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Highly selective photochemical synthesis of perfluoroalkyl bromides and iodides

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Abstract

Highly fluorinated alkyl iodides are conveniently synthesized by telomerization of a fluoroalkyl-iodide, RI, with, e.g., C_2F_4 . Normally, the reaction, often carried out in the liquid phase with a radical initiator, gives products with a broad distribution of molecular weights. In this work, we report a method that obtains selectively products of a desired molecular weight: this method is a photochemically induced reaction in the gas phase; the gas is circulated through a trap or a rectification still which continuously removes the heavier products, whereas the more volatile molecules return to the photoreactor. An analysis by rate equations shows which control parameters are important, and by a suitable choice of these parameters, we obtained a better selectivity for, e.g., $C_8F_{17}I$ than previously. This method also works with BrC_2F_4Br instead of an iodide. In this case, we demonstrated in a small laboratory setup with simple low-pressure Hg lamps (5×30 W), a productivity of more than 0.5 kg/day. In the telomerization of CF_3Br or HC_2F_4Br with C_2F_4 we found, however, a few percent of dibromide side products which are sometimes difficult to separate because of similar boiling points. For this case, it is better to synthesize the iodides instead, and then exchange the I for Br, if desired.

Keywords: Telomerization; Molecular weight distribution; Poisson distribution; Bromo-perfluoro octane

1. Introduction

Perfluoroalkyl iodides and bromides with 4-10 carbon atoms have a number of uses [1,2]. For instance, owing to its high solubility for oxygen and other gases, $C_8F_{17}Br$ is an excellent candidate as a blood substitute and, due to its Br content, for an X-ray contrast agent [3-6]. Such halocarbons are also used as intermediates. For example, ethylene can be easily inserted into the C-Hal bond [7], and the resulting compounds can be converted to cationic tensides (reaction with R_3N), to vinyl compounds (HX elimination) or carboxylic acids (oxidation of the vinyl compounds), whose salts are again surface active. For example, C_7F_1 , COO⁻ is used as a tenside in the suspension polymerization of $C_{2}F_{4}$. D functional compounds can be made from $Br(C_2F_4)_{\mu}Br[8]$ which may be of interest for preparing polymers. The perfluoroalkyl halides are also used as intermediates for water and oil repellents for fabrics, leather or paper.

The most convenient synthesis of perfluoroalkyl iodides is the radical induced telomerization [9,10], which has long been known [11,12], e.g.,

$$\mathbf{C}_{2}\mathbf{F}_{5}\mathbf{I} + (n-1)\mathbf{C}_{2}\mathbf{F}_{4} \rightarrow \mathbf{F}(\mathbf{C}_{2}\mathbf{F}_{4})_{n}\mathbf{I}$$
(1)

If a bromide is desired, the iodine can be exchanged, for example, using elementary bromine [1]. This has been the best synthesis of C₈F₁₇Br. Some reactive bromides can also be directly telomerized [7,9]. A disadvantage of reactions like (1) is that they give rise to products with a broad distribution of molecular weights. It is usually close to a Poisson distribution, since every product iodide can reenter into the reaction [9]. In the method presented in this work and in patents [13-17], the heavier molecules are continuously removed from the reaction mixture while refeeding the lighter ones and replenishing the reactants. This is done by carrying out the reaction in the gas phase and circulating the gases either through a cold trap or-to improve the separation selectivity—through a rectification still. In this way, most of the yield appears in a single compound of desired molecular weight.

As in our previous work [13–16], the reaction was initiated by a low-pressure mercury lamp of the so-called ozonefree type. This is a lamp of similar shape (and price) as a common fluorescent lamp. It has a high efficiency (30-35%of the electric power is emitted as the 254 nm line) and a

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long lifetime (>10 000 h). The ozone-free type suppresses the 185 nm line by using a wall (e.g., Vycor) which is opaque at this wavelength. This is important, since already very small powers at short wavelengths (<230 nm) would produce side products resulting from CC and CF bond splitting [13–16].

We have previously shown [13–16] how to optimize the reactant concentrations and light intensity in order to control the radical concentrations, which give the best yields of the desired products. In this work, we explain the background of these methods and apply them to the reaction (1) and the following reactions

$$\operatorname{BrC}_{2}\operatorname{F}_{4}\operatorname{Br}(n-1)\operatorname{C}_{2}\operatorname{F}_{4} \to \operatorname{Br}(\operatorname{C}_{2}\operatorname{F}_{4})_{n}\operatorname{Br}$$
(2)

$$\operatorname{CF}_{3}\operatorname{Br}+n\operatorname{C}_{2}\operatorname{F}_{4}\to\operatorname{CF}_{3}(\operatorname{C}_{2}\operatorname{F}_{4})_{n}\operatorname{Br}$$
(3)

$$HC_{2}F_{4}Br + (n-1)C_{2}F_{4} \rightarrow H(C_{2}F_{4})_{n}Br.$$
(4)

In reaction (1), we received a high yield of $C_8F_{17}I$ (up to 89 mol% relative to consumed C_2F_5I). For reaction (2), we found high yields (relative to the consumed BrC_2F_4Br) for $Br(C_2F_4)_nBr$ (94, 88 and 54 wt.% for n = 2. 3 and 4, respectively) with conditions optimized for n = 2 and 3. Reaction (3) was only briefly investigated for comparison. The reactions (3–4) required very small C_2F_4 concentrations in order to obtain low molecular weights ($\leq C_8$). The main difficulty in these two reactions is, however, that some dibromide side products are not easy to separate from monobromo products because of similar boiling points. If monobromides are needed (e.g., $C_8F_{17}Br$), the monoiodides can be prepared, with subsequent exchange of the halogen.

In the dibromide system, we have demonstrated in a small laboratory setup a productivity of more than 0.5 kg/day of telomers. The process is also economically feasible, e.g., for $C_8F_{17}I$ for which there is a growing need. The advantage of this method is that it reduces the waste (heavier products) by a factor of 5–10 compared to previous methods.

For simplicity, we abbreviate C_2F_4 in the following by f.

2. Experimental method and data

Commercial products HBr (Merck), CF_3Br (Merck) and C_2F_5I (Riedel de Haën) were used without further purification. BrC_2F_4Br was kindly given to us by Dr. K. von Werner (Hoechst) and Prof. Hu Changming (Shanghai Organic Chemistry Institute). To prepare C_2F_4 [18], BrC_2F_4Br was dropped into a suspension of Zn powder in C_2H_5OH and the gaseous product was passed through a trap (0–4°C) filled with Zn powder to scavenge unreacted BrC_2F_4Br and solvent. C_2F_4 was stored at pressures around 1 bar.

For the product analysis of the dibromides and iodides, we used a gas chromatograph with a heat conductivity detector. The 3 mm \times 215 mm stainless steel column was packed with 10% methylsilicone on acid-washed kieselguhr. The temperature was constant at 100°C for the iodides and 142°C for the dibromides. The carrier gas was H₂. More details are given in Ref. [19]. For the injection of the gas samples, we used a

syringe, which was preheated to 100–110°C in order to avoid condensation of the products.

The chromatography of the monobromides (as well as the iodides in a few experiments) was done using a gas chromatograph mass-spectrometer combination (masses 100–600 g/mol), using a 25-m capillary (inner diameter 250 μ m) coated with 5%-phenyl methyl silicone with a temperature rising from 90 to 200°C (40 K/min). In contrast to the iodides and dibromides, the sensitivity of the instrument has not been calibrated for the monobromides. Hence, the data overestimate the concentration of the heavier molecules to some extent.

IR spectra were measured in the gas phase in 10-cm glass cells equipped with two KCl windows, a valve for evacuation and a septum for the injection of the sample.

2.1. Reactors and operation

Fig. 1 shows the single-lamp reactor combined with distillation unit. The reaction is induced by the low-pressure mercury lamp (electrical power 30 W, length 770 mm) fixed in the axis of a cylindrical glass tube (inner diameter 94 mm, length 680 mm). The condensing liquid products leave the photoreactor via the siphon to the bulb of the small rectification still. The vapors leaving the column re-enter the reactor from the other end. The same reactor was also used for static experiments. For this purpose, the still was disconnected and the lower end of the reactor connected with a collection bulb.

The multi-lamp reactor consists of a cylindrical glass vessel (inner diameter 216 mm, length 1000 mm) with two end caps (length 340 mm each). It allows to fix two lamps on its axis or three of them parallel to it in an equilateral triangle or both sets together. The reactor has an inlet and an outlet as the single-lamp reactor and is arranged vertically.

These two reactors (single-lamp and multi-lamp) were mainly used for the dibromide system. After evacuation, they



Fig. 1. Reactor combined with passive recirculation (using convection and condensation) and a distillation still. The liquid in the siphon prevents the gas from flowing back.

were filled by the gaseous reactants BrC₂F₄Br and C₂F₄. 2–3 kPa of C₂F₄ was added during the reaction as soon as the pressure had dropped, until the predetermined added quantity was attained. After switching on the lamp(s), one observes some fog which quickly almost disappears (being transported to the collection bulb by the beginning convection, induced by the heat of the lamps). The temperature rises by 5–8 K and \leq 15 K in the single- and multi-lamp reactor, respectively. For analysis, all products were collected by condensation at 77 K.

