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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Photolysis of Perfluoropropylene-Methanol Mixture in Vacuum Ultraviolet¹

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Abstract—The products of reaction of C_3F_6 with CH₃OH, initiated by vacuum ultraviolet, were determined. The kinetics scheme of the process was proposed. The parameters of the kinetic processes were calculated. The feasibility of photochemical preparation of 2,2,3,4,4-hexafluoro-1-butanol was analyzed.

One of methods for introducing perfluoroalkyl groups in molecules of organic compounds is addition of these groups to unsaturated hydrocarbons in the course of radical telomerization [1, 2]. Many fluorinated organic compounds exhibit absorption only in the range of vacuum ultraviolet (VUV). A great number of compounds with required properties can be prepared by photoreactions of fluorinated organic compounds under exposure to VUV. In this work, we examined a new route to polyfluorinated 1-butanol: irradiation of a C_3F_6 -CH₃OH mixture with 185-nm light.

Perfluoroolefins, as well as lower alcohols, do not absorb in the range above 200 nm. Photolysis of C_2F_4 in VUV was studied in [3, 4]. Continuous absorption of C_3F_6 in VUV, determined in our works, suggests radical photolysis of this compound. Reactions of fluoroolefins with alcohols, usually initiated by peroxides or γ -radiation, yield telomers [5]. Photochemical initiation, unlike these methods, allows control of the process owing to selective activation of definite bonds. The aim of this study was do develop a new photochemical synthesis procedure. In particular, we studied possible reaction pathways, determined the yield of the reaction products and the irradiation efficiency, and constructed a mathematical model of the photolysis.

EXPERIMENTAL

Photochemical studies were performed in a cylindrical quartz reactor. A 70 W low-pressure mercury lamp [6] 0.9 m long was fixed at the reactor axis. The power of this lamp, measured at 185 and 254 nm, was 1 and 20 W, respectively. The photoreactor was equipped with a vacuum system used to fill the reactor with the initial reagents and to sample the reaction mixture. The photolysis products were analyzed on an HP5972 chromato-mass spectrometer with an HP-PLOT capillary column coated with Al_2O_3 . The mass spectra were assigned with the aid of WILEY.138.L library.

To understand the kinetics of synthesis of polyfluorinated 1-butanol, we studied perfluoropropylene photolysis. Initially we studied C_3F_6 photolysis at a pressure of 4 kPa and exposure time of 15 min. Under these conditions, C_3F_6 is quantitatively converted into perfluorocyclobutane derivatives (up to 45%) and perfluoroparaffin isomers.

Formation of perfluoromethylcyclobutane, 1,2-, and 1,3-bisperfluoromethylcyclobutane (in the ratio 1.6: 1.4: 1) can be described by the following scheme:

$$\begin{split} & C_{3}F_{6} + hv \rightarrow C_{3}F_{6}^{*}(+M) \rightarrow :CF_{2} + CF_{3}CF;, \\ & C_{3}F_{6}^{*} + (M) \rightarrow C_{3}F_{6}, \ 2:CF_{2} \rightarrow C_{2}F_{4}, \\ & CF_{3}CF; + (M) \rightarrow C_{2}F_{4}, \\ & C_{2}F_{4} + hv \rightarrow C_{2}F_{4}^{*}(+M) \rightarrow 2:CF_{2}, \\ & C_{2}F_{4}^{*} + (M) \rightarrow 2:C_{2}F_{4}, \end{split}$$

 $C_2F_4 + C_3F_6^* \rightarrow C_5F_{10}$ (perfluoromethylcyclobutane),

 $C_2F_4^* + C_3F_6 \rightarrow C_5F_{10},$

 $C_3F_6 + C_3F_6^* \rightarrow C_6F_{12}$ (perfluorodimethylcyclobutane isomers),

where perfluoropropylene in the electronically excited state is marked with an asterisk. This is probably the

