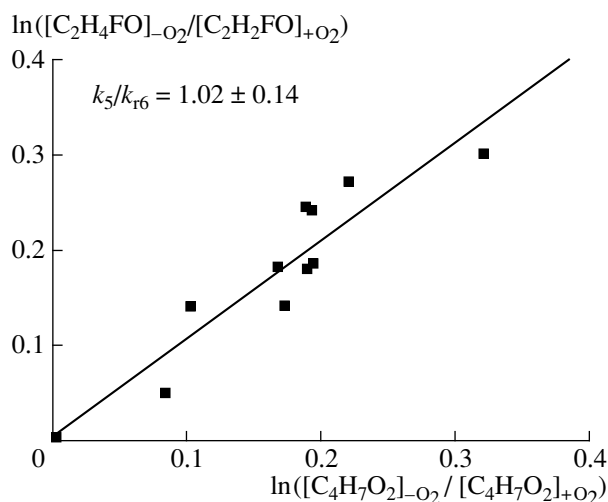
Fig. 6. Relationship between the consumption of the radicals with the general formula $C_2H_4F\dot{O}$ and the consumption of 1,4-dioxanyl in the reactions of these radicals with dioxygen at 298 K.
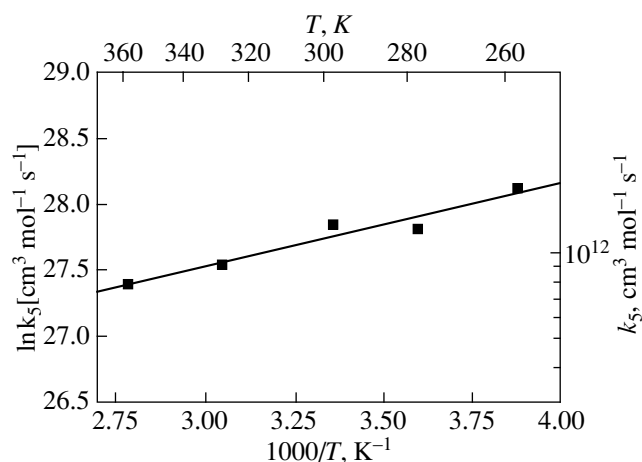
Fig. 7. Arrhenius plot of the rate constant of the reaction between dioxygen and the radicals with the general formula $C_2H_4F\dot{O}$.
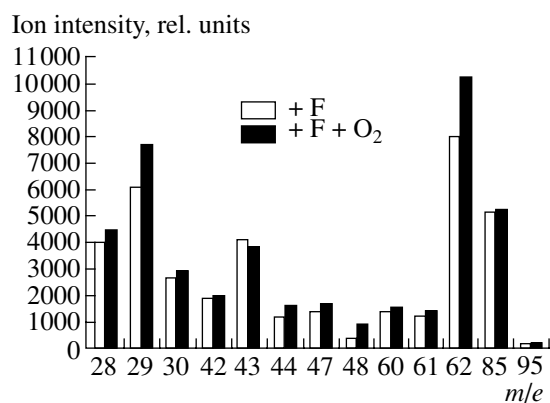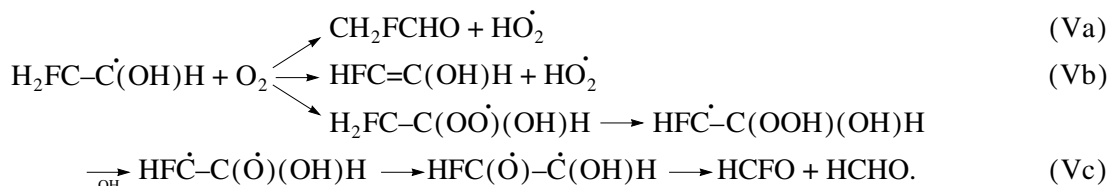

