The reaction of C_3F_6 with dioxygen under IR laser initiation

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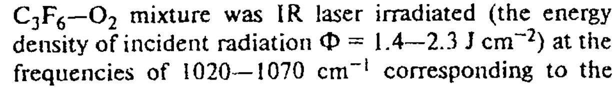
The mechanism of oxidation of C_3F_6 by molecular O_2 under IR multiphoton excitation was studied. The activation energy of C_3F_6 oxidation was estimated from the dependence of the reagent conversion on the O_2 pressure. The data obtained for the final reaction products, CF_3CFO and CF_2O, suggest the dioxetane mechanism of C_3F_6 oxidation.

Key words: perfluoroolefins, oxidation, dioxetane mechanism, IR multiphoton excitation, perfluorinated acyl fluorides, carbenes, kinetics, effective reaction temperature.

The mechanism and kinetics of oxidation of perfluoroolefins in the gas phase have been poorly studied. Only few works devoted to the interaction of simplest perfluoroolefins (C_2F_4, C_3F_6) with dioxygen in the gas phase are available in the literature.[1—7] In these studies, the rate constants of the reaction of carbene $:CF_2$ (formed from C_2F_4) with O_2 have been determined and refined, and two routes of oxidation have been suggested: the reaction of C_2F_4 with O atoms and the reaction of electron-excited $C_2F_4{}^*$ molecules with O_2 molecules.

Detailed information on the mechanism of interaction of perfluoroolefins with O_2 can be obtained from the analysis of oxidation of nonsymmetrical olefins. Similar studies have been performed for the single perfluoroolefin, C_3F_6. The SF_6-sensitized oxidation of C_3F_6 by molecular oxygen under continuous IR laser irradiation has been studied.[5] It has been found that C_3F_6 is oxidized to form CF_2O and CF_3CFO in the stoichiometric 1 : 1 ratio. The authors[5] believe that the reaction of C_3F_6 with O_2 occurs *via* the following scheme:



$$F_3C{-}CF{=}CF_2 \xrightarrow{O_2} \left[\begin{array}{c} O{-}O \\ F_3C{-}CF{-}CF_2 \end{array}\right] \longrightarrow F_3C{-}CFO + F_2CO.$$

This mechanism is favored by the fact that at the average effective temperatures of 600—700 K no O atoms are formed in the thermolyzed C_3F_6—SF_6—O_2 system, and olefin molecules are not electron-excited.

Quite different results have been obtained[6] when the C_3F_6—O_2 mixture was IR laser irradiated (the energy density of incident radiation $\Phi = 1.4$—2.3 J cm^{-2}) at the frequencies of 1020—1070 cm^{-1} corresponding to the absorption band of C_3F_6 molecules. It has been found that CF_2O and C_2F_4 are the final products of oxidation, and the fraction of the latter decreases as the O_2 content in the initial mixture increases. The absence of CF_3CFO among the final products is explained[6] by the oxidation *via* the scheme

$$C_3F_6 \xrightarrow{nh\nu} C_3F_6{}^* \text{ (IR multiphoton excitation)},$$

$$C_3F_6{}^* \longrightarrow C_2F_4 + :CF_2,$$

$$C_3F_6{}^* + O_2 \longrightarrow 2\,CF_2O + :CF_2,$$

$$C_3F_6{}^* + O_2 \longrightarrow C_2F_4 + CF_2O + O,$$

followed by secondary reactions of carbene $:CF_2$ and O atoms with olefins C_2F_4 and C_3F_6 resulting in the formation of CF_2O only.

Thus, the mechanism of oxidation of C_3F_6 remains unclear. Perhaps, diverse data[5,6] were obtained because of different methods of activation of the reagent molecules in the works cited. The purpose of this work is to reveal the mechanism and estimate the kinetic parameters of oxidation of C_3F_6 by molecular oxygen under IR multiphoton excitation (MPE) of the reagent molecules.