For the experiments with the premixed dibromide reactants, we used a modified filling procedure: after first filling in an initial quantity of BrfBr, more of it as well as the other components were added by bubbling C_2F_4 through a liquid thermostatted stock of a BrfBr/Brf₂Br mixture. This bubbler was also used for replenishing the reactants, and BrfBr was refilled to the liquid from time to time to restore the desired ratio.

For most of the experiments with the iodide and monobromide systems, an active circulation was employed, using a magnetically driven rotatory vane pump (Brey) with a graphite rotor and a pump capacity of $0.5 \text{ dm}^3/\text{s}$. A typical setup (for more details see Ref. [20]) is shown in Fig. 2. For the photoreactor, we used a desiccator of 5 dm³ volume with a low-pressure-Hg immersion lamp (Osram HNS, 'ozone-free' type) of 10 W electric power. When a larger reactor was needed, we used a 100 dm3 stainless-steel vessel (inner diameter about 350 mm) which normally served for storing liquid nitrogen; its 50-mm KF flange allowed insertion of a linear low-pressure-Hg lamp (Osram HNS 55 OFR, 'ozone-free' type, length 900 mm, 55 W electric power) and at the same time, the gas inlet (through a tube immersed to the bottom) and outlet. In one experiment with the iodides, we used the 1.05-dm³ reactor of Fig. 1 with a linear lamp (30 W), put vertically and combined with the Brey pump. In some cases, the gas flow was directed through a cell of 10 cm length which was placed in an IR spectrometer which monitored the content of C_2F_4 (at 1740 and 2110 cm⁻¹) and HBr (at 2607 cm^{-1}). The progress of the reaction was also monitored by gas chromatography; samples were taken (by a syringe through a septum) from the gas phase (mainly for the reac-



Fig. 2. Reactor (desiccator with U-shaped immersion lamp) combined with active circulation (vane pump), trap and IR absorption cell for monitoring the concentrations of the educts. The broken line indicates that C_2F_4 is replenished as soon as the IR absorption indicates that it has been depleted.

tants) and in the case of the iodides also from the liquid phase. The final composition of the products was determined from the condensates.

The products were collected by condensation at 77 K. The $H(C_2F_4)_n$ Br products were purified by distillation through a spinning-band column at normal (n = 1, 2) and reduced (8 kPa for n > 2) pressure. Due to the similarity of boiling points with the dibromide side products, a high reflux ratio (300) was necessary. Iodides and dibromides were distilled through a small Vigreux column.

2.2. Data

The UV spectra of some bromides are compiled in Fig. 3, which for comparison also contains C_2H_5Br . The spectra of the iodides all coincide with that of C_2F_5I (see Ref. [21]), which has its maximum at 262.5 nm and a half-width of 33 nm. Table 1 gives boiling points (T_b) and heats of evaporation ΔH^3 , some of which have been evaluated from the temperature-dependent vapor pressure according to

$$\frac{p_n}{101.3 \text{kPa}} = \exp\left(-\frac{\Delta H_n^{\nu}}{k_{\text{B}}} (T_{\text{b}}^{-1} - T^{-1})\right)$$
(5)

The measured ΔH^{v} followed sufficiently well Trouton's rule, that is $\Delta H^{v}/k_{\rm B} \approx hT_{\rm b}$, where h = 12.4 for the bromides and h = 11.0 for the iodides; the latter value is matched to the data compiled in Ref. [23]. Therefore the other ΔH^{v} were calculated from $T_{\rm b}$ using this proportionality. With this assumption, Eq. (5) can be reformulated:

$$\ln\left(\frac{p_a}{101.3\text{kPa}}\right) \approx -h\left(1-\frac{T_b}{T}\right)$$
(5a)



Fig. 3. UV spectra of some bromides. The higher $C_nF_{2n+1}Br$ and $H(C_2F_4)_nBr$ coincide with C_2F_5Br , while the higher dibromo-perfluoroalkanes differ from it just by a twice higher absorption cross-section.

in which the *n*-dependence is contained in $T_{\rm b}$. The boiling points reported previously (Table 1) have been confirmed in this work. For mass and IR spectra, see Ref. [20].

3. Results

3.1. $BrC_2F_4Br + C_2F_4$

This reaction was carried out with an excess of BrfBr. since more C_2F_4 favored the formation of heavier telomers. We used pressures p(BrfBr) = 25 kPa and $p(C_1F_4) = 2-3$ kPa. Due to the deviation from stoichiometry, the C_2F_4 was consumed at a faster rate than the other reactant. Each time, after its pressure had dropped below 2 kPa (monitored by gas chromatography, in one case also continuously by IR spectroscopy), it was replenished to 3 kPa. The sum of the additions are given in the tables. The reactions were carried out at 30°C.

3.1.1. Static system, single-lamp reactor

Table 2 shows the product composition as a function of conversion of BrfBr. It can be seen that the average molecular weight increases with the progress of the reaction. This is due to the fact that the initial products can reenter into the reaction. At low conversion, this effect is still unimportant, and the product ratio in this case will be just as shown in the first column of the table. This ratio can also be expected in a reactor with recirculation, in which the reactant concentrations are maintained and from which all products are continuously removed. In the setup below, however, the product Brf₂Br was also allowed to circulate, so that it was eventually consumed, too.

3.1.2. Distillation recirculation reactor

A simple trap in the recirculation system transmits the products in the ideal case in the ratio of their vapor pressures. At 0°C, this would be about 1:0.1:0.01 for the pure substances BrfBr:Brf₂Br:Brf₃Br (see Table 1). A better selectivity can be obtained with repeated condensation and evaporation. Instead of the trap, we used a distillation system with a small column (Fig. 1). The heavier products accumulate in the boiling bulb, whereas, the reactant BrfBr and a small part of the product Brf2Br leave the column and return to the photoreactor. In this way, the reactor contains mainly $BrfBr + C_2F_4$, so that light products will be favored. The results are shown in Table 3. It can be seen that even at a BrfBr conversion of 85%, the ratio of the first three products is still very near the initial product ratio in the static system (Table 2), as expected, since the ratio of reactants in the gas phase was kept nearly constant during the conversion. Fig. 4, which compares the static (closed symbols) with the circulation results (open symbols), represents this statement: open and closed symbols are close together for the products $n \ge 2$. even if the educt (n=1) concentration widely differs. The ratio of successive products (logarithmic slope in Fig. 4)

Table 1

Boiling points T_b and heats of evaporation ΔH^* . The ΔH^* data are either measured from the logarithmic slope of the temperature-dependent vapor pressure (Eq. (5)) or calculated by Trouton's rule (see text after Eq. (5)) from the boiling point. f stands for C_2F_4

	$T_{\rm b}/{ m K}~({ m at}~p/{ m kPa})$	$k_{ m B}^{-1} \Delta H^{ m v}/{ m K}$	Other
HfBr	285.5 (95.8)		IR 22
Hf ₂ Br	319.2 (95.8)	3946*	, ,
Hf ₃ Br	324.2 (8.0)	3995	
Hf₄Bτ	353.7 (8.0)	45864	
BrfBr	320.7 [7]	4031"	
Brf ₂ Br	371.2 [7]	4584"	
Bif,Br	415.2 [7]	4845	
Brf ₄ Br	458.2 [7]	5246	mp. 310 K
Brf _s Br	500.7 [7]	5736	mp. 346–350 K
Brf ₆ Br	407 (1.33) [7]		mp. 391–397 K
Brf ₇ Br	447 (1.33) [7]		1
$Ffl(=C_5F_5l)$	285.7 [1]	3143	
Ff ₂ I	340.2 [1]	3742	
FG	391.2 [1]	4292	
Ff₄I	436.2 [1]	4771	mp. 294 K [1]
FfsI	468.2 [1]	5177	mp. 338.7 K [1]
Ff.I	505.2	5557	1

^aUsing Eq. (5) and p_n measured at the boiling point and at room temperature.

Table 2

The reaction BrC₃F₄Br+C₃F₄ in the static cell (single lamp, 30°C, 25 kPa of BrC₂F₄Br, 2–3 kPa of C₂F₄), f stands for C₂F₄, Σ C₂F₄ is the total quantity of C₄F₄ added including the initial quantity, Brf₄, Br means Brf₈Br and heavier dibromides

Molar ratio $\Sigma C_2 F_4 / BrfBr$	0.50	1.00	1.50	
Conversion of BrfBr/%		28.6	42.8	65.1
Conversion velocity of Bri	9.3	7.4	6.6	
Product yield/wt.% of	$\mathbf{Brt} \cdot \mathbf{Br}$	76.9	70,5	62.5
converted BrfBr	\mathbf{B} rf \mathbf{B} c	46.0	56.8	52.0
	Brf_Br	13.9	23.4	29.1
	Brt Br		3.5	14.5

Table 3

The reaction $BrC_2F_4Br + C_2F_4$ with recirculation combined with distillation. For the conditions and explanations, see

Molar ratio $\Sigma C_2 F_4 / BrfBr$		0.52	0.92	1.49	2.39
Conversion of BrfBr/%	32.8 5.7	45.2	85.1 5.6	99.4 3.6	
Conversion velocity of BrfBr/g h		5.5			
Product yield/wt.% of	Brf ₂ Br	80.2	76.8	73.3	58.0
converted BrfBr	Brf.,Br	33.4	44.3	43.2	45.1
	Brf ₄ Br	8.4	13.2	14.9	16.7
	Brf ₅ , Br		3.2	12.9	49.2

surprisingly does not depend very much on the reactant ratio. Only the fraction of the heavier products Brf_nBr , $n \ge 5$ increases with the C_2F_4 content. As will be discussed below, this can be due to insufficient speed of circulation.

