Journal of Fluorine Chemistry, 61 (1993) 45–49

n-Alkyl perfluoroacyl nitroxides – EPR studies on electron transfer reactions of perfluorodiacyl peroxides with *O*-benzoyl-n-alkylhydroxylamines

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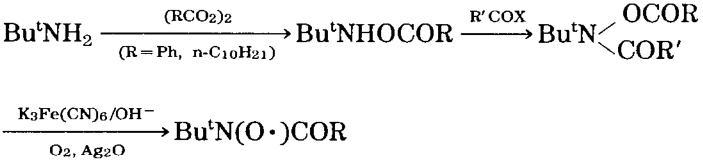
(Received January 30, 1992; accepted June 11, 1992)

Abstract

n-Alkyl perfluoroacyl nitroxides, n-RN(O•)COR$_F$ (n-R = n-C_4H_9, Pr^iCH_2CH_2, PhCH_2; R$_F$ = CF_3, C_2F_5, n-C_3F_7, n-C_7F_{15}, H$(CF_2)_2$, H$(CF_2)_4$ and H$(CF_2)_6$), have been generated by one-electron oxidation of *O*-benzoyl-n-alkylhydroxylamines by perfluorodiacyl peroxides. The EPR parameters of 15 useful new fluorinated nitroxides have been determined and the mechanism of their formation discussed.

Introduction

Acyl nitroxides, RN(O•)COR′, have been known from their EPR spectra for some years. The first group of t-alkyl acyl nitroxides isolated included Bu^{t}N(O•) COPh and Bu^{t}N(O•)CO$C_{10}H_{21}$. These are readily formed by oxidation of the corresponding hydroxamic acids as follows [1]:



$$Bu^tNH_2 \xrightarrow[(R=Ph,\ n\text{-}C_{10}H_{21})]{(RCO_2)_2} Bu^tNHOCOR \xrightarrow{R'COX} Bu^tN\begin{matrix}\diagup OCOR\\ \diagdown COR'\end{matrix} \xrightarrow[O_2,\ Ag_2O]{K_3Fe(CN)_6/OH^-} Bu^tN(O\bullet)COR$$

Variations of these procedures have allowed the isolation of some closely related acyl nitroxides such as t-butyl 3,5-dinitrobenzoyl nitroxide obtained as a green (λ_{max} = 662 nm; ϵ = 25.4) crystalline solid [2].

Acyl nitroxides have relatively high ρ_0 values (nitroxide) compared with those of dialkyl nitroxides [3], although some spin is found on the carbonyl oxygen [4].

Spin localization on nitroxyl oxygen should make these radicals more reactive than dialkyl nitroxides [5]. They oxidize organic substrates through

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0022-1139/93/$6.00

H-abstraction. Thus, they are useful agents for selective oxidations [6]. More interestingly, they have been used as chiral agents [7]. Recently, attention has been paid to the synthesis and application of acyl nitroxides.

However, most known acyl nitroxides are hydrocarbon derivatives. To our knowledge, the first group of fluorinated acyl nitroxides were the *p*-substituted benzoyl perfluoroalkyl nitroxides generated by making use of 'blue magic solution' containing $R_FN(O\cdot)R_F$ (H-abstracting agent) and R_FNO (spin-trapping agent) with *p*-substituted benzaldehydes in F113 ($CFCl_2CF_2Cl$) solutions at room temperature [8].

In this paper, we report a new type of acyl nitroxide containing perfluoroacyl groups (R_FCO), their EPR parameters and their formation mechanism.

Results and discussion

Many nitrogen-containing organic substrates can be oxidized by the strong organic peroxy oxidants, perfluorodiacyl peroxides, $(R_FCO_2)_2$, into various types of fluorinated nitroxides, such as bis(perfluoroalkyl) nitroxides from nitroalkane salts [9], pseudonitrile [10] and nitrite salts [11, 12], nitroalkyl perfluoroalkyl nitroxides from nitroalkane salts [9], alkyl perfluoroalkyl nitroxides from stable nitroxide [13], t-alkyl amines [14] and *O*-benzoyl t-butylhydroxylamine [15], primary and secondary alkyl perfluoroacyloxyl nitroxides from the corresponding primary amines [16].

Similar to the N-containing substrates mentioned above, *O*-benzoyl n-alkylhydroxylamines (**1**) undergo fast oxidation forming new perfluoroacyl nitroxides, $R_FCON(O\cdot)R$ (**3**), in F113 solutions of peroxides (**2**).