Fig. 8. Changes in the mass spectra of the reactants and products of the reaction $O_2 + C_2H_4FO$ caused by the introduction of dioxygen into the reactor.
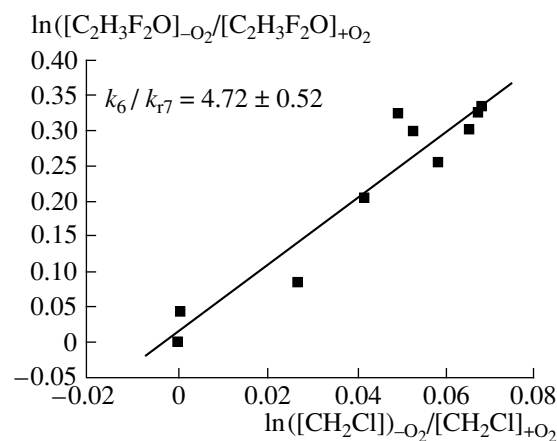
Fig. 9. Relationship between the consumption of the radicals with the general formula $C_2H_3F_2\dot{O}$ and the consumption of $\dot{C}H_2Cl$ in the reactions of these radicals with dioxygen at 300 K.

formyl fluoride (HCFO). The growth of the peaks at m/e 62 (CH_2FCHO^+), 61, and 60 is caused by the formation of the reaction product CH_2FCHO. The growth of the peak at m/e 44 is apparently due to secondary reactions yielding CO_2 as a final product.

The following mechanism of reaction (V) was deduced from the results of these experiments. There are three channels for the reaction between the $CH_2F\dot{C}HOH$ radical and dioxygen:

$$H_2FC\text{–}\dot{C}(OH)H + O_2 \begin{cases} CH_2FCHO + H\dot{O}_2 & \text{(Va)} \\ HFC\text{=}C(OH)H + H\dot{O}_2 & \text{(Vb)} \\ H_2FC\text{–}C(O\dot{O})(OH)H \longrightarrow HF\dot{C}\text{–}C(OOH)(OH)H \end{cases}$$

$$\xrightarrow[-OH]{} HF\dot{C}\text{–}C(\dot{O})(OH)H \longrightarrow HFC(\dot{O})\text{–}\dot{C}(OH)H \longrightarrow HCFO + HCHO. \quad \text{(Vc)}$$
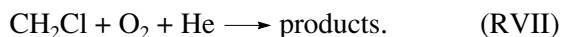
Table 3. Rate constants of the reactions between dioxygen and radicals at room temperature

Radical type	Rate constant, cm^3 mol^{-1} s^{-1}
$CF_3\dot{C}HOH$, $CF_3CH_2O^{\bullet}$	1.84×10^{10}
$\dot{C}F_2CH_2OH$, $CHF_2\dot{C}HOH$, $CHF_2CH_2O^{\bullet}$	1.32×10^{11}
$\dot{C}HFCH_2OH$, $CH_2F\dot{C}HOH$, $CH_2FCH_2O^{\bullet}$	1.23×10^{12}
$CH_3\dot{C}HOH$	1.15×10^{13}
$\dot{C}H_2OH$	5.66×10^{12}
$CH_3CH_2O^{\bullet}$	5.71×10^{9}
$CH_3O^{\bullet}$	1.16×10^{9}

Reaction (VI): $O_2 + C_2H_3F_2O \longrightarrow$ Products

The possible products of the reaction between fluorine atoms and CHF_2CH_2OH are $\dot{C}F_2CH_2OH$, $CHF_2\dot{C}HOH$, and $CHF_2CH_2\dot{O}$ (radicals with the general formula $C_2H_3F_2O$). The reaction of the $C_2H_3F_2O$ radicals with dioxygen, which was carried out at 300 K, a helium pressure of 1.37 Torr, and an oxygen partial pressure of $(0.75–4.5) \times 10^{-2}$ Torr, was investigated by the relative measurement method. The reference reaction was

$$CH_2Cl + O_2 + He \longrightarrow products. \qquad (RVII)$$

The low- and high-pressure limits of the rate constant of reaction (RVII) for nitrogen as the carrier gas