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τ _{ret} , min	<i>S</i> , %	Component	с, %
2.99 3.71 5.99 15.39 15.47 17.45 18.55 19.49 19.54	0.192 0.751 1.087 5.312 4.082 12.537 0.015 4.521 3.486	$C_{2}F_{6}$ $C_{2}F_{4}$ $C_{3}F_{8}$ <i>i</i> -C ₄ F ₁₀ $C_{4}F_{10}$ $C_{5}F_{10}$ (methylcyclobutane) $CF_{3}CF=CFCF_{3}$ <i>i</i> -C ₅ F ₁₂ $C_{5}F_{12}$	$ \begin{array}{c} 1.28 \\ 0 \\ 0.65 \\ 8.0 \\ 12.0 \\ 0 \\ 8.9 \end{array} $
19.66 19.97	10.734 7.774	C_6F_{12} (1,2-dimethylcyclo- butane) C_6F_{12} (1,3-dimethylcyclo- butane)	} 18.2
22.11 22.19 22.28	17.820 5.945 5.898	$C_{2}F_{5}CF_{2}CF(CF_{3})CF_{3}$ $C_{6}F_{14}$ $CF_{3}CF(CF_{3})CF(CF_{3})CF_{3}$	$ \begin{cases} 30.1 \\ (Sum of \\ C_6F_{14} \\ isomers) \end{cases} $
25.09 25.27 25.39 25.47	3.644 6.241 0.154 2.608	$\begin{array}{c} CF_3CF(CF_3)CF_2CF(CF_3)CF_3\\ C_2F_5CF_2CF_2CF_2CF(CF_3)CF_3\\ C_2F_5CF_2CF(CF_3)C_2F_5\\ C_7F_{16}\end{array}$	$\begin{cases} 9.2 \\ (Sum of \\ C_7F_{16} \\ isomers) \end{cases}$
30.26 30.57 30.93 31.41 36.57	0.688 2.189 2.337 1.169 0.764	$\begin{array}{c} CF_{3}CF(CF_{3})CF_{2}CF(CF_{3})C_{2}H_{5}\\ C_{2}F_{5}CF_{2}CF_{2}CF_{2}CF_{2}CF(CF_{3})CF_{3}\\ C_{2}F_{5}CF_{2}CF_{2}CF_{2}CF(CF_{3})C_{2}F_{5}\\ C_{8}F_{18}\\ \Sigma i\text{-}C_{9}F_{20}\\ \end{array}$	$ \begin{array}{c} 4.8 \\ (Sum of \\ C_8F_{18} \\ isomers) \\ 2.8 \end{array} $

Table 1. Chromatogram^{*} of the products of C_3F_6 photolysis and calculated component concentrations *c*

* (τ_{ret}) Retention time and (S) peak area.

triplet state that is involved in deactivation, predissociation degradation into radicals, and reactions with other molecules, ultimately resulting in cyclodimerization.

The presence of trace amounts of perfluoro-2-butene (~0.01%) and C_2F_4 (<1%) in the reaction mixture agrees with the reaction scheme, since C_2F_4 is converted incompletely and the perfluoro-2-butene formation by recombination of methylcarbene radical is considerably slower than the C_2F_4 formation. "Biradical" formation was detected in C_3F_6 pyrolysis [7], i.e., at significantly lower excitation energy of perfluoropropylene. Although cyclodimerization proceeds mainly by degradation of compounds containing a double bond to form saturated compounds and is typical of C_3F_6 pyrolysis ($T \sim 200^{\circ}$ C), it occurs in the course of C_3F_6 photolysis too. Photolysis of C_2F_4 under the same conditions occurs simslarly. The main product, perfluorocyclobutane, is formed after irradiation of perfluoroethylene for 3 min (the C_2F_4 conversion is ~15%). The process can be described by the above kinetic scheme, since, in both cases, predissociation degradation yields difluorocarbene. However, C_3F_6 photolysis is a more complex process and yields a series of paraffin isomers, from perfluoropropane to perfluorononane. This process involves an additional pathway initiated by the : CF_2 biradical and atomic fluorine formed in the primary photolysis step.

The weakest bonds of a molecule excited by a VUV quantum are ruptured owing to energy redistribution after molecular collisions. Several pathways of $C_3F_6^*$ dissociation are possible. The excess energy of photodissociation products was estimated on the basis of the energy balance and analysis of fluorocarbon fragments of saturated polyfluorinated products of C_3F_6 photolysis performed at a large excess of hydrocarbon. Based on the results of this estimation, we suggest the following scheme of $C_3F_6^*$ dissociation:

$$C_3F_6^*$$
 + (M) \rightarrow ·CF=CFCF₃ + ·F, E_{exc} 22 and
158 kJ mol⁻¹, respectively,

 $C_3F_6^* + (M) \rightarrow \cdot CF = CF_2 + \cdot CF_3$, E_{exc} 31 and 36 kJ mol⁻¹, respectively.

