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THERMOLYSIS AND UV-PHOTOLYSIS OF PERFLUORINATED IODO-ALKANES AND IODO-OXAALKANES: THERE IS A PREFERRED REACTION CHANNEL*

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SUMMARY

The thermal stability of perfluorinated iodides depends on their structure and decreases in the order of $R_FCF_2CF_2I > R_FCF_2CF(CF_3)I > R_FOCF(CF_3)I \approx R_FCF_2C(CF_3)_2I$. The major decomposition path consists of the elimination of an unsaturated compound ($CF_2{=}CF_2$, $CF_2{=}CF{-}CF_3$, $O{=}CF{-}CF_3$, $CF_2{=}C(CF_3)_2$, respectively) with concomitant formation of R_FI. The highest selectivities were found for tertiary iodides and 2-iodo-3-oxaalkanes, whose decomposition is virtually irreversible.

UV-photolysis of the iodo-compounds gave the same products as the thermolysis reactions.

INTRODUCTION

We have found recently that the thermolysis of the tertiary iodides **1a,b** at 250 °C in quartz ampoules gives **F**-isobutene and primary **F**-alkyl iodides in quantitative conversion (C) and with high selectivity (S = 95 - 97 %) [1]. Our suggestion for the mechanism is depicted in Scheme 1.

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[*] Dedicated to Professor Dr. W. Hilger on the occasion of his 60th birthday.

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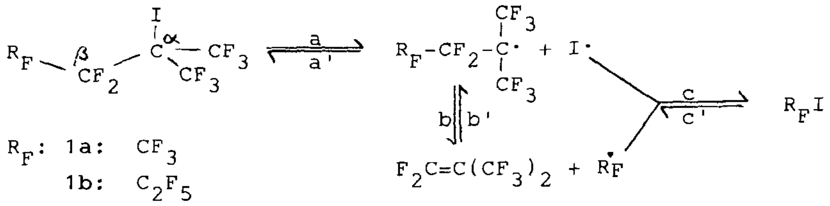


Scheme 1

The formation of a perfluororadical (step a) will be facilitated by the considerable steric strain in the molecules of **1a**,**b**, although a force field calculation of the minimum energy conformation of **1b** showed that this strain is somewhat relieved by lengthened CC-bonds at the tertiary carbon (0.03 Å on average) and a widened C_α-γ-angle Iodine is a very efficient trap for perfluoroalkyl radicals. Therefore, the recombination steps a' and c proceed fast[2]. The high selectivity of the overall reaction seems to be mainly caused by two factors: (i) The cleavage of the initially formed radical must occur almost exclusively through step b, and (ii), in regard to the rate constants, it is likely that k_c is much larger than $k_{b'}$. It is worth noting that the decomposition of **1a**,**b** leads to the thermodynamically most stable group of products.

The aim of the present studies was to find out if there possibly existed a basic principle ruling the decomposition pathways of different F-alkyl iodides. For comparison, we also performed some qualitative UV-irradiation experiments, that means, no quantum yields have been determined. The thermal cleavage of the carbon–iodine-bond of iodo-perfluoroalkanes gives very little excited (5- $^2P_{1/2}$) iodine atoms, in a Boltzmann-equilibrium, whereas UV gas-phase irradiation produces an excess of excited iodine. However, both methods of excitation create the same perfluororadical and may therefore afford the same end products. A short report on parts of our work has been presented earlier [3].

RESULTS AND DISCUSSION

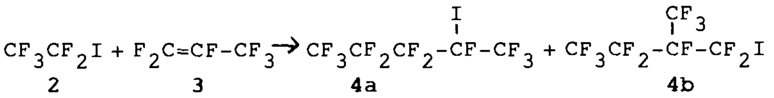
Tertiary Iodides

The highly selective thermolysis of two representatives of this class of iodides has been described in the introduction and in ref. [1].

UV-irradiation of compound **1b** at 254 nm did not induce any noticeable reaction. This is not surprising, since the intensity of the absorption curve of 1b (λ_{max} = 295 nm) at 254 nm is almost zero. However, when 1b was irradiated with an antimony lamp, whose emission contains components at 280 and 305 nm, we observed a slow formation of F-isobutene and of iodo-pentafluoroethane (S <u>ca.</u> 95 %).