Experimental

For IR MPE of C_3F_6 molecules, the radiation of a pulse CO_2 laser at the frequency $\omega_L = 1027.5$ cm^{-1} (9P40) corresponding to the absorption band of C_3F_6 was used. The energy density of incident IR laser radiation was 0.24—0.34 J cm^{-2}. The reaction of C_3F_6 with O_2 was carried out in a glass reactor with a diameter of 16 mm, a length of 60 or 120 mm, and BaF_2 windows. The mixture under study was irradiated in the multipulse regime with a pulse frequency of 0.15 Hz. The energy of radiation passed through the reactor was detected by an IMO-2N instrument for measuring the laser radiation power.

In experiments on irradiation of binary C_3F_6—O_2 and C_3F_6—N_2 and ternary C_3F_6—O_2—N_2 mixtures, the pressure of C_3F_6 was 5 Torr, and the pressure of O_2 and N_2 additives was varied within 0.5—25.0 Torr. The reaction mixture was analyzed during multipulse irradiation by spectrophotometry using a Specord 75-IR spectrophotometer. The consumption of C_3F_6 was monitored by the absorption at 1794 cm^{-1}, and the accumulation of CF_3CFO and CF_2O was detected at 1896 and 1954 cm^{-1}, respectively. For quantitative analysis of these substances, we used the extinction coefficients (σ) determined previously for characteristic absorption bands of C_3F_6 and acyl

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fluorides that formed: C_3F_6, $\sigma = 3.21 \cdot 10^{-19}$ cm^2; CF_3CFO, $\sigma = 3.11 \cdot 10^{-19}$ cm^2; CF_2O, $\sigma = 4.55 \cdot 10^{-19}$ cm^2;[8] and overlapping of absorption bands of CF_3CFO and CF_2O was taken into account.

After the end of laser irradiation, the reaction products were analyzed by GC on a 3700 chromatograph (a flame-ionization detector, a column filled with Porapak S). Only C_3F_6, C_2F_4, and C_4F_8 were observed by chromatography.

Results and Discussion

Since C_3F_6 can decompose during MPE,[9] we carried out a series of experiments on irradiation of C_3F_6 in mixtures with an inert buffer gas (N_2) without O_2 additives. In this case, C_3F_6 decomposes in the reaction

$$C_3F_6 \longrightarrow :CFCF_3 + :CF_2. \qquad (1)$$

C_2F_4 and traces of C_4F_8 were observed among the final products. They are formed in the reactions

$$2\ :CF_2 \longrightarrow C_2F_4, \qquad (2)$$

$$:CFCF_3 \longrightarrow C_2F_4, \qquad (3)$$

$$2\ :CFCF_3 \longrightarrow C_4F_8. \qquad (4)$$

The conversion of C_3F_6 in the irradiated volume was $7 \cdot 10^{-5}$—$2 \cdot 10^{-4}$ per laser pulse and decreased exponentially with an increase in the N_2 pressure (Fig. 1), which is characteristic of the multiphoton dissociation (MPD) of the reagent.[10]

In the presence of O_2 in both binary C_3F_6—O_2 and ternary C_3F_6—O_2—N_2 mixtures, the conversion of C_3F_6 under IR laser irradiation is 2 orders of magnitude higher and amounts $9.3 \cdot 10^{-3}$—$1.2 \cdot 10^{-2}$ (see Fig. 1). CF_3CFO, CF_2O, and traces of C_2F_4 and C_4F_8 were observed as the final products. Most likely, in the system under study, the reagent can be oxidized *via* two routes: (a) during interaction of C_3F_6 and O_2 molecules (dioxetane mechanism); (b) during decomposition of C_3F_6 followed by oxidation of carbenes formed. Under the conditions of our experiments, the direct interaction between the C_3F_6 and O_2 molecules in the reaction

$$C_3F_6 + O_2 \longrightarrow \text{Products} \qquad (5)$$

is a predominant process.