$\ln([C_2H_2F_3O])_{-NO}/[C_2H_2F_3O]_{+NO}$
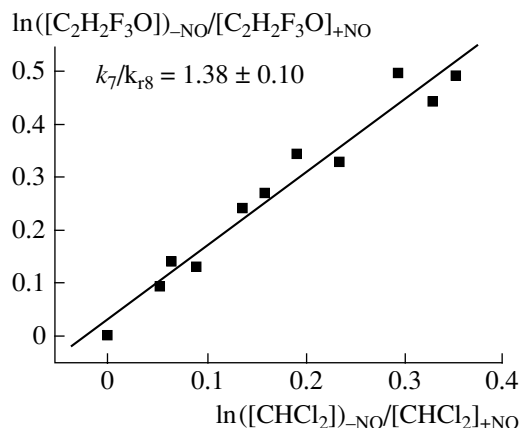
Fig. 10. Relationship between the consumption of the radicals with the general formula $C_2H_3F_2\dot{O}$ and the consumption of CH_2Cl in the reactions of these radicals with NO at 298 K.

are known from the literature: $k_{r7(0)} = 6.9 \times 10^{17}$ cm^6 mol^{-2} s^{-1} and $k_{r7(\infty)} = 1.75 \times 10^{12}$ cm^3 mol^{-1} s^{-1}. Based on these values, we estimated k_{r7} in the bimolecular approximation applied to our experimental conditions, using the Troe equation for helium as the carrier gas:

$$\log k_{r7} = \log\{k_{r7(0)}[He]/(1 + k_{r7(0)}[He]/k_{r7(\infty)})\}$$
$$+ (\log F_c)/(1 + [(1/N_c)\log\{k_{r7(0)}[He]/k_{r7(\infty)}\}]^2).$$

The following parameters were used in these calculations: $F_c = \exp(-T/C)$, $N_c = 0.75 - 1.27 \log F_c$, and $C = 255$. The rate constant of reaction (RVII) was thus estimated at $k_{r7} = 2.8 \times 10^{10}$ cm^3 mol^{-1} s^{-1}. The ratio of the rate constants of reaction (VI) and the reference reaction was determined using a formula similar to Eq. (2). The concentrations of $C_2H_3F_2O$ and $\dot{C}H_2Cl$ radicals were monitored as the intensities of the peaks at m/e 81 (for $C_2H_3F_2O^+$) and 49 (for CH_2Cl^+). The observed rate constant ratio, $k_6/k_{r7} = 4.72$ (Fig. 9), led to $k_6 = 1.32 \times 10^{11}$ cm^3 mol^{-1} s^{-1} at $T = 300$ K.

The rate constants of the reactions between O_2 and the radicals resulting from simplest PFAs are presented in Table 3. The same data available in the literature for methanol and ethanol are also presented there.

The effect of the composition of the terminal CX_3 (X = H, F) group on the rate constant of the reaction between the PFA molecule and the $\dot{O}H$ radical was estimated earlier: the rate constant changes from 1 to 0.32 and then to 0.1 (in relative units) in going from CH_2F to CF_3 (its logarithm is a linear function of the electronegativity of the terminal group). In the case of the radical–O_2 reaction, the effect of the CX_3 group is stronger: the rate constants are related as 1 : 0.11 : 0.02.

Reaction (VII): $NO + C_2H_2F_3O \longrightarrow$ Products

We carried out a kinetic study of the reaction of the $CF_3\dot{C}HOH$ and $CF_3CH_2\dot{O}$ radicals ($C_2H_2F_3O$) with NO. The rate constant of this reaction at room temperature and a helium pressure of 1.09 Torr was determined by the relative measurement method. The reference was the trimolecular reaction

$$\dot{C}HCl_2 + NO + He \longrightarrow products. \qquad (RVIII)$$
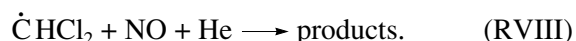
The rate of this reaction was determined by an independent experiment, again using the relative measurement method. The rate constant of reaction (RVIII) was compared to that of the reaction

