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THE CHEMISTRY OF DIACYL PEROXIDES — VIII. THE REACTIONS BETWEEN POLYFLUORODIACYL PEROXIDES AND 2-NITRO-2-NITROSOPROPANE--GENERATION OF BIS(POLYFLUOROALKYL) NITROXIDES

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SUMMARY

Thermal decomposition of 2-nitro-2-nitrosopropane (**4**) in F113 ($CCl_2F-CClF_2$) solution involves C-NO bond fission and forms acetone as the major product. In the presence of polyfluorodiacyl peroxide (**3**), the oxidation of **4** by **3** to 2,2-dinitropropane (**5**) is the predominant reaction and bis(polyfluoroalkyl) nitroxide(**1**) is generated as one of the by-products.

INTRODUCTION

Very recently, we have communicated a novel method for generating bis(polyfluoroalkyl) and nitroalkyl polyfluoroalkyl nitroxides [$R_FN(O)R_F$, **1** and $R_FN(O)CR^1R^2NO_2$, **2**] by making use of electron transfer reactions between polyfluorodiacyl peroxides **3** and carbanions derived from secondary nitroalkanes.[1] In order to rigorously establish the structures of the latter type of nitroxides(**2**), we tried to make them by trapping R_F radicals generated from thermal decompositions of **3** by 2-nitro-2-nitrosopropane **4** in F113 ($CCl_2F-CClF_2$) solutions. Unexpectedly, in our preliminary experiments, ESR indicated that 1 but not 2 was formed. The present work is an investigation of these reactions by product identification, kinetics and ESR studies.

RESULTS AND DISCUSSION

2-Nitro-2-nitrosopropane (**4**), the simplest 'Pseudonitrile', dimerises and appears as a white crystalline solid at room temperature. It monomerises rapidly and forms blue solutions in some inert solvents such as ether, benzene, CCl_4 and F113. Its redlight photodecompositions involve C-NO bond fission and exhibit dramatic changes of product distribution with the nature of the solvents.[2,3,4] Moreover, its reactions with some common oxidizing agents, such as permanganate and persulfate have been reported to form 2,2-dinitropropane (**5**) as the main oxidation product [4].

Our studies showed that **4** decomposed rather quickly in degassed dilute F113 solution (0.02M) at room temperature. The first order rate constant, k_1, as determined by integrating the diminishing signal of **4** (singlet at 1.6ppm) in a NMR tube maintained at 31° C, is $2.73 \times 10^{-5} S^{-1}$ ($t_{1/2}$ 423m).

If thermolysis of **4** in F113 involves C-NO bond fission as its photolyses do in other aprotic solvents,[2,3,4] one might expect that trapping 2-nitropropyl radical by **4** itself should lead to the formation of spin adduct, bis(2-nitro-2-propyl) nitroxide **6**. In fact, **6** could not be observed by ESR within a large temperature range (+30 to -40°C). However, under UV irradiation at -40° C well resolved spectra of **6** (Fig.1) have been recorded, and its life-times found to be less than 10 min., thus it is too short-lived and undetectable at higher temperatures.

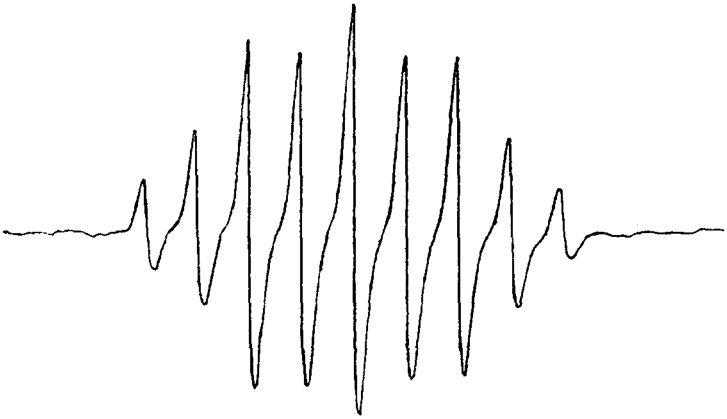


Fig.1 . ESR spectrum of nitroxide **6** in the photolysis of **4** in F113 solution at -40 °C. a_N = 10.40 G, $a_N^{NO_2}$ = 5.20 G.