This is indicated by the following experimental results. First, if the oxidation of C_3F_6 occurs mainly *via* channel (b), its conversion would be close by an order of magnitude to the degree of decomposition of C_3F_6 in the absence of O_2, which contradicts the experimental data (see Fig. 1). Second, the amount of C_2F_4 among the final reaction products is low and decreases as the conversion of C_3F_6 increases (Fig. 2). If the oxidation of C_3F_6 occurs only through the stage of carbene formation, then, since the reaction of $:CF_2$ with O_2 and its recombination are parallel, this would result in the accumulation of C_2F_4 as the reagent is consumed.

At least two possibilities for occurrence of reaction (5) exist under the conditions of the pulse IR laser initiation. On the one hand, during the IR MPE process, the vibration-excited $C_3F_6^*$ molecules can interact with O_2 molecules. On the other hand, after the end of vibrational relaxation of $C_3F_6^*$ molecules, the irradiated volume of the gas mixture is heated, and the standard thermal reaction of C_3F_6 with O_2 occurs. In the latter case, the action of laser irradiation is reduced to sensitized heating of the gas mixture (similarly to the conditions described previously[7]). Since vibrational relaxation of excited polyatomic molecules similar to C_3F_6 occurs anomalously rapidly,[11] the bimolecular reaction (5) of C_3F_6 with O_2 in the thermolyzed gas mixture makes the main contribution to the oxidation of C_3F_6.

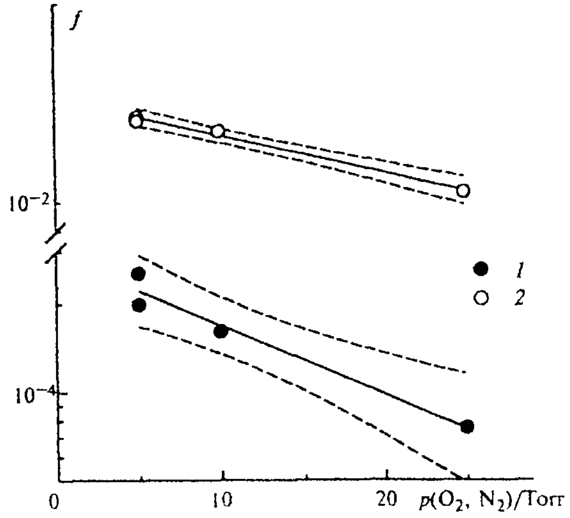

Fig. 1. Conversion (*f*) of C_3F_6 during one laser pulse in binary C_3F_6—(O_2, N_2) mixtures at different pressures of O_2 (*1*) and N_2 (*2*). Here and in Figs. 3—5, the dotted lines show the interval (95%) that contains all calculated values of ordinates.

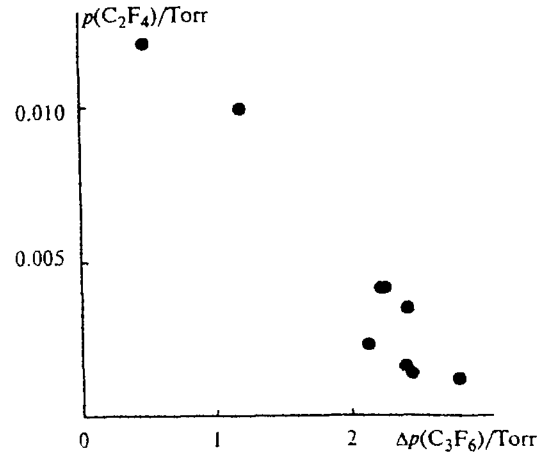

Fig. 2. Quantity of C_2F_4 formed due to laser irradiation of binary and ternary mixtures containing C_3F_6 (5 Torr) and O_2 (0.5—12.0 Torr) depending on a decrease in the reagent.

As seen in Fig. 1, the conversion of C_3F_6 in the presence of oxygen per laser pulse decreases as the O_2 pressure in the mixture increases. Since in these mixtures C_3F_6 is transformed in reaction (5), an increase in the O_2 pressure in the mixture should favor an increase in the reagent conversion. However, as the pressure of additives (O_2, N_2) increases, the total heat capacity of the gas mixture increases, which results in a decrease in its average effective temperature and, hence, a decrease in the rates of bimolecular reaction (5).

