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Di-t-BUTYL NITROXYL - RADICAL INDUCED HOMOLYSIS OF POLYFLUORODIACYL PEROXIDES

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SUMMARY

In the presence of di-t-butyl nitroxide (DTBNO) polyfluorodiacylperoxides undergo rapid decomposition in n-pentane or $CClF_2$-CCl_2F at -50 to +20 °C. The reactions are first order in peroxide and DTBNO. On the basis of ESR observation of t-butyl polyfluoroalkyl nitroxides as well as product analysis, it appears that the decomposition processes involve DTBNO induced homolysis of the peroxy bonds followed by product formation steps.

INTRODUCTION

Nitroxides of usual reactivity can induce homolytic cleavage of weak σ-bonds. It has been found that in di-t-butyl nitroxide (DTBNO) as the solvent or in molten 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxide, compounds such as benzoyl peroxide, N-bromosuccinimide (NBS) , allyl and benzyl bromides and even the less reactive secondary and tertiary alkyl bromides and iodides can be cleaved. These processes have been referred to as homosolvolyses [1]. Benzyl and allyl bromides afford the corresponding O-substituted hydroxylamines whereas the radicals derived from NBS or benzoyl peroxide abstract hydrogen atoms from unchanged DTBNO and lead to the formation of 2-methyl-2-nitrosopropane (MNP), an internal spin trap of succinimide or phenyl radicals [2].

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Our interests in the chemistry of polyfluorodiacyl peroxides have prompted us into some ESR studies on their homolysis in nitroxide-solutions of an inert solvent ($CClF_2$-CCl_2F). It is expected that peroxy bonds weakened by fluorination [3] would be more reactive than their hydrocarbon analogues in homosolvolysis and this is exactly what we have found in practice.

RESULTS AND DISCUSSION

0.15 ml (0.01M) of a yellow-brownish solution of DTBNO in F-113 was mixed in a degassed ESR tube with 0.30 ml (0.005M) of colorless solution of polyfluorodiacyl peroxide in F-113 at room temperature in the dark. The rapid development of a blue color in the reaction mixture would clearly indicate the presence of MNP. ESR examination minutes after mixing showed the disappearance of the DTBNO signal and the presence of a well-resoluted spectrum of stable *t*-butyl polyfluoroalkyl nitroxide,$R_FN(O)Bu^t$. From seven different peroxides, the same number of nitroxides of this type were easily identified. Their hfs values (a_N and a_F^{β})at various temperatures are presented in Table I. The spectral data of the nitroxides derived from perfluorodiacyl peroxides coincide with reported values [4, 5, 6]. However the nitroxides containing ω-H-fluoroalkyl groups are previously unknown. Evidently, all these fluorinated nitroxides are simply spin adducts of fluoroalkyl radicals (from decarboxylation of the corresponding fluoroacyloxy radicals) with the internally formed spin trapping agent, MNP.

As shown in Table I, the dependency of the a_N values on the nature of the perfluoroalkyl and ω-H-fluoroalkyl groups shows a consistent trend. In other words, if the electron-attracting power of the R_F groups is $CF_3 <$ secondary $R_F <$ tertiary R_F [7,8], then the decreasing order of the a_N values [$CF_3 > HCF_2CF_2 > C_2F_5$ and *n*-C_3F_7 , *n*-C_7F_{15} , $H(CF_2)_n(n=4,6)$] bears out the notion that in addition to geometric factors the polar effects may play an important role in affecting the a_N values. Naturally, these substituent effects become more important among the newly observed bis-[polyfluoroalkyl] nitroxides [9].

TABLE I

Hfs values of t-butyl polyfluoroalkyl nitroxides generated in DTBNO induced homolysis of $(R_FCO_2)_2$ in F-113 at various temperatures.