At 31°C when **3** (in F113, 0.1M) was added to the F113 solution (0.1M) of **4** (molar ratio **3**/**4** = 1:1), the decomposition was much accelerated. With the increase of molar ratio up to 6:1, the value of the first order rate constant for removal of **4** reached a maximum of 7×10^{-4} S^{-1}. The observed rate constants in the absence and presence of 3 are listed in Table 1. At each molar ratio, well resolved ESR spectra of nitroxides **1** were recorded. The spin yields, as determined by external manganese reference, are about 0.01 to 0.1%. The a_N, a_F^{β}, a_F^{r} values and g factors (see Table 2) all coincide with the previously reported data[1,5]. Furthermore, the spectra were satisfactorily simulated. There were no detectable amounts of asymmetrical nitroxides **2** [1,6] in the reaction mixtures (although **2** is formed if powdered activated copper is added to a F113 solution of **4** and excess 3). It has been found that the nitroxides can be

TABLE 1

Rates and main products of the reactions between **4** and **3** in F113 at 31 °C

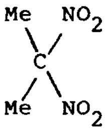
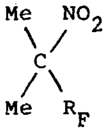
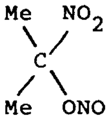
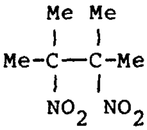
Molar Ratio 3/4	k_{obs}*10^5 s^{-1}	yields of main products, %				
		acetone	 **5**	 **8**	 **9**	 $Me_2C(NO_2)-C(NO_2)Me_2$ **12**
0:1	2.73	83	trace		17	trace
1:1	4.27	30	55	8	7	trace
3:1		22	67	11	trace	---
6:1	70.1	12	76	12	---	---
10:1	68.6	9	73	18	---	---

TABLE 2

ESR Parameters of bis(polyfluoroalkyl) nitroxides **1** generated in the reactions between **4** and **3** in F113

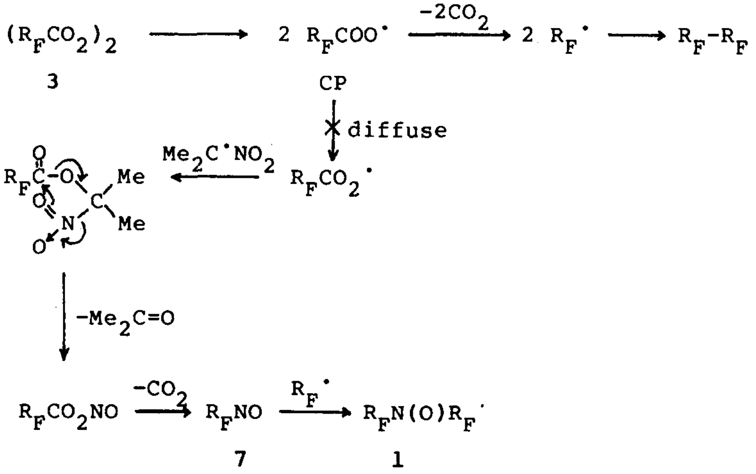
R_F in 1	CF_3	C_2F_5	n-C_3F_7	n-C_7F_{15}	$H(CF_2)_2$	$H(CF_2)_4$	$H(CF_2)_6$
T °c	10	10	30	10	19	19	19
g	2.0066	2.0069	2.0070	2.0070	2.0069	2.0069	2.0069
a_N (G)	9.56	8.79	8.70	8.71	9.71	8.80	8.61
a_F^{β} (G)	8.14	12.16	9.95	8.52	14.54	10.06	9.75
a_F^{γ} (G)		0.98	1.95	1.17		1.19	1.16

isolated from other products by flash chromatography on silica gel column and have life times of several days at r.t. in F113 solutions in the dark. Thus, the reactions of **4** with 3 may serve as yet another new method for generating these interesting nitroxides 1.