Mathematical processing of the experimental data on transformation of C_3F_6 in binary and ternary mixtures made it possible to estimate the kinetic parameters of reaction (5). Since the degree of decomposition of C_3F_6 in reaction (1) did not exceed 1—2% of the overall degree of its conversion, the contribution of reaction (1) was neglected in the estimation of the kinetic parameters of oxidation of C_3F_6. The rate constant of bimolecular reaction (5) can be presented in the form

$$k_5t = (a - b)^{-1} \cdot \ln\{b(a - x)/[a(b - x)]\}, \qquad (6)$$

where a and b are the initial concentrations of C_3F_6 and O_2, respectively; x is the concentration of the reacted C_3F_6; and t is the reaction time. In the multipulse irradiation regime, the reaction time t can be presented as $t = \tau n$, where n is the number of laser pulses, and τ is the characteristic time of reaction (5) after each pulse. The experimental data on the transformation of C_3F_6 were processed as the function $k_5t(n)$ (Fig. 3). At high degrees of conversion of C_3F_6, the effective temperature of the gas mixture decreases due to a decrease in the absorbed radiation energy, which results in a decrease in the calculated values of $k_5\tau$. Therefore, to estimate the kinetic parameters of reaction (5), we used only the initial regions of the $k_5t(n)$ dependences (see Fig. 3). The slope of this dependence is equal to $k_5\tau$.

During oxidation of C_3F_6, there is a temperature gradient in the irradiated volume in the reactor in both the space (due to heterogeneity of the laser beam) and time (due to cooling of the gas mixture). Therefore, for the estimation of k_5, the effective temperature of the mixture $<T>$ was used, which was calculated under the assumption of adiabatic transformation of the laser radiation energy into heat[13]

$$E_{abs} = \sum_i p_i \cdot \int_{298}^{<T>} C_{v,i} \cdot dT ,$$

where E_{abs} is the energy of absorbed laser radiation (calculated by the experimentally determined extinction coefficient $\sigma(C_3F_6) = (3.98 \pm 0.26) \cdot 10^{-19}$ cm^2); p_i and $C_{v,i}$ are the pressure and heat capacity of the ith components of the gas mixture, respectively; and $<T>$ is the initial temperature of the thermolyzed reaction mixture. It can be considered as the effective temperature of the reaction, because the transformation of the predominant portion of the reagent occurs at temperatures close to $<T>$ due to fast cooling of the gas mixture.

To check the assumption that reaction (5) is the main channel of transformation of C_3F_6, we studied ternary mixtures with the composition C_3F_6 (5 Torr) + O_2 (y Torr) + N_2 ($15 - y$ Torr). Since they are characterized by almost the same temperature ($<T> = 716$—723 K), the $k_5\tau$ value calculated for these mixtures should be independent of $p(O_2)$. As can be seen in Fig. 4, in ternary mixtures of C_3F_6 with excess O_2 ($y \geq 5$ or $p(O_2)/p(C_3F_6) \geq 1$), the calculated $k_5\tau$ value is independent, indeed, of the O_2 pressure and amounts $k_5\tau = 4.6 \pm 3.0$ L mol^{-1}. At a deficiency of O_2 ($y < 5$ or $p(O_2)/p(C_3F_6) < 1$), the $k_5\tau$ value increases rapidly as the fraction of O_2 in the mixture decreases. This is most likely related to a change in the mechanism of oxidation of C_3F_6: an increase in the effect of secondary processes on the main reaction (5) and an increase in the effective order of the reaction of C_3F_6 with O_2.