The secondary processes can involve reactions with "hot" radicals $\cdot CF_3$ and $\cdot F'$, with subsequent photodegradation of the fragments formed. The first photolysis step can be described by a superposition of the above reactions:

$$C_3F_6 + h\nu \rightarrow C_3F_6^*(+M) \rightarrow CF_3 + F_2F_2,$$

which agrees well with the kinetic scheme of formation of fluoroparaffin isomers presented in Table 1.

Subsequent transformations involve addition of fluorine atom to double bonds to form R_F radicals $(R_F, C_3F_7, C_2F_5, \text{ and } CF_3)$ recombining to give a series of paraffin isomers. The rate constants of radical recombination decrease appreciably in going from linear to branched structures and with increasing number of carbon atoms [8]. Therefore, recombination of branched radicals, C_4F_9 and higher, was disregarded in the kinetic scheme. The C_7-C_9 isomers may arise in the photolysis products in the step of formation of methylcyclobutanes, when R_F radicals recombine with the : C_6F_{12} biradical, which has no time to form a four-membered ring.

Photolysis of C_3F_6 to form detectable products is initiated to the same extent by difluorocarbene and atomic fluorine generated in primary photolysis steps. Generally C_3F_6 is photolyzed under the conditions when the rate of reactions of excited $C_3F_6^*$ molecules is comparable with that of predissociation degradation followed by secondary and tertiary radical reactions, which strongly complicates the photolysis mechanism. To understand the photolysis mechanism, mathematical modeling can be used.

A mathematical model of C_3F_6 photolysis was developed by comparing experimental and calculated data on the composition of the reaction products. The kinetics scheme includes 50 reactions whose constants were taken from the literature or were estimated by extrapolation of the known rate constants of homologs, taking into account the steric factors. A system of differential kinetic equations of these reactions was constructed and integrated by the Gear procedure [9].

The time dependeces of the concentration of the photolysis products are adequately described by the kinetic model (Table 1). The calculations show that C_3F_6 is completely decomposed after 100s of irradiation. The convergence of the calculated and experimental concentrations can be improved by varying the rate constants of the reactions and quantum yields of the products and by recording more exactly the absorption spectra of the radical products. A model calculation confirmed the occurrence of the main reactions of C_3F_6 photodissociation.

Synthesis of polyfluorinated 1-butanol by continuous irradiation of a C_3F_6 -CH₃OH mixture with VUV for 15 min was studied. Synthesis was performed at three ratios of the partial pressures of the components C_3F_6 : CF₃OH = 4 : 0.8, 4 : 4, and 0.8 : 4. Under these conditions, the ratio of the absorption coefficients of C_3F_6 and CH₃OH at 185 nm are 75, 15, and 3, respectively. This allows evaluation of the effect of the CH₃OH photolysis on the formation of the target product.

The fact that the chromatograms of the photolysis products of C_3F_6 and the initial mixture C_3F_6 : $CH_3OH = 4 : 0.8$ are similar indicates that CH_3OH is not involved appreciably in the radical process and is converted mainly by addition to the double bond

$$C_3F_6^* + CH_3OH \rightarrow CF_3CHFCF_2CH_2OH.$$

The yield of 2,2,3,4,4,4-hexafluoro-1-butanol is 20%. This reaction is responsible for formation of about 90% of the photolysis products. Telomerization

of $C_3F_6^*$ with CH_3OH is more intense than C_3F_6 dimerization. Side recombination reactions yield up to 1.5% fluorinated ethers $[(C_3F_6 + \cdot F) + CH_3O \rightarrow C_3F_7OCH_3, (C_3F_6 + \cdot CF_3) + CH_3O \rightarrow C_4F_9OCH_3]$ and up to 6.2% R_FH ($\cdot R_F = \cdot CF_3, \cdot C_4F_9, \cdot C_5F_{11}, \cdot C_6F_{13}$). Compounds R_FH are formed mainly by recombination with the $\cdot CHF_2$ radical

$$\begin{array}{rl} \cdot \mathrm{CHF}_2 \ + \ (\mathrm{C}_3\mathrm{F}_6 \ + \ \cdot\mathrm{F}) \ \rightarrow \ \mathrm{C}_4\mathrm{HF}_9, \\ \\ \cdot \mathrm{CHF}_2 \ + \ (\mathrm{C}_3\mathrm{F}_6 \ + \ \cdot\mathrm{CF}_3) \ \rightarrow \ \mathrm{C}_5\mathrm{HF}_{11}, \\ \\ \cdot \mathrm{CHF}_2 \ + \ (\mathrm{C}_3\mathrm{F}_6 \ + \ \cdot\mathrm{C}_2\mathrm{F}_5) \ \rightarrow \ \mathrm{C}_6\mathrm{HF}_{13}, \\ \\ (\mathrm{C}_3\mathrm{F}_6 \ + \ \cdot\mathrm{H}) \ + \ (\mathrm{C}_3\mathrm{F}_6 \ + \ \cdot\mathrm{F}) \ \rightarrow \ \mathrm{C}_6\mathrm{HF}_{13}. \end{array}$$