Product analysis (right after the disappearance of **4**) showed that the decomposition of **4** in F113 in the dark afforded less complicated products, i.e., mainly acetone (83%), nitroalkyl nitrite (**9**, 17%), trace amounts of 2,3-dimethyl-2,3-dinitrobutane and **5**. The formation of such radical products indicates that the decomposition is also initiated by homolysis of the C-NO bond followed by subsequent radical reactions as reported in the literature [2,3,4].

It was found that in the presence of 3, e.g., $(\underline{n}\text{-}C_3F_7CO_2)_2$, 5 became the major product (eq.3) and its yield increased with the increase of the molar ratio, whereas reactions, e.g., eq.1, 2, 9 and 16, became less important. Also it is worthy to mention that while the yields of acetone decreased greatly with the increase of the molar ratio, a radical coupling product, 2-heptafluoropropyl-2-nitropropane (**8**) was formed in increasing yields (from 8 to 18%). The yields of the products as determined by ^{1}H NMR after the completion of decomposition of **4** are given in Table 1.

Based on rate, ESR and product studies, we propose that in the absence of 3, **4** first undergoes unimolecular homolysis and the major product acetone comes from decomposition of the unstable coupling product, nitroalkyl nitrite **9** (eq. 7 and 13 in Scheme 2) as reported previously [2,3]. But in the presence of 3, there are at least two parallel reactions which compete with the oxidation of **4** (eq.3). One is the aforementioned unimolecular decomposition of **4** (eq.2) which provides 2-nitropropyl radicals and nitric oxide, the other, is the unimolecular decomposition of **3** (eq.1) which has been studied previously [7]. Taking the decomposition of perfluorobutyroyl peroxide as an example , its first order rate constant measured in dilute F113 solution is 8.5×10^{-5} S^{-1} ($t_{1/2}$ 138 m) at 30 ± 0.05 °C, about 2 times faster than that of **4**. A detailed product analysis had proved that the decompositions of the perfluorodiacyl peroxides involve homolytic scission of the peroxy bond and afforded CO_2 and R_F-R_F as the major products (~80%). Since the decarboxylation of polyfluoroacetoxyl radicals is extremely fast ($k \sim 10^{10}$ s^{-1}, much faster than diffusion rate, 10^7-10^8 s^{-1}) in the original solvent cage,[8] they can not diffuse to the bulk and couple with 2-nitropropyl radicals to form nitroalkyl carboxylic ester, which has been found[1] to be an unstable intermediate, and a source of nitrosoperfluoroalkane, R_FNO (**7**) (see Scheme 1).



Scheme 1

Although many reactions which lead to the formation of nitroso compounds are best understood on the basis of the combination of nitric oxide with an appropriate free radical (e.g., eq.9), we may presume that in the studied reactions, induced decomposition of **4** by R_F radicals (eq.5) may enhance the decomposition of **4** and thus contribute to the formation of spin traps (**7**). And nitroxides **1** are spin-adducts of R_F radicals to spin traps (**7**) internally formed in the systems.

All in all, the decomposition of **4** in the presence of **3** is so complicated that only some tentative mechanistic paths can be proposed (Scheme 2). Thus we arrive at the following points:

1. Thermal decomposition of **4** in F113 solution is similar to those reported in other aprotic solvents such as ether,benzene,etc.
2. With a large excess of **3** present, the process becomes mainly the fast oxidation of **4** by **3** to **5**.
3. In the presence of **3**, bis(polyfluoroalkyl) nitroxides (**1**) are generated by spin trapping of $R_F^{\bullet}$ by R_FNO (**7**). The formation of **1** is significant spectroscopically but probably of relatively minor importance for the kinetics of the studied reactions.