As indicated above, in the C_3F_6—O_2 mixtures with excess O_2, a decrease in the reagent obeys the second-order equation. For the estimation of the kinetic parameters of reaction (5), we used the $k_5\tau$ values in the binary mixtures of C_3F_6 (5 Torr) with excess O_2 (5—20 Torr), the average effective temperatures of which lie in the range $<T> = 680$—840 K. Since the $<T>$ temperature range is sufficiently narrow, it can be accepted that the τ value remains almost unchanged, and the temperature dependence of the $k_5\tau$ value (Fig. 5) characterizes the temperature dependence of the k_5 constant. Since it is impossible to determine the characteristic time of reaction (5) τ under our experimental conditions, we cannot estimate the value of the k_5 constant (more exactly, the pre-exponential factor A). However, the linear dependence of $\ln(k_5\tau)$ on $1/<T>$ makes it possible to estimate the activation energy of reaction (5): $E_a = 28.1 \pm 3.3$ kcal mol^{-1}. Since only the data on consumption of

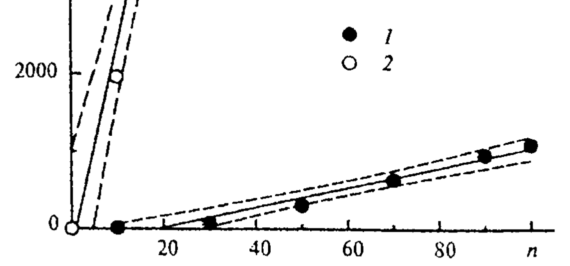

Fig. 3. Values of k_5t calculated from Eq. (6) depending on the number (n) of laser pulses for binary C_3F_6—O_2 mixtures: $p(O_2) = 1$ Torr (1) and 10 Torr (2).

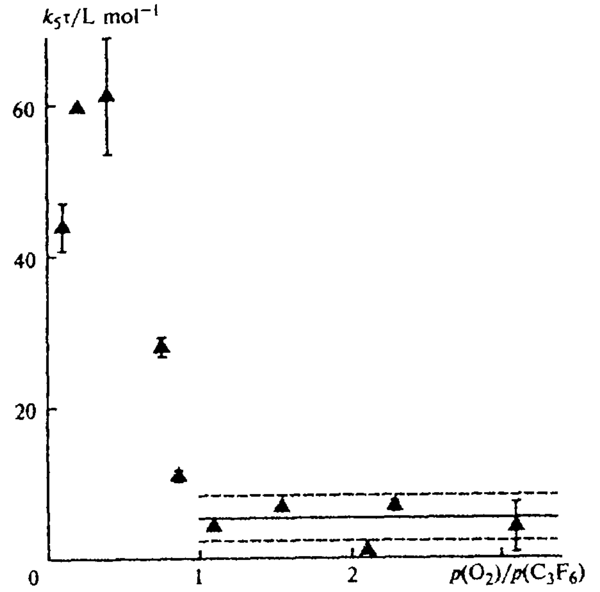

Fig. 4. Value of $k_5\tau$ for ternary mixtures with the same temperature $<T>$ at different C_3F_6 to O_2 ratios in the starting mixture. The average $k_5\tau$ value for mixtures with excess O_2 is shown by the solid line.

C_3F_6 during oxidation were used for the calculation of the E_a value, the activation energy estimated characterizes precisely the direct interaction of C_3F_6 with O_2 under conditions of IR MPE of reagent molecules.

The second part of our work was associated with the study of oxygen-containing products, CF_3CFO and CF_2O, formed by the oxidation of C_3F_6 in binary mixtures with an excess and deficient of O_2 (Fig. 6). In the mixtures deficient in O_2, we observed a decrease in the concentration of CF_3CFO formed and an accelerated increase in the concentration of CF_2O at conversions higher than 75—80%. For the mixtures with $p(C_3F_6)/p(O_2) \geq 5$, all CF_3CFO is consumed until the end of the reaction (see Fig. 6). In the case of ternary mixtures, these dependences have the same shape, but for the mixtures with $p(C_3F_6)/p(O_2) \geq 5$, CF_3CFO is consumed to a less extent. Note that these data can explain the disagreement of the results of the previous works[5,6] concerning the presence of CF_3CFO among the final products of oxidation of C_3F_6. The products of C_3F_6 oxidation were analyzed[6] only in the end of multipulse irradiation of the reagent, and the dynamics of transformations of the reagent and products was not monitored. In addition, all experiments were carried out at a high excess of C_3F_6, which should result in the single acyl fluoride among the final products: CF_2O (see Fig. 6).