R_F in $(R_FCO_2)_2$	$R_FN(O)Bu^t$	T (°C) ±2	a_N ±0.1G	a_F^β ±0.1G
CF_3	$CF_3N(O)Bu^t$	+19	12.4	12.4
		-40	11.8	12.8
		-60	11.8	13.3
		-60	12.03[a]	12.34[a]
C_2F_5	$C_2F_5N(O)Bu^t$	+19	11.3	22.7
		-10	11.3	23.0
		-30	11.28[a]	22.27[a]
		-40	11.5	23.9
		-60	11.5	23.3
n-C_3F_7	n-$C_3F_7N(O)Bu^t$	0	11.4	19.2
		-30	11.5	19.0
		-30	11.44[a]	17.80[a]
n-C_7F_{15}	n-$C_7F_{15}N(O)Bu^t$	+10	11.4	19.7
		-30	11.4	19.9
		-30	11.10[b]	17.95[b]
$H(CF_2)_2$	$H(CF_2)_2N(O)Bu^t$	+19	12.1	21.9
		0	12.0	21.9
		-20	12.0	22.1
		-30	11.9	22.3
$H(CF_2)_4$	$H(CF_2)_4N(O)Bu^t$	-20	11.8	20.5
$H(CF_2)_6$	$H(CF_2)_6N(O)Bu^t$	0	11.5	19.7
		-30	11.5	19.7

[a] From Ref.[4], in CH_2Cl_2. [b] From Ref.[5].

Quite large changes of β-fluorine splitting constants with temperature have been observed for some of the nitroxides. Both decrease and increase in a_F^β value have been noted with decrease in temperature. For example, in the same temperature range (+19 to -60° C), t-butyl trifluoromethyl nitroxide shows a decrease in a_N value and an increase in a_F^β value with temperature decrease; whereas t-butyl pentafluoroethyl nitroxide shows an exceedingly large increase in a_F^β while a_N remains nearly constant with temperature decrease. These changes coincide with previously reported data and can be rationalized in terms of preferred structural conformations at different temperatures as well as fluorine-nitrogen p-π interactions as discussed in the literature [4, 6, 10, 11].

At room temperature, the reactions between fluorinated diacyl peroxides and DTBNO were very fast. At the freezing point of F-113, -38° C, they were still too fast to allow rate measurement. However, when n-pentane (m.p.-130°C) was used as solvent, the homolysis could be carried out at much lower temperatures (-50 to -70° C) and we could measure rate constants. A typical procedure was, 0.15 ml solution of $(\underline{n}\text{-}C_3F_7CO_2)_2$ (0.005M) and 0.15ml solution of DTBNO (0.01 M) were quickly mixed in an ESR tube at -78°C (dry-ice trap) and it was inserted in the ESR cavity maintained at -50 ± 2°C. The diminishing signals of DTBNO (triplet with a_N 15.1 G) were repeatedly scanned. Since the recorded ESR lines had similar line widths, the disappearance of DTBNO was simply monitored by measuring its peak heights, a (at '0' time) and a-x (x stands for net decrease in peak height at each time interval). By plotting x/(a-x) against t, the slope thus obtained(r=0.999, confidence level 99.8 %) was the second-order rate constant, $k_2=(6.74\pm0.68)*10^{-3}\ m^{-1}.l.s^{-1}$. The data used for the calculation of k_2 are shown in Table II.

For product studies, 1.0 ml solution (0.2 M in F-113) of DTBNO and 1.0 ml solution (0.2 M in F-113) of $(\underline{n}\text{-}C_3F_7CO_2)_2$

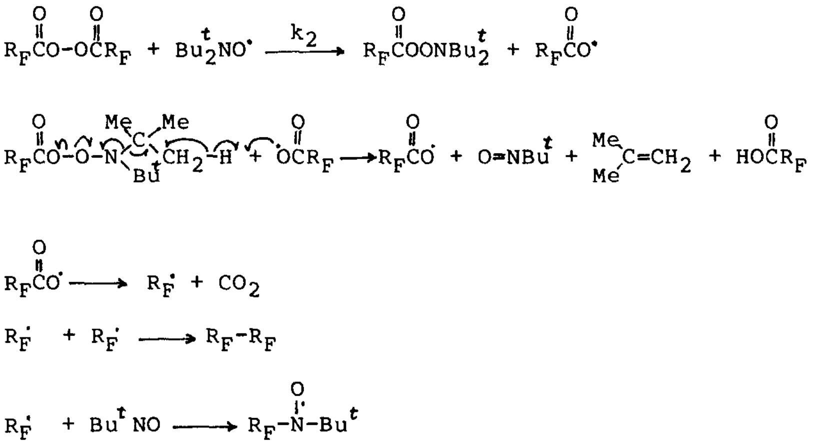
TABLE II

ESR peak heights of DTBNO, as recorded from induced homolysis of ($\underline{n}$-$C_3F_7CO_2)_2$ in $\underline{n}$-pentane at −50±2°C