EXPERIMENTAL

Polyfluorodiacyl peroxides **3**,[7] 2-nitro-2-nitrosopropane **4** [12] (m.p. 74-76 °C) and 2,2-dinitropropane **5** [13] were prepared as reported previously. F113 was purified and redistilled.

Sample solutions both in NMR and ESR tubes were degassed on a standard vacuum line and handled in the dark . Rate studies were performed on a Varian EM-60 NMR spectrometer at constant temperature (30-31 °C) by integrating ^1H NMR peaks of **4** (S, 1.6

Homolysis

$$(R_FCO_2)_2 \longrightarrow \overline{2\ R_FCO_2^{\bullet}} \longrightarrow R_F^{\bullet} + CO_2 \qquad [1]$$

3

$$Me_2C(NO_2)NO \longrightarrow Me_2C^{\bullet}NO_2 + NO \qquad [2]$$

4

Oxidation

$$\mathbf{4} + 3 \longrightarrow Me_2C(NO_2)_2 + \text{other product(s)} \qquad [3]$$

5

$$NO \xrightarrow{[O]} NO_2 \qquad [4]$$

Radical induced reactions, e.g. :

$$\mathbf{4} \xrightarrow{R_F^{\bullet}} Me_2C^{\bullet}NO_2 + R_FNO \qquad [5]$$

7

$$\mathbf{4} \xrightarrow{R_F^{\bullet}} Me_2C(NO_2)R_F + NO \qquad [6]$$

8

Radical recombination (or coupling)

$$Me_2C^{\bullet}NO_2 + NO_2 \longrightarrow \mathbf{5} + Me_2C(NO_2)ONO \qquad [7]$$

9

$$Me_2C^{\bullet}NO_2 + R_F^{\bullet} \longrightarrow \mathbf{8} \qquad [8]$$

$$R_F^{\bullet} + NO \longrightarrow \mathbf{7} \qquad [9]$$

$$R_F^{\bullet} + NO_2 \longrightarrow R_FNO_2 + R_FONO \qquad [10]$$

10 **11**

$$2\ Me_2C^{\bullet}NO_2 \longrightarrow Me_2C(NO_2)C(NO_2)Me_2 \qquad [11]$$

12

$$2\ R_F^{\bullet} \longrightarrow R_F{-}R_F \qquad [12]$$

13

Scheme 2

(continued)

Scheme 2 (cont.)

Decomposition of the unstable intermediates

$$\mathbf{9} \longrightarrow \text{Acetone} + NO_2 + NO \qquad [13]$$

$$\mathbf{11} \longrightarrow R_FO^{\bullet} + NO \qquad [14]$$

14

$$\mathbf{14} \longrightarrow CF_2O + R_F^{\bullet} \qquad [15]$$

Formation of nitroxides

$$\mathbf{7} + R_F^{\bullet} \longrightarrow R_FN(O)R_F \qquad [16]$$

1

ppm), acetone (S, 2.05ppm), **5** (S, 2.18ppm)[14] and other products at each time interval. The slopes of the straight lines obtained by plotting ln C_o/C_t vis time represent the first order rate constants, k_1, at different concentrations of 3.

When NMR detection was finished, the NMR sample tubes were kept in a thermostat maintained at 31 °C until the disappearance of **4** in the tubes was found. Then the solutions in the tubes were subjected to GC and IR analyses. GC analysis was conducted on Shanghai Analytical Instrument, GC-102G by using PEG 20,000 (10%) on chromosorb at 80-150 °C. IR spectra were recorded on Shimadzu IR-440 spectrometer.

ESR spectra were recorded on a Varian E-112 spectrometer with quartz tube (3mm ID) and 100 KHz modulation at ~20 °C. Satisfactory spectral simulations were carried out by employing Varian E-935 Software Program NO.929970-11.

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