3.1.3. Multi-lamp reactor, influence of lamp power

For preparative purposes, we designed and operated a reactor with five lamps (see Section 2) with and without recirculation. The irradiation results (Table 4) show that in this



Fig. 4. Mole fractions x_n of Br(C₂F₄)_nBr with (open symbols) and without (closed symbols) circulation. The parameter is the ratio $[C_2F_4]/[B(C_2F_4Br], n=5 actually means <math>n \ge 5$. The data have been calculated from the weight concentrations of Tables 2 and 3; the sum of x_n for the data sets circ1.5 and circ2.4 is only 0.9, which is an estimated normalization factor accounting for the heavier products of unknown molecular weight.

reactor, the selectivity is as good and the efficiency (production rate per lamp) is even better than in a single-lamp reactor (compare the second and last columns of Table 4). This greater efficiency is probably a consequence of the larger dimensions, providing more pathlength for light absorption. The table also shows that the product distribution depends on the light power density (compare columns with 5. 3 and 1 lamp): higher power favors smaller molecular weights. This effect has been previously noticed [13,24] and will be discussed below. The last four columns concern static reactors, the first column reports the results in the recirculation system with distillation. This column shows that with 59% of BrfBr conversion, the yield of Brf_2Br reaches 94 wt.% (68 mol%).

3.7.4. Premixing BrfBr and Brf₂Br for increasing the Brf₃Br yield

Increasing the average molecular weight of the educts will also increase the average molecular mass of the radicals and Table 5

Premixing BrfBr and Brf₂Br as reactants. For explanations, see . Reactor with five lamps, temperature 37–38°C, total pressure 25–28 kPa with 2–3 kPa of C_2F_4 , $\sum C_2F_4/(2 BrfBr + Brf_2Br) \approx 0.48$

Molar ratio Brf ₂ Br/BrfBr		2.00	1.02	0.67
Conversion of BrfBr/%		46.4	43.6	51.2
Product yield/wt.% of	Brf ₂ Br	-54.4°	1.0	29.2
converted BrfBr	Brf ₃ Br	94.4	87.7	67.6
	Brf₄Br	66.8	53.4	40.0
	$\mathbf{Brf}_{5+}\mathbf{Br}$	61.0	19.1	13.7

"Negative sign means consumption.

the products. Therefore, we added some Brf_2Br to the BrfBr. Note in this context that due to a neighbor group effect, BrfBr has an about five times higher absorption cross-section than the higher dibromides (Fig. 3: note also figure caption). In Table 5, it can be seen that the Brf_3Br yield increases with the $Brf_2Br/BrfBr$ ratio, and that Brf_2Br is consumed when this ratio is > 1. At a ratio of 1, the quantity of Brf_2Br does not change, giving the impression that BrfBr would be directly converted to Brf_3Br and the higher telomers.

3.2. Monobromides

The success with the dibromides suggested to study also the monobromides. Our main efforts involved HC_2F_4Br as a starting material. Compared to hydrogen-free compounds, the expected products will have less potential for destruction of the stratospheric ozone, since they will be attacked directly in the troposphere by the OH radical. This may be important, if the compounds will be used in large quantities for medical purposes or in another way with eventual release to the atmosphere. For comparison, we also briefly investigated CF_3Br and got very similar results.

 HC_2F_4Br (abbreviated: HfBr) was synthesized from $HBr + C_2F_4$ in our photoreactor, as previously described [25–27]. We only report some additional observations and the preparation of higher telomers. There are also some interesting differences to the other telomerization systems studied in this work.

Table 4

The reaction $BrC_2F_4Br + C_2F_4$ in a multilamp reactor. For the conditions (except number of lamps) and explanations, see

		Recirculation	Static syste	m		
Nu nber of lamps		5	5	3	,	1
Reactor volume/dm ³		56	56	56	56	55
Vo.ume/lamp/dm ³		11.2	11.2	18.7	28.0	5.5
Absorbed fraction of light/%		57	57	60	66	42
Molar ratio $\Sigma C_2 F_4 / BrfBr$		0.96	0.86	0.94	1.00	1.00
Conversion of BrfBr/%		59.1	42.6	41.5	41.0	42.7
BrfBr conversion velocity/g(h lamp)		11.1	9.1	9.4	11.8	7.4
Product yield/wt.% of converted BrfBr	$Brf_{2}Br$	93.9	73.3	64.0	54.3	70.5
	Brf ₃ Br	32.2	51.9	48.8	50.2	56.8
	Brf ₄ Br	8.1	20.0	23.4	28.0	23.4
	$\mathbf{Brf}_{r+}\mathbf{Br}$	1.6	6.0	8.9	15.3	3.5

3.2.1. $HBr + C_2F_4$

The photochemical synthesis of HfBr in the gas phase, using a 1:1 mixture of the reactants, is very rapid. We observed quantum yields of several thousands, being greater at higher pressures. To obtain some higher telomers, we applied a varying excess of C_2F_4 . The resulting product distributions are shown in Fig. 5.

In addition to these main products, we observed small quantities of the dibromides Brf_nBr (altogether 1–4% of the products), whereas dihydrides Hf_nH were hardly detectable. For stoichiometric reasons, these two side products should be generated in equal quantities. But probably the lacking hydrogen eluded the analysis in the form of H_2 , since the reaction of H with HBr is very rapid [28].

Most of the distributions of Fig. 5 are close to exponential. This means that rephotolysis is negligible (see also Section 4). So, the higher telomers cannot be obtained as the main products. Nevertheless, with a 10–25-fold excess of C_2F_4 , the quantity of Hf₄Br is already appreciable. Under these conditions, we observed a quantum yield for its production of about 100. (For HfBr, the best quantum yield was about 2500). So, the productivity of this reaction is guite attractive for preparative purposes, in particular if the small selectivity for the higher telomers is acceptable. The product distribution with $HBr/C_2F_4 = 0.04$ noticeably deviates from the exponential shape. This is an indication that the primary products have been rephotolysed. In fact, the 7% conversion of C_2F_4 implies that all the HBr has already been consumed. So, in this stage of the reaction, the radicals are not further scavenged by the HBr, but are added to the olefin. Conformingly, at such extreme reactant ratios, we observed solid deposits of higher telomers if the irradiation was not stopped already after few minutes. To avoid deposits in a preparative procedure, it is obviously necessary to replenish the HBr, as soon as its concentration drops.

This task was accomplished in the setup of Fig. 1: we monitored the IR absorption bands of HBr and C_2F_4 and kept their ratio constant by adding suitable quantities of HBr every 10–20 min. Over several batches, it turned out that the circulation speed needed to be as high as possible in order to avoid solid deposits. Using 8 kPa HBr + 80 kPa C_2F_4 , we converted altogether 8.4 mol of HBr and 5.8 mol of C_2F_4 . The collected products were distilled to isolate the various telomers. It turned out that the Hf_nBr have nearly the same boiling points as the side products Brf_{n-1}Br, which were found in quantities of 1–4% altogether. So, this preparative procedure is recommended only where dibromides are not harmful.

At this point, it may be worth mentioning some characteristic side products observed when a high-pressure Hg–Xe lamp or a not ozone-free low-pressure Hg lamp were used. Both lamps emit a few percent of their radiation below 220 nm, the latter at 185 nm. In addition to some HCF₂Br, we observed in this case, dihydrides, all of which had an odd number of carbon atoms (HCF₂f_nH, n = 0-2). This indicates the mechanism of their formation: the short wavelengths can



Fig. 5. Composition c_a of the gaseous products Hf_aBr (not calibrated) from $HBr + C_2F_4$. The inset indicates the $[HBr]/[C_2F_4]$ ratio, the pressures of HBr and C_2F_4 in kPa and the conversion of C_2F_4 . c_a is probably intermediate between wt.% and mol%.

photolyse C_2F_4 (UV spectrum: Ref. [29]), producing both singlet and triplet CF_2 [30]. Whereas, the former can directly insert into HBr, forming HCF₂Br, the triplet carbene will scavenge an H atom from HBr:

$^{3}CF_{2} + HBr \rightarrow HCF_{2} + Br.$

The radical HCF_2 can then add C_2F_4 and/or scavenge an H atom from HBr. thus, forming the dihydrides with odd number of C atoms. Previously [13–16], we also postulated the photolysis of the intermediate radicals at short wavelengths. In fact, CF_3 has a broad and weak absorption around 200 nm [31]. Whereas, the assumption of radical photolysis is needed to explain the CF bond splitting observed in Ref. [13], it cannot explain why in the present experiment, the odd-numbered side products contained practically no Br (except HCF_2Br). The observation again underlines that only a few percent of short-wavelength radiation can be harmful, since the absorption cross-sections can be much higher than at longer wavelengths.