This system of three-step consecutive reactions accounts for the absence of C_2HF_5 and C_3HF_7 in the photolysis products. The radical CHF_2 is effectively formed by the reactions $:CF_2 + \cdot H \rightarrow \cdot CHF_2$, $:CF_2 + CH_3O \rightarrow \cdot CHF_2 + CH_2O$. Formation of C_2HF_3 traces is due to the reactions $C_2F_2 + \cdot F \rightarrow \cdot C_2F_3$, $\cdot C_2F_3 + CH_3OH \rightarrow C_2HF_3 + CH_3O$, or $\cdot CF'_3 + CH_3O \rightarrow C_2HF_3 + H_2O$. CH_3CF_3 is formed by the reactions $\cdot CF_3 + \cdot CH_3 \rightarrow CH_3CF_3$ or $\cdot CF'_3 + CH_3O \cdot \rightarrow CH_3CF_3 + O$: ($\cdot CF'_3$ is "hot" radical). Methanol is involved in photolysis and in reactions with fluorine radicals:

$$\begin{array}{rcl} \mathrm{CH}_{3}\mathrm{OH} \ + \ h\nu \ \rightarrow \ \mathrm{\cdot H} \ + \ \mathrm{CH}_{3}\mathrm{O} \cdot \ (79\%), \\ \mathrm{CH}_{3}\mathrm{OH} \ + \ h\nu \ \rightarrow \ \mathrm{CH}_{2}\mathrm{O} \ \mathrm{H}_{2} \ (20\%), \\ \mathrm{CH}_{3}\mathrm{OH} \ + \ h\nu \ \rightarrow \ \mathrm{\cdot CH}_{3} \ + \ \mathrm{\cdot OH} \ (1\%) \ [10], \\ \mathrm{\cdot R}_{\mathrm{F}} \ + \ \mathrm{CH}_{3}\mathrm{OH} \ \rightarrow \ \mathrm{R}_{\mathrm{F}}\mathrm{H} \ + \ \mathrm{CH}_{3}\mathrm{O} \cdot \ (85\%), \\ \mathrm{\cdot R}_{\mathrm{F}} \ + \ \mathrm{CH}_{3}\mathrm{OH} \ \rightarrow \ \mathrm{R}_{\mathrm{F}}\mathrm{H} \ + \ \mathrm{CH}_{2}\mathrm{OH} \ (15\%) \ [11]. \end{array}$$

The main reactions competing with the formation of the fluornated alcohol are cyclodimerization of C_3F_6 and predissociation decomposition of C_3F_6 . Photolysis of CH₃OH has virtually no effect on the synthesis. Chromatograms of the products formed in photolysis of the C_3F_6 -CH₃OH system are presented in Table 2 in order of increasing retention time.

The yield of 2,2,3,4,4,4-hexafluoro-1-butanol decreases to 11.5% with increasing CH_3OH content in the initial mixture ($C_3F_6: CH_3OH = 4: 4$). The total content of the products of chemical reactions of the photolysis products increases to 60%, and the selectivity of the alcohol formation decreases from 90 to 19%. Among the photolysis products, 2,2,3,4,4,4-