Secondary iodides

It is known that primary F-alkyl iodides can be added to the double bond of hexafluoropropene by simple heating to give 2-iodo-perfluoroalkanes [4]. When we employed this method to prepare F-2-iodo-pentane (**4a**) from pentafluoroethyl iodide (**2**) and HFP (**3**), in a molar ratio of 1.5 : 1, at 220 °C in a stainless steel autoclave, complete consumption of HFP could not be achieved. Beside unreacted starting materials, the reaction mixture contained the desired product **4a**, small amounts of its isomer F-1-iodo-2-methyl-butane **4b** and higher telomers (equation 1):

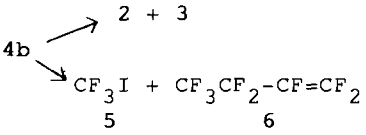


$$\underset{\mathbf{2}}{CF_3CF_2I} + \underset{\mathbf{3}}{F_2C{=}CF{-}CF_3} \rightarrow \underset{\mathbf{4a}}{CF_3CF_2CF_2{-}\overset{I}{\overset{|}{C}}F{-}CF_3} + \underset{\mathbf{4b}}{CF_3CF_2{-}\overset{CF_3}{\overset{|}{C}}F{-}CF_2I} \qquad (1)$$

+ telomers

Higher reaction temperatures and prolonged times did not complete the reaction, but led mainly to more side products. This gave us the impression that the addition reaction was basically reversible, the decomposition of secondary iodides being catalyzed by the wall metals.

Because we were unable to separate **4a** from **4b** by distillation, a mixture of these compounds (**4a**/**4b** = 93.5 : 6.5, b.p. 93 - 94 °C) was used in our experiments. After this mixture was heated in a Pyrex tube (300 °C, 12 h), a conversion of 53 % and a selectivity of 72 %, with regard to the formed amounts of 2 and 3, were found. Compound **4b**, having two carbons in γ-position to iodine, can be expected to undergo two different decompositions:



The compounds **5** and **6** were indeed identified among the products. The relatively low selectivity of the overall reaction can be explained by the addition of trifluoromethyl iodide **5** to fluoroolefins, followed by thermolysis reactions of the resulting iodides.

UV-photolysis of the **4a,b**-mixture at 254 nm also yielded compounds 2 and 3 as the main products.

F-isopropyl iodide (**7**), which does not possess a carbon in γ-position to iodine, is thermally more stable than **4a** or **4b** It slowly decomposes at 300 °C under exclusive formation of **F**-2,3-dimethyl-butane (**8**) and of iodine (equation 2).

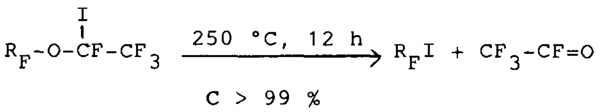
$$\underset{\mathbf{7}}{2(CF_3)_2CF\text{-}I} \xrightarrow[10\ h]{300\ ^{\circ}C} \underset{\mathbf{8}}{(CF_3)_2CF\text{-}CF(CF_3)_2} + I_2 \qquad (2)$$

$$C = 6{,}5\ \%,\ S > 99\ \%$$

The same reaction has been shown to be responsible for the slow consumption of 7 as a lasing agent in UV-powered infrared lasers [5].

F-2-iodo-3-oxa-alkanes

These compounds (**9a-c**) can be regarded as quasi-secondary iodides, where one of the carbons in β-position to iodine is replaced by oxygen. They are thermally less stable than the secondary iodides and decompose with high selectivity according to equation 3:



$$R_F\text{-O-}\overset{I}{C}F\text{-}CF_3 \xrightarrow[C\ >\ 99\ \%]{250\ °C,\ 12\ h} R_FI + CF_3\text{-}CF{=}O \qquad (3)$$

9a-c **10a, b** **7** **11**

R_F: **9a**: $CF_3CF_2CF_2$

9b: $CF_3CF_2CF_2\text{-O-}CF(CF_3)CF_2$

9c: $(CF_3)_2CF$

S: **10a,b** >99 %

7 *ca*. 95 %

In the case of **9c**, small amounts of compounds **5** and **8** were formed as by-products. The F-4-methyl-3-oxa-pentyl-2 radical, thought to be a transient intermediate during the pyrolysis of **9c**, has been shown to fragment very easily into the perfluoroisopropyl radical and trifluoroacetylfluoride **11** [6].