3.2.2. $HC_2F_4Br + C_2F_4$

In this reaction, rephotolysis of the products plays a role and the resulting product distribution (Fig. 6) shows some tendency to a Poisson form, though with deviations at low molecular weight (see also the predicted distributions in Section 4). The figure also shows that a large excess of HfBr is necessary, if one wants to avoid the heavier products Hf_nBr, $n \ge 5$, which tend to form deposits. Due to this deviation from stoichiometry, to obtain larger conversions of HfBr, one must replenish C₂F₄ whenever its concentration has dropped. The reconversion of the products again offers the chance to concentrate the products in a small range of molecular weights, using a circulation system with a trap. We briefly investigated and demonstrated this effect, using the setup of Fig. 2. The C₂F₄ was refilled about every 20 min, after the IR absorption, monitored continuously, indicated that more than 30% had been consumed. In this experiment, we again noticed deposits, if the pumping speed was too slow: in one experiment with an irradiation vessel of 100 dm^3 and a 55-W lamp instead of 5 dm³ and 10 W, our pump ($0.5 \text{ dm}^3/\text{s}$) was not sufficient to avoid deposits.

In the irradiation of $HC_2F_4Br + C_2F_4$, we again observed dibromides as side products, in particular at high HfBr excess. Their over-all concentration was of the order of 5% of the products with HfBr/ $C_2F_4 = 10$. As mentioned, they are difficult to separate from the monobromides due to the similar boiling points. This problem can be avoided, if the telomerization is first carried out using the corresponding iodides, and then the iodine is replaced by Br. As a model system, we preferred a fully fluorinated iodide (C_2F_5I) instead of HC_2F_4I . The latter would, however, be available commercially (Fluorochem) or from thermal or photochemical addition of HI to C_2F_4 [32].

$3.3. C_2 F_5 I + C_2 F_4$

The kinetics of this reaction in a static cell is described in detail in Ref. [33]. Here, we report the selective preparation of $C_8F_{17}I$ in a circulation system. In one series of runs, we used the setup of Fig. 2. The irradiation vessel was heated to 100°C to avoid condensation of the iodides with six and more carbon atoms. The trap in this experiment was actually a three-necked bulb with condenser and bulb cooled to -20° C and equipped with a septum for taking samples from the liquid. The system was filled with 26 kPa C_2F_5I+31 kPa $C_{2}F_{4}$. The ratio of the educt concentrations in the gas was monitored by IR spectroscopy. C₂F₄ was replenished whenever 2 kPa of it had been consumed. Less than about 50% of the C_2F_5I was consumed during the experiment, and this consumption was not compensated. In the condensate, we determined the ratio $C_8F_{17}I/C_{10}F_{21}I$. It is given in Table 6. Heavier iodides were not found, and more volatile iodides represent no loss since they can be reconverted.

Obviously, this ratio decreases with progressing conversion of the educts. This is probably because an increasing average molecular weight of the feed favors heavier products. For compensation, it would certainly be better to replenish also the C_2F_5I or not to substitute the full consumption of C_2F_4 .

The magnitude of this ratio deserves special attention. A ratio of 8 at 27% conversion of the starting iodide (last line of the table) means that only 1/9 = 11% of the products are lost in the form of heavier products. This should be contrasted with the losses in the thermal process which are often much greater than 50% (see for example Refs. [34,35]: for a thermal process with recirculation see Ref. [17]).

In another investigation of this system, we used higher trap temperatures (room temperature and 40°C, reactor: 100°C, circulation system similar to Fig. 1), so that the lower product iodides did not condense. The irradiation was continued until much higher conversion of C_2F_5I (up to 98%). The results Fig. 6. Composition c_n of the gaseous products Hf_nBr (not calibrated) from $HfBr + C_2F_4$. The inset indicates the $[HfBr]/[C_2F_4]$ ratio, the pressures of HfBr and C_2F_4 in kPa. The conversion of C_2F_4 was always smaller than 20%, that of HfBr smaller than 10%. c_n is probably intermediate between wt.% and no0%.

Table 6

Product ratio $C_8F_{17}I/C_{10}F_{21}I$ (determined in the condensate; higher iodides not detectable) as function of conversion of the gaseous educts C_2F_5I and C_2F_4 . 10 W U-shaped lamp, temperature of the reactor (Fig. 2) 100°C, of the trap -20°C. Initial pressures 26 kPa C_2F_5I (decreasing during irradiation) and 31 kPa C_2F_4 (maintained by successive addition of doses of 2 kPa). ΣC_2F_4 means the total (i.e., initial + added) quantity of C_2F_4 . Estimated quantum yield for C_2F_5I consumption: 0.1

$\Sigma C_2 F_4 / k Pa$	31	41	49	
C_2F_4/C_2F_5I conversion/9	% 30/14	48/27	50/34	
Irradiation time/min	150	300	480	
$C_8F_{17}I/C_{10}F_{21}I$	12.5/1	8/1	6/1	

are shown in Table 7 and Fig. 7. It can be seen that the larger the depletion of C_2F_5I and the light iodide products, the more the maximum of the distribution shifts to larger molecular weight. At 98% depletion the maximum is at $C_8F_{17}I$. It is natural that in this case, the next member is less abundant by only a factor of 3. On the other hand, it is worth noting that without the circulation system, a much broader product spectrum (a Poisson distribution) is expected for such high conversion [9] (see also Section 4) and has been observed in Refs. [34.35] in telomerization without circulation. It has the form

$$x_n = \exp(-m) \frac{m^n}{n!} \tag{6}$$



Table 7

Reactor		Static	Recirculation		
Reactor volume/dm ³		1.06	1.71	1.71	1 71
Trap temperature/°C		_	22	40	21
Molar ratio $\Sigma C_2 F_4 / C_2 F_5 I$ (initial)		26.7/26.7	26.7/26.7	26.7/26.7	40/40
Molar ratio $\Sigma C_2 F_4 / C_2 F_5 I$ (Total)		a	66.7/26.7	100/26.7	128/53.3
Irradiation time/min		120	240	308	300
Conversion of C ₂ F ₅ I/%		42.5	94.4	97.9	92
Product yield/mol% of converted C ₂ F ₄ I	C _i E ₀ I	36.9	26.3	5.0	34.6
	C.,F ₁₃ I	5.5	40.1	26.9	40.3
	$C_3F_{17}I$	0.0	21.6	44.5	13.8
	$C_{10}F_{21}I$		6.5	15.8	3.2
	$C_{12}F_{25}I$		0.0	5.8	0.0
Molar ratio $C_8F_{17}I/C_{10}F_{21}I$			3.3	2.8	4.3
Quantum yield of C_2F_4 consumption		0.025	0.10	0.10	0.14

Product distribution from the reaction $C_2F_3I + C_2F_4$ in a static and recirculation reactor. ΣC_2F_4 means the total (i.e., initial + added) quantity of C_2F_4 . Lamp 30 W, reactor of Fig. 1 (but vertical), reactor temperature 100°C, pressures measured at the reactor temperature

"No replenishment. During the reaction, the pressures of C_3F_4 and C_3F_5I dropped from 26.7 to 1.2 and 15.4 kPa, respectively.



Fig. 7. Mole fractions x_n of $C_2F_5(C_2F_4)_nI$ from $C_2F_5I + C_2F_4$ in the static and recirculation system. Parameter is the conversion $1 - x_0$. A Poisson distribution with m = 3.3 (Eq. (6)) is shown for comparison.

and is also shown in Fig. 7. x_n is the mole fraction of the products and *m* is the number average of *n*. The ratio of C₈-to C₁₀-iodides for the Poisson distribution would be near 1, which is three times worse than in our experiment with circulation.

Table 7 also shows a remarkable result: in spite of the broader distribution (compared to Table 6), the product $C_8F_{17}I$ corresponds to 100 wt.% of the consumed C_2F_5I at 98% conversion. An even better result (more than 200 wt.%) can be expected, if the distribution is narrowed down as discussed below.

4. Discussion

The experiments demonstrate that with circulation, a much better ratio of heavy products is obtained than without, and that this ratio can be further influenced by the conditions. It is helpful to consider a simplified kinetic scheme for understanding these influences and other observations, such as the difference between the three halides HBr, organic bromides and iodides. We will also use rate equations to find out the parameters controlling the process. Quantitative predictions are not intended. Hence, we can make many simplifying assumptions such as optically thin conditions and rates independent of molecular weight.

4.1. Kinetics

Telomerizations are chain reactions which include not only the customary initiation, propagation and termination steps, but usually also a chain transfer. The latter either transfers a hydrogen atom (from HBr) or a halogen atom to a radical. In spite of this similarity, the system HBr+C₂F₄ behaves differently from the other reactions. For interpretation, we use the two kinetic schemes in Schemes 1 and 2. For the considerations to follow, we assume for simplicity that the rate constants do not depend on the size of the molecules (see end of Section 4.1.3 for effects caused by this approximation).

4.1.1. Fast chain transfer: $HBr + C_2F_4$

This reaction differs from the other systems in several respects.

- The chain transfer (in this case, an H transfer) is very rapid and can easily compete with the chain termination (radical combination). Therefore, the kinetic chain length (= propagation rate over termination rate) and the quantum yield are very large.
- 2. The reactive species (Br) directly generated by chain transfer can only recombine by a three-body collision, a process which is slow. This increases the chain length further.