In addition, the mechanism of oxidation of C_3F_6 with the equimolar formation of various acyl fluorides, which was suggested[5] for conditions of continuous laser irradiation, is not fulfilled under the conditions of our experiments. As seen in Fig. 6, CF_3CFO and CF_2O are formed in different stoichiometric ratio. The dependences of $p(CF_3CFO)/p(CF_2O)$ ratios calculated at low degrees of conversion of the reagents for binary and ternary mixtures on the composition of the mixture are shown in Fig. 7. It is seen that an excess amount of CF_3CFO as compared to that of CF_2O is formed for both types of the mixtures at any initial composition.

The experimental results presented in Figs. 6 and 7 can be explained as follows. At the first stage of oxidation of C_3F_6 (reaction (5)), dioxetane appears as an intermediate species. It is most likely that along with its decomposition to two acyl fluorides in the 1 : 1 stoichiometric ratio, there is another channel of its transformation to form either only CF_3CFO, or CF_3CFO and CF_2O in a

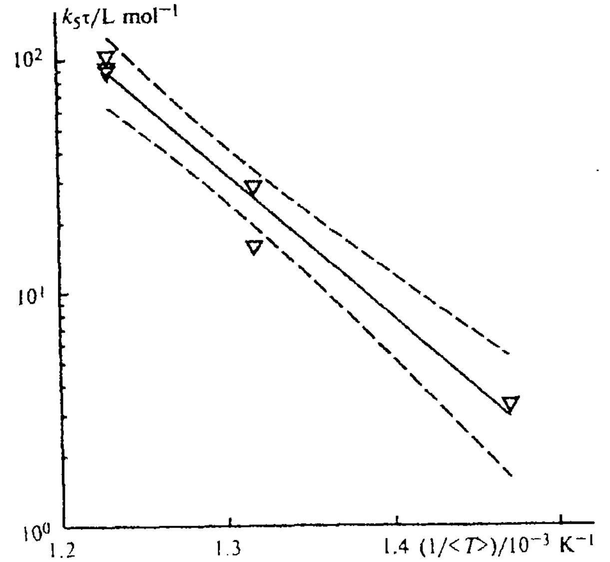

Fig. 5. Dependence of the $k_5\tau$ value for binary mixtures with excess O_2 on $1/<T>$.

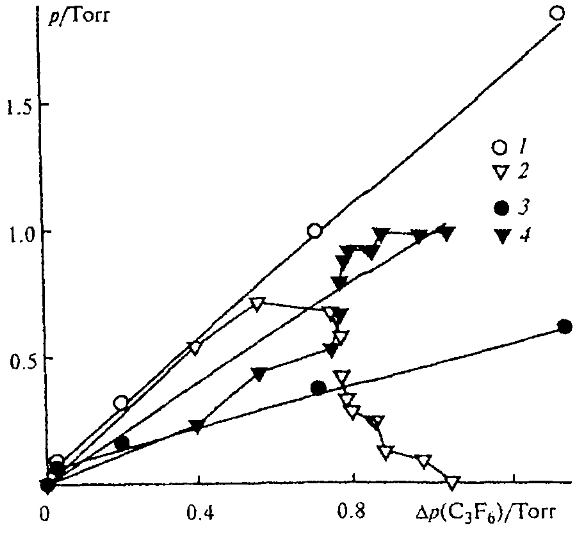

Fig. 6. Typical curves of accumulation of CF_3CFO (*1, 2*) and CF_2O (*3, 4*) with consumption of C_3F_6 in binary mixtures at $p(O_2)$ = 10 Torr (*1, 3*) and 1 Torr (*2, 4*).