The bromo-analogue (**9d**) of compound **9b** decomposed rather slowly at 300 °C in a Pyrex tube, but it reacted rapidly at 450 °C in a quartz flow reactor to give the known compound F-2-bromo-3-oxa-hexane beside **11**, in essentially quantitative yield. A very similar reaction (equation 4) has been found by Resnick [7]:

$$CF_3CF_2CF_2\text{-O-}CFBr\text{-}CF_2Br \xrightarrow{\Delta} CF_3CF_2CF_2Br + CF_2Br\text{-}CFO \quad (4)$$

UV-irradiation of the iodide 9a at 254 nm afforded the same products as its thermal reaction. In a gas laser, driven by UV flashlamps, the lasing qualities of 9a and of perfluoroisopropyl iodide (7) were similar, however, 9a was much faster degraded than 7 [8].

Several attempts at a reversion of the process described by equation 3 remained unsuccessful, both under thermal or photolytic conditions.

Interestingly, 1-iodo-3-oxa-butane that contains oxygen instead of carbon in the γ-position to iodine reacts through a different fragmentation route, giving pentafluoroethyl radicals and difluorophosgene [9].

Primary iodides

The thermolysis of these iodides requires higher temperatures. Butler and Snelson used a platinum reactor to study the pyrolysis of n-perfluoropropyl iodide at very low pressure in the 450 - 600 °C range. The products were investigated by IR matrix techniques and C_3F_7, CF_3 and CF_2 radicals could be identified beside substantial amounts of tetrafluoroethene [10], however, no complete description of the overall reaction has been given. Our own experiments were performed in a quartz reactor at normal pressure. F- 1-iodo-hexane (12) was chosen as a model compound. We used relatively long residence times, with the consequence of a high number of collisions in the gas phase. As shown in Table 1, the reaction is very specific at 400 - 500 °C in regard to the formation of linear iodides having even numbers of carbon atoms. Above 500 °C, the selectivity drops sharply and large amounts of iodine, odd-numbered iodides, F-alkanes and F-alkenes (including perfluoroisobutene) are formed.

TABLE 1

Thermolysis of n-$C_6F_{13}I$ (flow reactor, medium residence time *ca*. 3.5 min)

T (°C)	Resulting $CF_3(CF_2)_nI$ (%, determined by GLC)					
	n: 1	3	5	7	9	Σ
400	0.3	3.5	92.8	2.8	0.2	99.6
450	0.9	6.1	86.3	5.8	0.5	99.6
480	1.4	12.2	70.7	11.9	1.7	97.9
500	4.3	18.7	45.5	18.7	5.7	92.9
520	11.9	19.8	26.5	14.3	4.2	76.7

The distributions of even-numbered iodides obtained from the first four experiments in the table form flattening Gaussian curves, their maxima corresponding to the values of compound **12**. A plausible explanation for this homologation process is outlined below, assuming that the elimination of TFE (**13**) from linear perfluororadicals is the predominant key step.

$$\underset{\mathbf{12}}{C_6F_{13}I} \xrightarrow[-I^{\bullet}]{\Delta} C_6F_{13}^{\bullet} \longrightarrow C_4F_9^{\bullet} + \underset{\mathbf{13}}{F_2C{=}CF_2}$$

$$C_4F_9^{\bullet} + I^{\bullet} \longrightarrow C_4F_9I$$

$$C_6F_{13}^{\bullet} + \mathbf{13} \longrightarrow C_8F_{17}^{\bullet} \xrightarrow{+I^{\bullet}} C_8F_{17}I$$

Scheme 2

This mechanism is corroborated by photochemistry: Gas phase irradiation of 12 at 254 nm resulted in a slow formation of F-butyl iodide beside small amounts of the C_2- and C_8-iodides and of **13**.

EXPERIMENTAL

The starting materials have been prepared by known procedures (for **1a,b** see [1], for **9a-d** see [11]). The inhalation toxicity of **9a-d** is low, judged from pre-screening results with NRMI-mice. All halogeno-compounds have been carefully purified by fractional distillation, e.g. **12** to 99.9 %.

All experiments were run under strict exclusion of moisture and oxygen. Due to the high toxicity of several compounds, all operations have been performed in well-vented fume hoods, using protective gloves and glasses.

The products were analyzed by means of GLC, IR and ^{19}F-NMR (at 75.393 MHz, vs. external CF_3CO_2H), in some cases also by ^{13}C-NMR. Low temperature NMR-spectra were obtained at -60 °C in $CDCl_3$-solutions. The identification of the products was facilitated by our extensive collection of spectral data. Whenever the interpretation of GLC data was doubtful, the retention times were counterchecked using pure reference samples on the same column.

Thermolysis reactions

In order to determine a suitable temperature range for the decomposition reactions, a set of several experiments had to be undertaken for each group of F-alkyl iodides. DSC-measurements in Monel-cells proved of little value, since metallic walls tend to lower the decomposition temperature and also to favour unwanted side reactions. Therefore, quartz or Pyrex glass had to be the materials of choice.