$$\dot{C}H_2F + NO + He \longrightarrow products. \qquad (RIX)$$
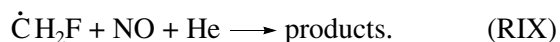
The rate constant of the latter is known from the literature: $k_{r9(0)} = 1.5 \times 10^{17}$ cm^6 mol^{-2} s^{-1} [14]. We found that $k_{r8}/k_{r9} = 0.81 \pm 0.19$. The radicals $\dot{C}HCl_2$ and $C_2H_2F_3O$ were obtained by reacting fluorine atoms with dichlo-

romethane and trifluoroethanol, respectively. The k_7/k_{r8} ratio was determined using the equation

$$\ln([C_2H_2F_3O]_{-NO}/[C_2H_2F_3O]_{+NO})$$
$$= k_7/k_{r8}\ln([CHCl_2]_{-NO}/[CHCl_2]_{+NO}), \quad (3)$$

where k_7 and k_{r8} are the rate constants of reactions (VII) and (RVIII), $[C_2H_2F_3O]_{-NO}$ and $[CHCl_2]_{-NO}$ are the initial concentrations of $C_2H_2F_3O$ and $\dot{C}HCl_2$, and $[C_2H_2F_3O]_{+NO}$ and $[CHCl_2]_{+NO}$ are the concentrations of these species during their reactions with NO. The concentrations of radicals were monitored in the same way as in the case of the reactions with O_2. The data thus obtained are presented in Fig. 10. The slope of the straight line implies $k_7/k_{r8} = 1.38 \pm 0.10$. Assuming that the rate of reaction (RVIII) is a linear function of the helium concentration, we found the low-pressure limit of the rate constant of this reaction in the bimolecular approximation: at 298 K, $k_{r8} = (1.21 \pm 0.28) \times 10^{17}$ [He] cm^6 mol^{-2} s^{-1}. These data enabled us to calculate the rate constant of reaction (VII) at 298 K: $k_7(298) = 9.7 \times 10^9$ cm^3 mol^{-1} s^{-1} ([He] $= 5.8 \times 10^{-8}$ mol/cm^3). Note that the rate of reaction (VII) is of the same order as the rate of the trimolecular reaction (RVIII). The value of k_7 at 298 K can be compared with the