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τ _{ret} , min	Composition, %, at indicated C_3F_6 : CH ₃ OH ratio, kPa : kPa				
	4:0.8	4:4	0.8 : 4		
5.67		CH ₂ =CF ₂ (3.2%)			
14.21	C_2HF_3 (0.13%)	$C_2 \tilde{H}F_3$ (3.9%)			
14.74	$CHF_{3}(0.27\%)$	CHF ₃ (2.3%)	CHF ₃ (6.9%)		
16.52	CF_3CH_3 (0.13%)	$C_2H_3F_3$ (3.1%)	$C_2H_3F_3$ (12.1%)		
17.13	$C_{3}F_{7}OCH_{3}$ (0.32%)	200	2 0 0		
19.35	$C_4 HF_9$ (1.65%)	$C_4 HF_9$ (10%)	$C_4HF_9 (+C_3H_2F_6) (8.1\%)$		
19.38		$CF_3CHFCF_2C(O)H$ (30.7%)			
19.63		$C_2 F_5 CH_3$ (4.6%)	$C_{3}H_{3}F_{5}$ (13%)		
20.02		$\overline{CF_2} = \overline{CFCHF_2}$ (1.5%)			
20.24	$C_4F_9OCH_3$ (1.25%)				
20.38		$CH_2 = CFCF_3$ (2%)			
21.60	C_5HF_{11} (1.2%)	$C_{5}HF_{11}$ (4.9%)	$C_{5}HF_{11}$ (5%)		
21.62	$CF_3CHFCF_2CH_3$ (0.6%)	$C_4H_4F_6$ (1.1%)			
22.22		$C_{3}F_{7}CH_{3}$ (3.4%)	$C_4H_3F_7$ (6.7%)		
22.30			$CHF_2CF_2CH_2F$ (5%)		
22.35	$CF_3CHFCF_2CH_2OH$ (90.8%)	$C_4 H_4 F_6 O$ (19%)			
23.77			$CHF_2CF_2CH_3$ (10.5%)		
23.84	C_6HF_{13} (3.1%)	$C_{6}HF_{13}$ (6.5%)	C_6HF_{13} (11.2%)		
24.40	$CHF_2CF_2CF(CF_3)CHF_2$ (0.5%)	$C_5H_2F_{10}$ (3.5%)			
25.75			$CH_3CF_2CF_2CH_3$ (10.7%)		

Table 2. Chromatograms of identified products of photolysis of C_3F_6 -CH₃OH mixture at various partial pressures of the components

hexafluorobutanal is characterized by the maximal yield (30%). As the temperature increases, this compound can be formed by the reaction

$$C_3F_6^* + CH_3OH \rightarrow CF_3CHFCF_2C(O)H + H_2$$

or the secondary reaction

$$C_3F_6^* + CH_2O \rightarrow CF_3CHFCF_2C(O)H.$$

The number of the products of radical reactions increases by approximately a factor of 5. The total content of $R_{\rm F}H$ compounds increases to 24%. New compounds R_FCH_3 with total content of up to 12% are formed instead of ethers by recombination $\cdot R_F + \cdot CH_3 \rightarrow R_F CH_3$, where $\cdot CH_3$ is generated by the reaction $\cdot H + CH_3OH \rightarrow \cdot CH_3 + H_2O$. These compounds can also be formed by reactions $R_{\rm F}$ + $CH_3O \rightarrow R_FCH_3 + O$: The contribution of these reactions increases with temperature. The heating of the reaction mixture is due to a stronger absorption in the system owing to an increase in its optical density. The increase to approximately 10% in the content of polyolefins (CF₂=CFCHF₂, CH₂=CFCF₃, C₂H₂F₂, C_2HF_3 formed in reactions like $CF_3 + CH_3 \rightarrow$ $C_2H_2F_2$ + HF) that were not subjected to photolysis is due to intensification of the pyrolytic processes. The kinetic model of the process becomes severely

complicated, since CH_3OH photolysis and some temperature-dependent reactions should be taken into account.

No products of addition to the double bond of C_3F_6 were detected in the reaction mixture of photolysis at C_3F_6 : CH₃OH = 0.8 : 4. All the products of the reaction of C_3F_6 with CH₃OH are formed by radical reactions initiated by the photolysis products of C_3F_6 and CH₃OH. The content of R_FH and R_FCH₃ increases to 31 and 32%, respectively. The other products are polyfluorinated paraffins and olefins. Trace amounts of CH₂O, CO₂, HF, H₂O, CF₃OCF₃, etc. are also formed. The chromatograms of the main reaction products are presented in Table 2.

CONCLUSIONS

(1) Photolysis of perfluoropropylene by vacuum ultraviolet was studied. The photolysis products were determined. The kinetic scheme of the process was proposed.

(2) Irradiation of a C_3F_6 : CH₃OH mixture (4 : 0.8) with vacuum ultraviolet yields 2,2,3,4,4,4-hexafluoro-1-butanol in 20% yield. The yield of this compound decreases with increasing CH₃OH content in the mixture. The calculated composition of photolysis products agrees well with the composition of the products formed in the photochemical reactor.

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