t(s)	a−x	$\frac{x}{a-x}$
0	198− 0	0
42	198− 32	0.19
84	198− 60	0.44
126	198− 83	0.72
168	198−101	1.04

were mixed and kept at −30°C for about 30 min. Then the reaction mixture, a blue solution, was analyzed quantitatively by ESR, NMR, and GC. ESR showed a good spectrum of $\underline{t}$-butyl heptafluoropropyl nitroxide mixed with a small amount of DTBNO. ^1H NMR showed MNP (mixed, 9H, at 2.10 ppm) and $\underline{n}$-$C_3F_7CO_2H$ (singlet at 11.6 ppm). GC analysis with authentic samples showed the formation of CO_2, $\underline{i}$-butene, $\underline{n}$-C_6F_{14} and MNP.

Based on ESR, kinetic and product studies all mentioned above, a tentative mechanism for the DTBNO induced homolysis of the polyfluorodiacyl peroxides can be proposed as follows:



$$R_F\overset{O}{\overset{\|}{C}}O\text{-}O\overset{O}{\overset{\|}{C}}R_F + Bu^t_2NO^\bullet \xrightarrow{k_2} R_F\overset{O}{\overset{\|}{C}}ONBu^t_2 + R_F\overset{O}{\overset{\|}{C}}O^\bullet \qquad (1)$$

$$R_F\overset{O}{\overset{\|}{C}}O\text{-}O\text{-}\underset{Bu^t}{N}\text{-}\overset{Me\ \ Me}{C}\text{-}CH_2\text{-}H + {}^\bullet O\overset{O}{\overset{\|}{C}}R_F \longrightarrow R_F\overset{O}{\overset{\|}{C}}O^\bullet + O{=}NBu^t + \begin{matrix}Me\\Me\end{matrix}\!\!>C{=}CH_2 + HO\overset{O}{\overset{\|}{C}}R_F \qquad (2)$$

$$R_F\overset{O}{\overset{\|}{C}}O^\bullet \longrightarrow R_F^\bullet + CO_2 \qquad (3)$$

$$R_F^\bullet + R_F^\bullet \longrightarrow R_F\text{-}R_F \qquad (4)$$

$$R_F^\bullet + Bu^tNO \longrightarrow R_F\text{-}\overset{O^\bullet}{\overset{|}{N}}\text{-}Bu^t \qquad (5)$$

Obviously, R_F radicals and their spin adducts with MNP might also induce the homolysis of the peroxides but their participations are negligible. This is because, although decarboxylation of the fluoroacyloxy radicals (step 3) competes with H-abstraction from the peroxy intermediate (reaction 2) and consequently produces R_F radical, a considerable proportion of $R_F^{\cdot}$ thus formed undergoes fast and effective coupling (4) and in the same time only a certain amount of them is trappped by MNP. Therefore, in the bulk, both $R_F^{\cdot}$ and their spin adducts are present in small concentrations, so they could not make the homolysis process deviate from the second-order kinetics.

EXPERIMENTAL

DTBNO was purchased from Aldrich Chemical Company and used as received. MNP was gift from The Lanzhou University. Solvents, F-113 and n-pentane were purified by conventional methods. Polyfluorodiacyl peroxides and $\underline{n}$-C_6F_{14} were prepared as described previously [3].

ESR spectra were recorded on a Varian E-112 X-band spectrometer with 100 KH_Z magnetic field modulation. Temperature studies were achieved with a Varian E-257 variable temperature accessory. Temperature was calibrated by a Ni-Cr/Ni-Al thermocouple. Spectral simulations were performed using Varian E-935 software program, No 929970-11.

Proton NMR spectra were recorded on a JEOL FX-90Q spectrometer. GC analysis was conducted on a perfluorotriazine column (3m*4mm) at 60°C or room temperature (for gaseous products).

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