rate constant of the reaction between NO and the methoxyl radical at 1 Torr. In the reaction NO + CH_3O, there is a probability of an H atom being abstracted to yield $HNO + CH_2O$. The rate constant of this process at a helium pressure of 0.7–8.5 Torr is $k = 1.9 \times 10^{12}$ cm^3 mol^{-1} s^{-1}. Apparently, a similar bimolecular channel exists in the reaction NO + $C_2H_2F_3O$; however, k_7 is two orders of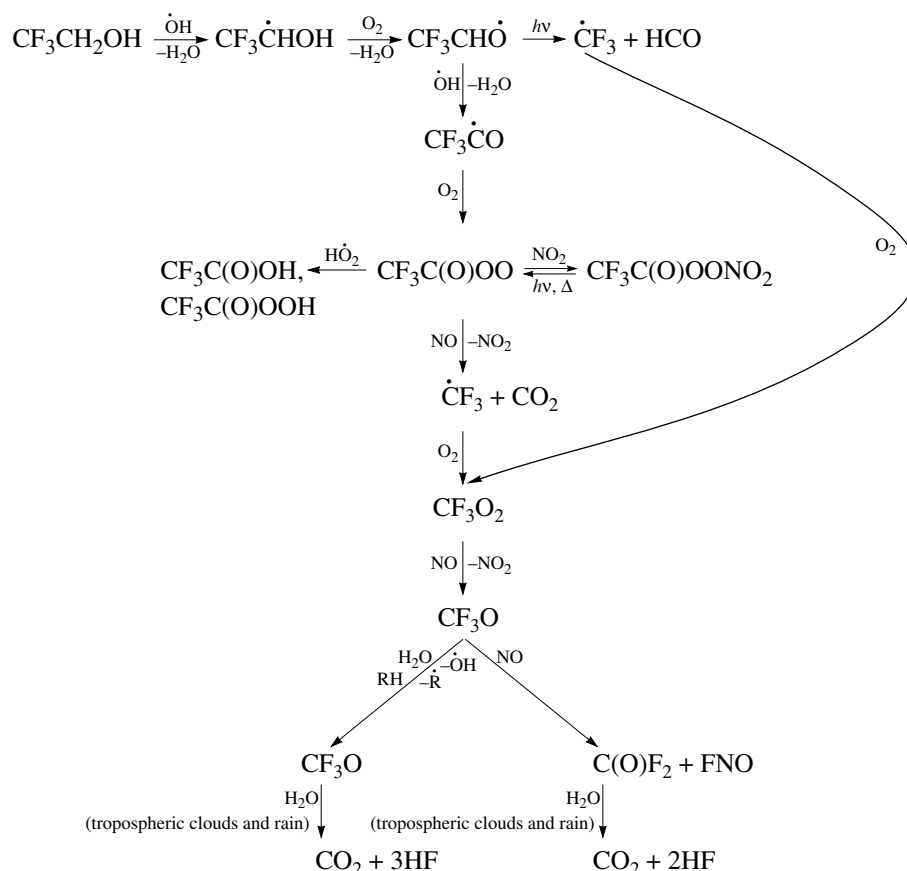 magnitude smaller than k. As in the case of the $\dot{O}H$ + PFA reactions, this can be explained by the inductive effect exerted by the CF_3 group on the electron density in the transition complex during the abstraction of an H atom (C–H bond breaking). Furthermore, for the reaction NO + CH_3O, there is a channel leading to an adduct, specifically, methyl nitrite (CH_3ONO). The formation rate of the adduct depends on pressure and on the nature of the carrier gas. At a helium pressure of 1.09 Torr, the low-pressure limit of the bimolecular rate constant is $k_{(0)}$[He] $\approx 3 \times 10^{11}$ cm^3 mol^{-1} s^{-1} [15]. Thus, the $k_7(298)$ value obtained in this study is more than one order of magnitude smaller than $k_{(0)}$[He]. Miyoshi et al. [16] measured the rate constant of the reaction $CH_3\dot{C}HOH$ + NO under similar carrier-gas pressures ([He] $= 12.24 \times 10^{-8}$ mol/cm^3). The rate constant of this reaction was pressure-independent within the experimental error and was equal to 3.8×10^{13} cm^3 mol^{-1} s^{-1}, three orders of magnitude larger than k_7 at 298 K. The reaction products were not identified. It was only assumed that the dominant reaction channel is the abstraction of an H atom from the radical, yielding