Due to the large chain length, most Br atoms are generated by chain transfer. The contribution by HBr photolysis is below 0.1%, concluded from the quantum yields above 1000. Initiation:

$$\begin{array}{rcl} HBr &+ h\nu &\rightarrow &H + Br & (\sigma I [HBr]) \\ H &+ HBr &\rightarrow &H_2 + Br \\ \hline \\ Chain propagation and chain transfer: \\ Br &\stackrel{f}{\longrightarrow} Brf &\stackrel{f}{\longrightarrow} Brf_2 &\stackrel{f}{\longrightarrow} Brf_3 &\stackrel{f}{\longrightarrow} & (k_{pr}[f]) \\ &\downarrow + HBr &\downarrow + HBr &\downarrow + HBr & (k_{tr}[HBr]) \\ &\downarrow + HBr &Hf_2Br &Hf_3Br \\ &+ Br &+ Br &+ Br \end{array}$$

$$\begin{array}{c} Chain termination: \\ R &+ R' &\longrightarrow &RR' & (k_{trr}[R']) \end{array}$$

Scheme 1. The most important reaction steps for HBr + C_2F_4 , C_3F_4 is abbreviated by f. Since practically all hydrogen atoms are consumed by the very efficient scavenger HBr [28], this step has been listed under initiation. The most efficient third body M in this system is Br₂.

Initiation: $(\sigma I [RI])$ RI + hvR + IChain propagation and chain termination: $R \xrightarrow{f} Rf \xrightarrow{f} Rf_2 \xrightarrow{f} Rf_3 \xrightarrow{f}$ $(\mathbf{k}_{pr}[f])$ $+1_{2}$ (k₁₂[12]) + 12 + I₂ Rfl Rf₂I Rf₃I Halogen recombination: 1 + I + M $I_2 + M$ ->

Scheme 2. The most important reaction steps for $RI + C_2F_4$. C_2F_4 is abbreviated by f. For the bromides, the terminations consist of the recombination R + R' and the reaction $R + Br_2$, the relative contributions of which depend on the conditions.

Therefore, one can also neglect the photolysis of the primary products, unless HBr is used in very small concentrations or has nearly been used up after high conversion.

In the case of high conversion, the initially formed bronides are rephotolysed in the presence of HBr. However, they will not eventually form the higher bromides, but (di)hydrides, since the radicals rapidly abstract an H atom from HBr. So, in the presence of HBr, rephotolysis combined with continuous separation of the higher bromides is not suitable for selective preparation of the latter. With negligible rephotolysis, an exponential product distribution over the degree of polymerization is expected. In fact, the curves for low conversion in Fig. 5 are fairly well approximated by exponentials. The ratio of the quantities of successive bronides is [9]

$$\frac{[\mathbf{H}\mathbf{f}_{n}\mathbf{B}\mathbf{r}]}{[\mathbf{H}\mathbf{f}_{n+1}\mathbf{B}\mathbf{r}]} = \mathbf{I} + \frac{k_{tr}[\mathbf{H}\mathbf{B}\mathbf{r}]}{k_{pr}[\mathbf{C}_{2}\mathbf{F}_{4}]}$$
(7)

where the rate constants for H transfer k_{tr} and addition of C₂F₄ k_{pr} ('propagation') were assumed to depend only little on *n*. From the logarithmic slopes in Fig. 5, we get $k_{tr}/k_{pr} = 15-20$.

This large ratio is responsible for the relatively small molecular weight of the products. Obviously, the slope of the distribution is controlled by the concentration ratio $\gamma = [HBr] / [C_2F_4]$. A small such ratio requires replenishment of HBr from time to time to keep γ constant and also demands a good gas circulation to avoid local depletion of HBr. A small γ allows convenient preparation of the higher bromides with good quantum yield, though not selectivity. This has been demonstrated in the previous section. The conversion rate of HBr and production rate of the bromides has been derived in Refs. [26,27] from the assumption of stationary Br and radical concentrations to be

$$-\frac{\mathbf{d}[\mathbf{H}\mathbf{B}\mathbf{r}]}{\mathbf{d}t} = k_{\mathrm{tr}} \cdot [\mathbf{H}\mathbf{B}\mathbf{r}]^{3/2} \cdot (\sigma t/2k_{\mathrm{RR}})^{1/2}$$
(8)

where k_{tr} and k_{RR} are the rate constants for H transfer and radical combination, σ is the absorption cross-section of HBr and I the intensity in photons cm⁻² s⁻¹. Dividing by the absorbed power σI [HBr] gives the quantum yield

$$\varphi_{\rm HBr} = k_{\rm tr} \cdot [{\rm HBr}]^{1/2} \cdot (2k_{\rm RR}\sigma I)^{-1/2}.$$
(9)

For our conditions (0.1 W cm⁻², 25 kPa HBr), one calculates $\varphi \approx 7500$. We actually found somewhat smaller values (2500). A possible reason for this deviation can be a small Br₂ content which could scavenge a fraction of the radicals.

4.1.2. Negligible chain transfer rates: iodides

A much slower chain transfer is characteristic for all the other reactions studied here. In fact, it turned out that under our conditions (gas phase, not too small conversion), it is even negligible. It would involve the transfer of a halogen atom from the educt to a radical. This is easiest for the iodides and, due to a neighbor-group effect, also for BrfBr. But in the kinetic work on $C_2F_5I + C_2F_1$ [33] it has been shown that under practical conditions (non-negligible conversion), another reaction of the radicals wins the competition with this transfer: the reaction of the radicals with accumulated molecular iodine. This reaction is so fast that even the radical dimerization can be neglected (in case of a low-intensity lamp, which produces only a low radical concentration). Therefore, we omitted the chain transfer and the radical combination from Scheme 2. Due to its kinetic simplicity, we concentrate on the iodide system in this section.

The reaction $R + I_2$ can be considered as terminating the chain, since the iodine atoms produced are relatively unreactive. Formally, the iodine recombination is also part of the termination. Its rate is slow, since it requires a third body M. (The most efficient M is I_2 itself [36]). It is, however, not necessary to know this rate for calculating the I_2 concentration, since after a short time the latter will, for stoichiometric reasons, simply be equal to the concentration of radical dimers [33]:

$$[I_2] = [R_2]$$

unless it is limited, e.g., by its vapor pressure in the cold trap.

The ratio of the propagation rate over the termination rate is called the kinetic chain length ν . For the iodide system it can be written:

$$\nu = k_{\rm pr} [C_2 F_4] / (k_{12} [I_2]) \tag{10}$$

It is equal to the average number of C_2F_4 units added to the starting iodide to form the telomer products. If there is no rephotolysis of the products, one expects an exponential distribution of $x_n = [Rf_nX]/\Sigma_i[Rf_iX]$. In fact, the distribution observed at low conversion (42% in Fig. 7, even better at lower conversion) is close to exponential. Denoting by *q* the ratio of successive products (see also Eq. (A1)), one can write (see Appendix A)

$$x_0 = \exp(-\tau) \tag{11}$$

$$x_n = (1 - q)q^{n-1}(1 - x_0) \tag{12}$$

where $q = \nu/(\nu + 1)$ (13)

and
$$\tau = \sigma I q t$$
 or $\sigma I t$. (14)

In normalized time τ , the factor q should be omitted if the chain transfer dominates (if the I_2 concentration is negligible), whereas it should be added if the back-formation of the starting halide RX from the primary radical R cannot be neglected, such as with non-negligible { I_2 }. In the latter case, q is equal to the quantum yield φ for conversion of RI.

4.1.3. Negligible chain transfer rate: bromides

Also with the bromides, the halogen atom transfer to a radical is only slow. In the chain termination, there are, however, differences to the iodides. Since the addition of Bratoms to C_2F_4 is probably fast, molecular bromine cannot accumulate much. If there is any accumulation, there can be at best a steady-state bromine concentration, which will increase with the photolysis rate (intensity and absorption cross-section). A termination by radical combination has been suggested for the telomerization of $BrC_2F_4Br + C_2F_4$, and the intensity dependence of the product molecular weight was successfully modelled with such kinetics [24]. On the other hand, the kinetics of this and similar systems with pulsed laser excitation was interpreted in terms of some contribution of Br₂ [8,37]. The two channels of product formation can be distinguished in the system $HC_2F_4Br + C_2F_4$. Radical combination forms dihydrides and dibromides, scavenging by Br₂ forms monobromides (Hf_nBr). We found a ratio of dibromides/monobromides of typically 0.05 under our conditions (see Section 3); but using a focused 1-kW Hg-Xe lamp this ratio was up to 0.4 [20]. So, we believe that the contribution of radical combination is non-negligible, especially when using BrC₂F₄Br with its high absorption cross-section.

Product formation via radical combination makes product distributions $(x_n \alpha nq^n)$, if the rates do not depend on n) deviating from exponential to favor higher molecular weights. Another deviation is caused in the dibromide system by the n-dependence of the photolysis rate, being about five times larger for BrfBr than for the products Brf_nBr. Also, the addi-

tion of Brf to C_2F_4 is noticeably faster than that of the heavier Brf_n [24]. But the analysis in the previous and following sections is still qualitatively correct, in the sense that the parameters controlling the molecular weight distributions are the kinetic chain length ν (= propagation rate/termination rate), the conversion and the molecular weight or composition of the starting bromides.