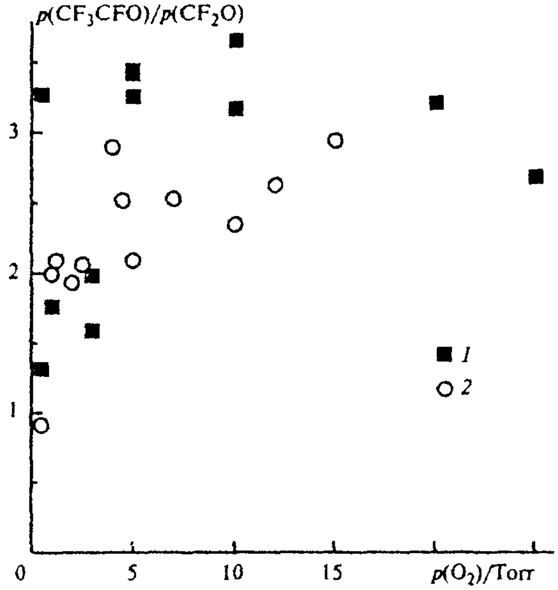

Fig. 7. Ratio of pressures of acyl fluorides formed at the initial stages of C_3F_6 conversion in binary (*1*) and ternary (*2*) mixtures at different O_2 pressures.

ratio not less than 4 : 1 as the final oxygen-containing products. This channel can be associated with the transformation of dioxetane into perfluoropropylene oxide, which decomposes, under these conditions, to CF_3CFO and :CF_2 only,[13] and with the interaction of dioxetane with O atoms, perfluorocarbenes, and probably the initial reagent, which initiates the chain free-radical reaction. In this case, when the O_2 pressure in the starting mixture increases (hence, the number of O atoms during free-radical reactions suggested increases as well), the fraction of the alternative channel of dioxetane transformation and the $p(CF_3CFO)/p(CF_2O)$ ratio should increase, which is observed in the experiment (see Fig. 7).

The facts observed by us for the consumption of CF_3CFO and accelerated formation of CF_2O during the deep oxidation of C_3F_6 only at a deficiency of O_2 (see Fig. 6) can be explained as follows. Although CF_3CFO molecules do not absorb IR laser radiation under the conditions of our experiments, they can accumulate an energy higher than the dissociation level due to vibrational relaxation of excited C_3F_6 molecules, in particular, during V—V-exchange of energy. As known,[14,15] CF_3CFO can decompose to form CF_2O. Therefore, acyl fluorides observed in experiments on oxidation of C_3F_6 could appear due to reaction (5) and simultaneous transformation of CF_3CFO. If the fraction of CF_3CFO decomposed during a pulse is constant, the occurrence of the reaction indicated does not change the linear character of the dependence of accumulation of acyl fluorides (see Fig. 6). In mixtures with excess O_2, the oxidation of C_3F_6 and accumulation of acyl fluorides occur until the energy absorbed by C_3F_6 is enough for effective heating of the mixture and occurrence of reaction (5). In the case of mixtures deficient in O_2, when its predominant amount is consumed, reaction (5) of oxidation of C_3F_6 and accumulation of acyl fluorides cease, and the decomposition of CF_3CFO can be continued, since excess C_3F_6 still provides effective heating of the gas mixture. Therefore, the character of accumulation of acyl fluorides changes precisely for mixtures with a deficiency of O_2. The heating of the gas mixture and efficiency of decomposition of CF_3CFO should increase as the density of IR laser radiation energy increases. In this connection, in the work discussed above[6] where the radiation density was 4—5 times higher than that in our experiments, CF_3CFO should not appear among the products of C_3F_6 oxidation.

Thus, the activation of perfluoroolefin molecules by sensitized laser heating or IR MPE does not change basically the mechanism of oxidation. It is most likely that the bimolecular reaction with O_2 is the determining process in oxidation of perfluoroolefins, and the difference in the presence or ratio of final products is due to secondary reactions, which depend on laser-chemical experimental conditions only.

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