HNO and CH_3CHO. As is mentioned above, the difference between the rates of the $CH_3\dot{C}HOH$ + NO and $C_2H_2F_3\dot{O}$ + NO reactions is likely due to the effect of the CF_3 group on the electron density in the transition complex. Our $k_7(298)$ determination procedure is based on rate constant data for the reference reaction (RVIII). Compare the low-pressure limit of the rate constant of the reaction NO + $\dot{C}HCl_2$, which was found to be 1.21×10^{17} cm^6 mol^{-2} s^{-1}, to the rate constant of the reaction $\dot{C}FCl_2$ + NO + $N_2 \longrightarrow$ products, which is reported to be 3.6×10^{18} cm^6 mol^{-2} s^{-1} [17]. The value of $k_{(0)}$ is larger for the reaction involving $\dot{C}FCl_2$ than for the reaction involving $\dot{C}HCl_2$. The same is true for the reactions of $\dot{C}HCl_2$ and $\dot{C}FCl_2$ with dioxygen: their rate constants in the low-pressure limit are, respectively, 1.56×10^{17} and 2.0×10^{18} cm^6 mol^{-2} s^{-1} [9, 10].

Atmospheric Degradation of PFAs

From the results of our experiments and literature data, it is possible to derive a scheme of atmospheric PFA degradation, including tropospheric and stratospheric processes. The following key question should be answered by this scheme: What is the effect of the PFA degradation products on the Earth's ozone layer? Furthermore, it is important to find out whether the degradation products contain free radicals that can decompose ozone and whether this process can yield long-lived products capable of enhancing the greenhouse effect.

For the sake of simplicity, the above scheme of atmospheric PFA degradation is limited to 2,2,2-trifluoroethanol conversions. The main channel of 2,2,2-trifluoroethanol degradation is the reaction with the hydroxyl radical [5]. The resulting $C_2H_2F_3O$ radical reacts rapidly with atmospheric dioxygen (reaction (IV)), yielding trifluoroacetaldehyde, $CF_3CH\dot{O}$. The latter can decompose into $\dot{C}F_3$ and $CH\dot{O}$ under the action of $\lambda > 290$ nm light or react with hydroxyl to produce the trifluoromethylacyl radical $CF_3\dot{C}O$. Next, an acyl peroxy radical results from the reaction between $CF_3\dot{C}O$ and oxygen. The reactions involving $CF_3C(O)OO$ are detailed elsewhere [18]. The rapid reaction between this radical and NO yields trifluoromethyl and carbon dioxide. The main intermediate in 2,2,2-trifluoroethanol degradation is the $\dot{C}F_3$ radical, which is converted to CF_3O via reactions with O_2 and NO. The removal of CF_3O from the atmosphere is due to reactions of this radical with minor components of the atmosphere, such as water vapor, methane, and nitric oxide. The products—trifluoromethanol and carbonyl fluoride—disappear in the troposphere through physical processes and

$$CF_3CH_2OH \xrightarrow[-H_2O]{\dot{O}H} CF_3\dot{C}HOH \xrightarrow[-H_2O]{O_2} CF_3CH\dot{O} \xrightarrow{h\nu} \dot{C}F_3 + HCO$$

$$\Big\downarrow \dot{O}H \;\; -H_2O$$

$$CF_3\dot{C}O$$

$$\Big\downarrow O_2$$

$$CF_3C(O)OH, \xleftarrow{H\dot{O}_2} CF_3C(O)OO \underset{h\nu,\Delta}{\overset{NO_2}{\rightleftarrows}} CF_3C(O)OONO_2$$
$$CF_3C(O)OOH$$

$$\Big\downarrow NO \;\; -NO_2$$

$$\dot{C}F_3 + CO_2$$

$$\Big\downarrow O_2$$

$$CF_3O_2$$

$$\Big\downarrow NO \;\; -NO_2$$

$$CF_3O$$

RH $\overset{H_2O}{\underset{-\dot{R}}{\diagup}}$ $\dot{O}H$ $\overset{NO}{\diagdown}$

$$CF_3O \qquad\qquad C(O)F_2 + FNO$$

$$\Big\downarrow {}^{H_2O} \qquad\qquad \Big\downarrow {}^{H_2O}$$
(tropospheric clouds and rain)   (tropospheric clouds and rain)

$$CO_2 + 3HF \qquad\qquad CO_2 + 2HF$$

($h\nu$ and Δ designate photolysis and thermal decomposition, respectively.
Near arrows, reactants are given the sign + and one
of the products appears with the sign –.)

Scheme of the main CF_3CH_2OH degradation processes in the atmosphere.

hydrolysis, which play a more significant role than photolysis or reactions involving the hydroxyl radical. Note that the ultimate products of these processes are HF and CO_2. Hydrogen fluoride will then dissolve in raindrops to leave the atmosphere as precipitation, while CO_2 will accumulate in the atmosphere to add to the greenhouse effect. We make the following general conclusions from the above results: Owing to the presence of H atoms in PFA molecules, PFAs react rapidly with hydroxyl radicals in the troposphere. It is these reactions that determine the lifetime of a PFA in the troposphere and, accordingly, the possibility of its transfer to the stratosphere.

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