4.2. Rephotolysis

In this and Section 4.3, we will again consider in detail only the iodide system. If all the iodides are photolysed at the same rate σI and if C_2F_4 is kept constant by replenishing, then the mean number $\langle n \rangle$ of C_2F_4 units contained in educt (0 units) and products increases linearly with time, with a rate proportional to ν :

$$\frac{\mathrm{d}\langle n\rangle}{\mathrm{d}t} = \nu\sigma I. \tag{15}$$

For the mole fraction x_n of the products, we derive in Appendix A an exponential multiplied by a polynomial $P_a^{(n)}(\tau)$ of degree *n*, containing *q* as a parameter:

$$x_n = P_a^{(n)}(\tau) \exp(-\tau). \tag{16}$$

These functions are represented in Fig. 8. With increasing τ , Eq. (16) describes the continuous transition from an exponential to a Poisson distribution. The term with highest power in τ has the form $\exp(-\tau) + ((1-q)\tau)^n/n!$. That is, at long times or high conversions, one expects a Poisson distribution (Eq. (6)), whose maximum and average *n* are proportional to time. Numerically, one finds that the curve with $\tau=5$ is close to a Poisson distribution with m=4.5. It is evident from the figure that the distributions quickly become broader as the conversion proceeds. This broadening is even faster with a larger value of *q*. So, to limit the products of high molecular weight, the mixture should be sent to the trap at an early stage of the conversion.

The experimental distributions x_n of the iodides in Fig. 7 are narrower than a Poisson distribution and do not broaden



Fig. 8. Mole fractions of $C_2F_5(C_2F_4)$. If rom $C_2F_5I + C_2F_4$ with rephotolysis, calculated using Eqs. (16). (A1.8) and (A1.10) with q = 0.1 for different normalized reaction times τ .

with time. This is due to the effect of the trap (see below). However, $\langle n \rangle$ grows proportional to time ($\tau = -\ln(x_0)$) and the maximum of x_n shifts accordingly, and at early time, the transition from exponential to a distribution with maximum can be observed. Whereas, in the dibromide system (Fig. 4), the latter feature is also noticeable, the shape and maximum of x_n are fairly insensitive for the conversion $1 - x_0$. This may be due to the fact that the (re)photolysis of the higher bromides is about five times slower than that of BrfBr. This is in contrast to the iodides and the *n*-independence of the rates assumed above.

We can also conclude from this section that both the conversion $1 - x_0$ (or $\tau = -\ln(x_0)$) and the kinetic chain length ν are control parameters for the molecular weight. For the iodide and bromide systems, $\nu \alpha [C_2F_4]$ and for the iodides also $\nu \alpha [I_2]^{-1}$, which can be controlled by the trap temperature. Other control parameters are expected to be the starting ratio of halides (if a mixture is used) and the properties of the separation system (trap). They will be discussed below.

4.3 Circulation system

In the circulation system, the heavier products Rt_aI will be continuously removed, if their partial pressure comes close to the vapor pressure p_n at the trap temperature. (In a mixture, due to solution effects, it is not necessary to reach the full p_n of the pure components). These vapor pressures depend almost exponentially on n, since the heat of evaporation ΔH^{v} is proportional to the boiling temperature $T_{\rm b}$ (at 101.3 kPa) and the latter increases by about 45 K for unit increase of n. The functional dependence is given by Eqs. (5) and (5a). It is shown in Fig. 9 in relative units, denoted S_n (= $p_n/101.3$ kPa) for trap temperatures T = 273 and 313 K, together with the product distributions x_{μ} generated in the reactor at low conversions. Approximately, p_n is a limiting line: the trap will influence the iodide partial pressures $x_n p_{tot}$ ($p_{tot} = sum$ of iodide pressures), if the latter comes close or even exceed the p_n line, either due to increasing conversion or to a choice of a high $[C_2F_4]/[I_2]$ ratio or to lowering the trap temperature (which shifts the p_n line). However, p_n also has a more quantitative meaning: if, as in practice, the separation unit almost completely condenses the heavy products, the composition of the condensate will be just as produced in the reactor. The vapor passing through will be depleted by a separation factor S_n . If the separation unit (trap or still) has a number $n_{\rm pl}$ of theoretical plates.

$$S_n c(p_n^{n_{\mathbf{P}}}). \tag{17}$$

Multiplying x_n by S_n means adding the curves in the logarithmic plot, so that the distribution returning to the reactor has a steeper slope at high *n*. The S_n lines shown in the figure correspond to $n_{pl} = 1$. To convert to pressure units, multiply S_n by the normal pressure (101.3 kPa) and x_n by the total pressure p_{tot} of the iodides, for which 10 and 1 kPa have been assumed in the Fig. 9a and b, respectively (p_n is treated here

Fig. 9. Mole fractions of $C_2F_5(C_2F_4)$, ff from $C_2F_4I + C_2F_4$ with rephotolysis, calculated as in Fig. 8 with q = 0.1 (a) and 0.3 (b). The separation factor S_n is the vapor pressure p_n of the iodides in relative units. (a) at 40°C, (b) at 0°C. To convert to pressure units, multiply the S_n scale by the normal pressure (101.3 kPa) and x_n by the total pressure p_{tot} of the iodides. If $p_{tot} = 10$ kPa (a) or 1 kPa (b), the curves for the partial pressures ($x_n p_{tot}$) and vapor pressures ($p_n = S_n \times 101.3$ kPa; will have the relative positions just as shown in the figures. An increase of p_{tot} shifts the curves $x_n p_{-n}$ vs. p_n so that condensation sets in at earlier times τ .

as a variable which is easy to measure, although in principle, it can be calculated from the x_n and the trap temperature).

The figure shows that with q = 0.1 and $p_{tot} = 10$ kPa, condensation of Rf₄I begins around $\tau = 1.1$ (i.e., with a conversion of $1 - e^{-\tau} = 67\%$), but with q = 0.3 and $p_{tot} = 1$ kPa, it begins already around $\tau = 0.4$ (conversion 33%), and even earlier at higher pressure. This is a consequence of the fact that a larger q enhances the heavier products. It also shows that the higher quantum yield ($\varphi = q!$) requires an acceleration of the circulation more than proportionally to the higher conversion rate. To avoid high molecular weights, one should profit from the steepness of x_n at small τ and induce condensation as early as possible. This can be attained not only by making S_a steeper (by lowering the trap temperature or increasing $n_{\rm pl}$), but also by increasing the total iodide pressure, since x_n must be multiplied by it to convert them to partial pressures. Actually, p_{tot} was higher in the experiments than in Fig. 9. The low pressure in this figure was only chosen because it allows to better illustrate the principles.



We can draw several more conclusions from these considerations.

- 1. Since the product distribution depends on $\nu \alpha |C_2F_4| / [I_2]$, any change of $[I_2]$ by varying the trap temperature requires a proportional change of $[C_2F_4]$ to avoid change of the product spectrum. We found this effect in the $C_2F_5I + C_2F_4$ system: at room temperature, without circulation and low conversion, the ratio $[C_2F_5I]/[C_2F_4]$ optimal for $C_8F_{17}I$ formation was 1:3 [20]. whereas, with circulation and a trap temperature of $-20^{\circ}C$ (reactor temperature 100°C), it was 1:1.5 (Table 6). In the former case, the I₂ concentration varied during conversion (being visible by its violet color) and was certainly higher on the average than in the latter case.
- 2. If R in Scheme 2 already contains a number n_0 of C_2F_4 units, the above analysis including the resulting distribution (as a function of *n*) will not change; but the maximum will shift by n_0 to the right. if plotted versus the total number $n + n_0$ of monomer units. So, the product distribution can also be controlled by injecting products of intermediate molecular weight. This has been demonstrated for Brf_nBr.
- 3. If the conversion is too high in one cycle, or equivalently, if the circulation is too slow, molecular weights higher than desired may be produced before condensation can begin in the trap. In such cases, we observed condensation already in the reactor. Deposits on the UV windows or the lamps would be serious, since they can be further photolysed and increase their molecular weight, so that it may eventually be difficult to remove them. Besides accelerating the circulation, also heating the windows (lamps) to a temperature above that of the surrounding helps to prevent deposits.

In one version of our circulation system, we used a small rotatory vane pump with a throughput of up to 0.5 dm³/s. An elegant circulation method, which is capable of very high speeds and does not need moving mechanical parts. uses thermal convection: if a vertical external tube (length *l*, diameter *d*), connected at both ends with the reactor, would be colder by ΔT than the reactor, the difference in hydrostatic pressure is

$$\Delta p = \Delta \rho g l = (\Delta T/T) \rho g l \tag{18}$$

 $(\rho = \text{gas density}, g = 9.8 \text{ m/s}^2)$, which for instance with $\Delta T = 100 \text{ K}$ and ρ corresponding to atmospheric pressure would drive a flow of 26 dm³/s in a tube of d = 50 mm (calculated using Poiseuille's law). The flow would be even faster with condensation, or if the temperature difference would be between the walls of the reactor and its axis. In one of the setups (Fig. 1), we used a passively driven flow with condensation. To maintain the separation efficiency in spite of the fast flow, one should initially precipitate only the condensable material and distill this in a separate unit.