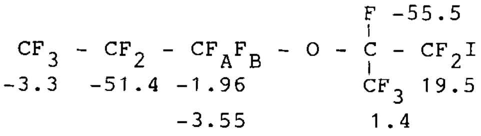
Method A: Thermolysis in Pyrex ampoules

Example: Synthesis of F-1-iodo-2-methyl-3-oxa-hexane (**10b** n.c.) from **9b**

Compound **9b** (6.0 g, 10.4 mmol) was placed in a 15 ml thick-walled Pyrex ampoule and was degassed at -70 °C in vacuo. The ampoule was sealed and transferred to a 100 ml steel bomb, containing a perfluoroether oil as heat-transfer fluid. The bomb was pressurized with 1.0 MPa of nitrogen, electrically heated to 250 °C and kept for 12 h at this temperature. After cooling to room temperature, the ampoule was taken out and cooled to -70°C. Then it was opened under nitrogen, connected to a -70°C trap and then slowly warmed up to 40 °C. A colorless gas condensed within the receiver. This was identified as trifluoroacetyl fluoride by -60 °C-^{19}F-NMR (δ CF_3: 2.8 ppm, δCF : 93.5 ppm), gas phase-IR (νc=o : 1890 cm^{-1}), and its facile hydrolysis to give trifluoroacetic acid.

The residue that had remained in the ampoule was successively washed with dilute sodium bicarbonate solution and water, dried over molecular sieve (3 Å) and filtered. 4.6 g of a fluid were obtained (99.7 % purity, based on GLC-analysis). It was assigned the following structure by ^{19}F-NMR (in $CDCl_3$).

δ ^{19}F (ppm):



$$\begin{array}{ccccccccc} & & & & & & & \mathrm{F}\ \ -55.5 & \\ & & & & & & & | & \\ \mathrm{CF_3} & - & \mathrm{CF_2} & - & \mathrm{CF_AF_B} & - \ \mathrm{O} \ - & & \mathrm{C} & - \ \mathrm{CF_2I} \\ & & & & & & & | & \\ -3.3 & & -51.4 & & -1.96 & & & \mathrm{CF_3} & 19.5 \\ & & & & -3.55 & & & 1.4 & \end{array}$$

$^2J(F_AF_B)$ = 148.5 Hz

Analysis: found: C 15.4 %, F 53.1 %, I 27.6 %,
calcd. for $C_6F_{13}IO$: C 15.6 %, F 53.5 %, I 27.5 %.

Method B: Thermolysis in a quartz flow reactor

Description of the apparatus:

A three-necked evaporator flask (50 ml) was equipped with an inlet for pure nitrogen, the flow of which could be adjusted with a flowmeter, an injector unit to dose the starting material, and an exit ending in a nozzle which opened into the pyrolysis tube. This quartz tube

(20 mm inner diameter) was divided by a perforated disk, having a 3 mm-wide hole in its center, into a 30 cm-preheating zone and a 40 cm-pyrolysis zone. The outlet of the latter zone was connected to a descending cooler (40 cm) that ended in another three-necked flask that could be cooled with an ice-bath. One neck of the flask bore a rubber septum, through which gas samples could be drawn with a syringe. The exit of the flask led into two -70 °C-traps, followed by a bubbler filled with silicone-oil.

In typical experiments with F-hexyl iodide **12**, 20 g of **12** were used. The evaporator flask was kept at 180 °C, the preheating zone at 350 °C and the pyrolysis zone at the desired temperature (accuracy of T: ± 5 °C).

UV-photolysis

A slender, cylindrical quartz reactor of 23 cm height and 3.6 cm inner diameter was used. This reactor possesse a flat bottom and four necks at the top. The rod-shaped UV-sources could be inserted through the widest neck. The other necks carried a thermometer, a rubber septum for taking samples, and a cock that could be connected to a cooled receiver. The free usable gas volume was 120 - 130 ml, depending on the size of the UV source.

In each experiment a 10 g-sample of the liquid perfluoroalkyl iodides was used that had been treated with copper powder to remove any free iodine. It was carefully degassed, then nitrogen or argon was filled in. The sample was stirred with a magnetic bar, and the reactor was thermostatted to 40 ± 2 °C during the irradiation. Samples for GLC-analysis were taken from the gas phase in 2 h-intervals. The composition of the liquid phase was analyzed at the end of the experiment.

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