4.4. Continuous process

In the experiments with recirculation, the reactants were replenished, but the products accumulated in the system. In a really continuous process, the products also should be withdrawn. A steady state can be reached if the iodide feed is equal to the product stream of the product iodides altogether (both in mol/h). This follows from the material balance of the iodine atoms. It is easy to calculate for this case the iodide mole fractions $x_n^{(l)}$ in the liquid products (for calculating the gas-phase composition, multiply these $x_n^{(l)}$ by p_n). This has been done in the Section A.2 under simplifying assumptions, and the result is shown in Fig. 10. The parameter r is the ratio of photolysis rate over feed rate and 1/(r+1) is the depletion of the feed iodide (RI) in the steady state; s characterizes the separation efficiency (vapor-pressure ratio of successive iodides) and q is as before (Eqs. (12) and (13)). One can see that r and s influence the distribution of the light products. but the ratio of heavy products (logarithmic slope) is always = q. independent of conversion and separation efficiency. This ratio is equal as in the case of low conversion in the static case. This may be unexpected at first sight. But *a* is also equal to the relative probability that a radical adds another C_2F_4 compared to the total reaction rate (Eq. (A1)). which does not depend on the circulation and separation, since the time scales are very different.

The predicted constancy of slopes agrees remarkably well with the experimental results of (a semilog version of) Fig. 7, the effective q varying only little: from 0.22 to 0.33 with the conversion dramatically increasing (the slight variation could have to do with the fact that in the experiment, the products were allowed to accumulate, so that their concentration was not stationary). The shapes and shifts of the curves in dependence on the conversion show a similar agreement. Thus, also the shape which was found to be narrow compared to a Poisson distribution is explained as a consequence of the exponential distribution.



Fig. 10. Calculated mole fractions $x_{\perp}^{(\ell)}$ of $R(C_2F_4)_{\mu}I$ in the liquid phase produced by combined action of the photoreactor and the trap in the circulation system. For the parameters see the text.

The calculation assumed for simplicity that the feed consists (together with the necessary C_2F_4) only of RI (= C_2F_5I). The heavy-product ratio would be the same, if one injected a heavier iodide, as well as if a mixture of them was used. The resulting distributions would look similar to those of Fig. 10 for higher r (higher conversions). This result is useful for a practical improvement of the process: whereas in the calculation, the liquid product stream still contains light iodides, in a production process one would separate them externally and reinject them to the reactor. As a result, the net feed would only consist of $C_2F_5I + C_2F_4$ and the product would be the desired heavier iodide, the quantity of even heavier side products being characterized by the effective q.

A patent [17] using a long reactor for thermal telomerization of $C_2F_5I + C_2F_4$ claimed a similar quality of product distribution as in this work. The intermediate iodides were externally separated by rectification and then individually refed at different positions to the tubular reactor, so that the heavier the intermediates, the shorter was the additional reaction time. However, as we have shown, the ratio of heavier product depends only on q, not on the reaction time. On the other hand, q also depends on [1₂]. Probably, this concentration increases along the reactor (longitudinal flow), so that the iodides injected near the exit will experience a smaller q (steeper logarithmic slope for the products). A direct control of [1₂] would probably be simpler.

5. Concluding remarks

Dolbier says in his recent review on reactions of fluoroalkyl radicals: "What remains to be done in this area is a tough job: to find conditions for optimization of production of telomers with various specific degrees of polymerization." [10] This task has been solved in this work for the special case that the primary products can re-enter into the reaction and that the products can be continuously separated by fractional condensation or distillation. We have demonstrated several examples in a laboratory setup in batch operation. The method is, however, even more attractive for continuous operation. In this case, one would replenish the reactants (e.g., C_2F_4 + halides of low molecular weight) and selectively remove the product halides of high molecular weight. The composition in the reactor would be completely stationary. Hence, the net reaction would be the conversion of one or several different light halides to a narrow distribution of heavier ones. The ratio q^{-1} of the desired product to the next heavier one only depends-in the idealized theory --on the primary distribution produced in the reactor which is controlled by the kinetic chain length $\nu (q^{-1} = 1 + \nu^{-1})$. In practice, we found slightly narrower distributions (smaller effective q) at lower conversions. In batch operation, it is desirable to have a high conversion of the starting materials. In the system $C_2F_5I + C_2F_4$, we have demonstrated that even with 98% consumption of C_2F_5I , one has still a molar ratio of \Im :1 for the C₈ over the C₁₀ iodides, if the circulation system is used (Table 7). This is clearly much better than in the static case. In continuous operation, however, there is no necessity to have a low C_2F_5I concentration in the reactor. In this case, the selectivity for the desired product can be much better than in the batch process, if again, the average molecular weight is kept at low values by choosing a low $\nu \alpha [C_2F_4]/[I_2]$. We have demonstrated a value of up to 12.5 for the ratio of $C_8F_{17}I$ to the higher iodides (Table 6).

The process works very well for the systems $C_2F_5I + C_3F_4$ and $BrC_{3}F_{4}Br + C_{3}F_{4}$, so that higher iodides and dibromides can be selectively prepared in this way, up to the limit where the products are no longer volatile. With monobromides, however, one always observes substantial quantities (5%) of $Br(C_{3}F_{4})_{n}Br$ as side products. Of course, with $BrC_{3}F_{4}Br$ as educt, they are identical to the main products. But if the desired product is a monobromide with even number of CF₂ groups, the dibromides are difficult to separate due to accidentally almost equal boiling points. With CF₃Br as starting material, however, the main products have an odd number of CF₂ groups, in contrast to the dibromide side products; the smallest difference of boiling temperatures is about 20 K, so that separation should be feasible. In other cases, one may wish to exchange the Br by another substituent and the separation may be possible afterwards. In general, however, it will be preferable to prepare the monobromides via the corresponding iodides [1].

To control the process, the composition in the reactor should be kept constant. A very convenient method provides in the trap a liquid stock of iodide(s) or bromide(s) whose partial pressure is then determined by the temperature. The olefin pressure can then simply be monitored and controlled by the total pressure. (We used this method with $BrC_2F_4Br + C_2F_4$ in several preparative runs not reported here). In particular, in cases where an extreme ratio of the reactants was required, we used a more advanced analysis technique such as infrared spectroscopy or gas chromatography. However, in the systems $C_1F_4 + C_2F_5I$ or BrC_2F_4Br , the required ratio of the reactants is not far from stoichiometric, so that replenishment is not often necessary and can even be done by hand.

That the ratio $[C_2F_4]/[I_2]$ is a control parameter in the iodide system was derived from the assumption that the final products RI form by reactions of the radicals R with the molecular iodine. This mechanism implies that the quantum yield φ for conversion of the starting halide never exceeds 1. The difference to 1 is due to the scavenging of the primary radical by I₂. (Compared to this reaction, the loss by radical combination can almost be neglected with the small [R] produced by the low intensities) With the trap cooled to below room temperature, we reached $\varphi = 0.5$. Much higher quantum yields can be predicted. if [I₂] is further reduced until its reaction with the radicals is slower than the chain transfer (iodine transfer) in R + RI and $\varphi > 1$ is feasible in this case. Using the rate constants of Refs. [33,28] and [RI] corresponding to atmospheric pressure, we find

$$k_{I_2}[I_2] \le k_{tr}[RI] \text{ if } [I_2] \le 2 \times 10^{-7} \text{ mol/dm}^3$$
 (19)

 $(I_2 \text{ pressure } 0.5\text{Pa}).$

This corresponds to the vapor pressure of iodine at -20° C. To keep [I₂] so low is probably feasible by washing the iodine out by a counterflow of the liquid iodides. In this case, the control parameter will be $\nu' = k_{pr}[C_2F_4]/k_{tr}[RX]$ and the C_2F_4 concentration must be appropriately reduced to keep $q = \nu'/(\nu' + 1)$ below 0.1–0.2. With sufficiently small [I₂], φ will be limited only by the radical recombination. With [R] similar to ours, one can deduce the chain length from the ratio of iodide products to recombination products; the ratio given in Ref. [38] for the very similar system $CF_3I + C_2H_4$ implies $\varphi \le 200$, if [I₂] = 0. We believe that at least $\varphi = 1$ should be practically feasible.

The quantum yield may not seem important in view of the small photon costs: a low-pressure Hg lamp of 55 W electric power (15 W or 0.11 mol/h of UV quanta at 254 nm) costs about 50 USD including power supply and has a lifetime of 10 000 h. Using the data of Table 7 ($\varphi \approx 0.1$, not optimized), one calculates a production of 6 g of C_8F_{17} per hour in a single-lamp reactor. With the moderate improvement of φ to 0.5 by lowering $[I_2]$ and with a 10-lamp reactor (which is still a laboratory setup; a reactor with five lamps has been demonstrated), one calculates a $C_8F_{17}I$ production of 0.3 kg/ h. It would be desirable to check experimentally whether better washing out of I_2 would increase φ and the productivity even more, as suggested. An alternative would be to take a lamp of higher power per unit length, but with a spectrum which is still in a narrow range and is fully absorbed. A good candidate would be an excimer lamp (KrF at 248 nm or XeCl at 308 nm) with its similar efficiency, but a power around 1 kW per m of length [39,40].¹

These numbers also demonstrate that in contrast to a widespread opinion, the throughput in a gas-phase reactor can be substantial. Its dimension is not much larger than with a liquid: the necessary diameter is only a small multiple of the absorption length of the light, which was kept below 3 cm in this work by choosing a not too small pressure of the halide. Thus, the space-time yield calculated for the example above is only 2–4 times smaller than in the conventional methods disclosed in the patents [17,35]. It should also be noted that the separation in the circulation system by means of the vapor pressures does not require that the reaction itself is also carried out in the gas phase, nor is it necessary to choose a photochemical reaction. One may also think of an IR-laser induced reaction [41–44].

Finally, we should also mention that the photochemical reactions studied here are very clean. That is, with due care, there is no darkening of windows or lamp walls due to decomposition products. This is in contrast to (radical) photochemistry of compounds with many CH bonds, where the radicals can frequently disproportionate, giving rise to unsaturated compounds with higher absorption at the irradiation wavelength. In fluorocarbon chemistry, such disproportionations do not occur at normal temperatures. The necessary care involves:

- avoiding (by suitable temperatures and circulation speeds) deposit of the heavier products on the windows or lamps; once deposited, they would be photochemically converted to even less volatile products;
- avoiding hydrocarbons including traces of pump oil. Perfluoropolyethers (e.g., Fomblin, Ausimont) as pump oil present no problems;
- 3. avoiding wavelengths shorter than about 230 nm, especially the 185 nm Hg line. These would give rise to side reactions such as photolysis of C_2F_4 (to singlet and triplet CF_2) and of the intermediate radicals (causing CC and CF bond splitting). Such wavelengths are suppressed in the commercial so-called ozone-free lamps, which employ glasses (such as Vycor or Heralux) opaque below about 240 nm:
- avoiding corrosion sensitive metals or protecting them (e.g., by enamel) from halogens;
- 5. avoiding oxygen. Its reaction with a fluorinated radical RCF_2 finally produces an acid fluoride RCFO (along with IF or BrF in the presence of a halide), which can hydrolyse to HF. The latter attacks glass, enamel and ceramics.

Under such conditions, we have run a production of dibromides in the kg scale over several days without any indication of degradation. More than 20 yr of operation of the photochemical iodine laser with its very similar chemistry (photolysis of iso-C₃F₇I, megajoule flashlamps, Heralux quartz glass) in our institute in Garching point to the same direction.

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Appendix A

A.1. Telomer distribution produced in the reactor (without and with rephotolysis)

Using the steady state approximation for the radicals in the reaction Scheme 1, i.e., in the absence of rephotolysis, we get

for
$$n \ge 1$$
: $\frac{d[\mathbf{Rf}_n]}{dt} = 0 = k_{pr}[C_2F_4][\mathbf{Rf}_{n-1}]$
 $-(k_{12}[I_2] + k_{pr}[C_2F_4])[\mathbf{Rf}_n]$
or $\frac{[\mathbf{Rf}_n]}{[\mathbf{Rf}_{n-1}]} = \frac{k_{pr}[C_2F_4]}{k_{12}[I_2] + k_{pr}[C_2F_4]} =:q$ (A1.1)

and
$$[\mathbf{R}] = \frac{\delta T}{k_{1,2}[\mathbf{I}_2] + k_{pr}[\mathbf{C}_2 \mathbf{F}_1]} [\mathbf{R}\mathbf{I}]$$
 (A1.2)

⁴ Such lamps are commercially available from Heraeus Noble Light (Hanau) and Osram (Munich).

From Eq. (A1.1) we obtain

$$[\mathbf{R}]_{n} = q^{n} [\mathbf{R}] \tag{A1.3}$$

which can be combined with Eq. (A1.2). The product formation rate can also be written in terms of q, as well as the educt consumption. Using Eq. (A1.3) and Eq. (A1.2), we obtain:

$$\frac{\mathrm{d}[\mathrm{RI}]}{\mathrm{d}t} = -\sigma I[\mathrm{RI}] + k_{1_2}[\mathrm{I}_2][\mathrm{R}] = -\sigma tq[\mathrm{RI}]$$

or $\frac{\mathrm{d}x_0}{\mathrm{d}\tau} = -x_0$ (A1.4)

$$n \ge 1: \frac{\mathrm{d}[\mathbf{R}\mathbf{f}_n\mathbf{I}]}{\mathrm{d}t} = k_{1_2}[\mathbf{I}_2][\mathbf{R}\mathbf{f}_n] = \sigma I(1-q)q''[\mathbf{R}\mathbf{I}]$$

or $\frac{\mathrm{d}x_n}{\mathrm{d}\tau} = Qq''x_0$ (A1.5)

In the second form of Eqs. (A1.4) and (A1.5) we have introduced Q = (1-q)/q, the normalized time $\tau = \sigma l q t$ and the mole fractions

$$x_n = |\mathbf{R}f_n\mathbf{I}| / \sum_{i} |\mathbf{R}f_i\mathbf{I}| = |\mathbf{R}f_n\mathbf{I}| / |\mathbf{R}\mathbf{I}|_0$$
(A1.6)

These equations have the solutions (11-14) in the text. To include rephotolysis, one adds a term $\sigma I[Rf_n1]$ generating the radical Rf_n to the steady state Eq. (A1.1). After some algebra, one derives the differential equations

$$\frac{\mathrm{d}[\mathrm{Rf}_{n}\mathrm{I}]}{\mathrm{d}\tau} = -[\mathrm{Rf}_{n}\mathrm{I}] + Q\sum_{i=0}^{n-1} q^{n-i}[\mathrm{Rf}_{i}\mathrm{I}]$$
(A1.7)

Eq. (A1.7) can also be understood in a straightforward way: the second term represents the production of Rf_v from all the lighter iodides together (compare Eq. (A.5+)). This set of equations has the solution Eq. (16) in the text, in which the coefficients a_{vi} of the polynomial

$$n \ge 1: P_q^{(n)}(\tau) = \sum_{i=1}^n a_{ni} \tau^i$$
 (A1.8)

$$n=0: P_a^{(0)}(\tau)=1$$

can be found by the insertion of Eq. (16) into Eq. (A1.7) and comparison of coefficients for each τ^i . The resulting set of algebraic equations

$$ja_{nj} = Q \sum_{i=j-1}^{n-1} q^{n-i} a_{i,j+1} \qquad (n \ge 1.0 \le j \le n)$$
 (A1.9)

has the solution

$$a_{nj} = \binom{n-1}{j-1} \frac{Q^j q^n}{j!} \tag{A1.10}$$

with the special values $a_{n1} = Qq^n$ and $a_{nn} = (Qq)^n/n!$. For x_n the term $a_{nn}\tau^n$ dominates over $a_{n,n-1}\tau^{n-1}$ if $\tau \gg Q/(n-1)$. It yields a Poisson distribution when multiplied by $e^{-\tau_n}$.

A.2. Telomer distribution produced by combined action of reactor and trap

In a continuous process, a steady state can be reached for the gas- and liquid-phase concentrations of all components. We assume that only C_2F_5I (=RI) is fed into the reactor (together with the necessary C_2F_4), at a rate (mol/h) which we write for convenience in the form *FV*, containing the reactor volume *V*. From the material balance of iodine atoms (neglecting the loss due to molecular iodine) one infers that the product stream of all iodides together will be equal to the feed, due to the steady state, and the stream of the individual liquid components will be $FVx_n^{(1)}$. If in the steady state, feed rate \ll condensation rate (= rate of evaporation + feed), then the gas phase concentrations $|Rf_nI|$ are connected with the liquid-phase mole fractions $x_n^{(1)}$ via the saturated vapor density of the pure substances (to receive it, multiply Eq. (5) by 101.3 kPa/k_BT):

$$[Rf_nI] = [Rf_nI]_{sat} x_n^{(I)}$$

= [RI]_{sat} sⁿ x_n^{(I)}. (A2.1)

For simplicity, we assumed here the exponential dependence of the vapor pressure on n, which was already mentioned. The net change of concentrations, which will be 0 in the steady state, is a sum of the feed rate, the product stream and the conversion rate in the reactor. The latter is given by the right-hand side of Eq. (A1.7). Abbreviating the ratio of the (fictive) conversion rate of the saturated vapor over the feed rate by

$$r \coloneqq \frac{\sigma Iq[R1]_{sat}}{F}$$
(A2.2)

we have (dropping temporarily the upper index *l* of $x_n^{(l)}$:

$$n=0: F - \sigma Iq | \mathbf{R1} | -Fx_0 = 0 \text{ or}$$
 (A2.3)

$$x_0 = (r+1)^{-1}$$
 (A2.4)

$$n > 0; \ \sigma Iq Q q^n \sum_{i=0}^{n-1} q^{-i} [\mathbf{R}\mathbf{f}_i \mathbf{I}]_{sat} x_i - \sigma Iq [\mathbf{R}\mathbf{f}_n \mathbf{I}]_{sat} x_n - \mathbf{F} x_n = 0$$

(A2.5)

or

$$x_n = (rs^n + 1)^{-1} Qq^n r \sum_{i=0}^{n-1} s^i q^{-1} x_i.$$
 (A2.6)

This system of equations can be explicitly solved for the unknown $x_n^{(t)}$ by successive insertion (Eq. (A2.4) into Eq. (A2.6) with n = 1, then the next n, etc.). But more conveniently, it can also be used directly for the calculation of Fig. 10. By dividing two of the Eq. (A2.6) with two successive n, we note that the ratio of successive $x_n^{(t)}$ for high molecular weights (high n) is = q, the corresponding ratio for small conversion:

$$x_{n+1}^{(n)}/x_n^{(n)} \approx q.$$
 (A2.7)

Surprisingly, this is independent of s, i.e., of the quality of separation (provided that it is good enough), and of r, i.e., of the conversion rate compared with the feed rate.

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