In a typical experiment, the oily substrate **1** was mixed with 0.20 ml of F113 solution of **2** (*c*. 0.2 M, flushed with N_2) in an EPR tube at 25 °C. After vigorous shaking for several minutes, the strong EPR signal of the required nitroxide could be detected. The nitroxides **3** were found to be quite stable, and could be kept in a refrigerator for weeks without significant decay. The EPR parameters of nitroxides **3** are given in Table 1 and the EPR spectra of some representative nitroxides **3** are shown in Fig. 1.

As shown in Table 1, the magnitude of the g factors clearly indicates that the radicals detected are nitroxides. The a_N values are those of typical acyl nitroxides. The a_N values are smaller than those of nonfluorinated acyl nitroxides (7.5 ~ 8.5 G) because of the more powerful electron-withdrawing perfluoroacyl group (compare with nonfluorinated acyl) in the nitroxides.

The smaller a_N values mean a greater spin density on the nitroxyl oxygen atoms and thus probably a higher reactivity in H-abstraction and other radical steps, as we have found in our extensive studies on the chemical reactivity and applications of reactive fluorinated nitroxides [17].

As far as the substituent effects of R_F on the a_N values are concerned, we again found the same trend of decreasing a_N values in the order $CF_3 > C_2F_5 > n\text{-}C_3F_7 \approx n\text{-}C_7F_{15}$; thus the electronegativity increases in the order $CF_3 < C_2F_5 < n\text{-}C_3F_7 \approx n\text{-}C_7F_{15}$. Similar trends are found for analogs containing

TABLE 1

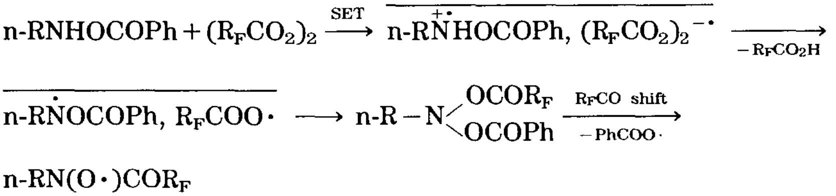
EPR parameters of $R_FCON(O\cdot)R$ (**3**)[a]

R_F	R	a_N	a_F^β	g
CF_3	n-C_4H_9	7.37	5.75	2.0065
C_2F_5	n-C_4H_9	7.57		
n-C_3F_7	n-C_4H_9	7.33	5.68	
n-C_7F_{15}	n-C_4H_9	7.26	5.68	2.0064
$H(CF_2)_2$	n-C_4H_9	7.40	5.54	
$H(CF_2)_4$	n-C_4H_9	7.19	5.62	2.0067
$H(CF_2)_6$	n-C_4H_9	7.22	–	2.0065
CF_3	$Pr^iCH_2CH_2$	7.26	6.07	
n-C_3F_7	$Pr^iCH_2CH_2$	7.21	5.80	2.0066
$H(CF_2)_2$	$Pr^iCH_2CH_2$	7.40	–	
$H(CF_2)_6$	$Pr^iCH_2CH_2$	7.31	5.74	2.0064
CF_3	$PhCH_2$	7.27	4.96	2.0065
C_2F_5	$PhCH_2$	7.25	4.68	
n-C_3F_7	$PhCH_2$	7.22	4.68	
$H(CF_2)_2$	$PhCH_2$	7.49	4.65	

[a] At 25 °C; hfsc are in gauss (±0.05).

ω-H atoms. The unusually large a_N values for $H(CF_2)_2CON(O\cdot)R$ arise because of intramolecular hydrogen bonding as suggested previously [9, 11, 13].

Based on the EPR results, we can obtain much information about the mechanism of formation of nitroxides **3**. The reactions are initiated by electron transfer from electron-rich substrates **1** to peroxides **2**. After the elimination of perfluorocarboxylic acid, which may sometimes cause smoke in the EPR tube during mixing, further radical steps involving cage recombination, cage elimination and 1,2-acyl shifts may lead to the formation of nitroxides **3**, sometimes accompanied by side-reactions forming other nitroxides in trace amounts (e.g. n-alkyl perfluoroacyloxyl nitroxide [16], $Bu^nN(O\cdot)OCO$-C_3F_7-n, $a_N = 9.90$, $a_H^\beta = 6.98$, $g = 2.0066$).



$$\text{n-RNHOCOPh} + (R_FCO_2)_2 \xrightarrow{\text{SET}} \overline{\text{n-R}\overset{+\bullet}{N}\text{HOCOPh}, (R_FCO_2)_2^{-\bullet}} \xrightarrow[-R_FCO_2H]{}$$

$$\overline{\text{n-R}\overset{\bullet}{N}\text{OCOPh}, R_FCOO\bullet} \longrightarrow \text{n-R}-N\begin{matrix}\diagup OCOR_F\\ \diagdown OCOPh\end{matrix} \xrightarrow[-PhCOO\bullet]{R_FCO\text{ shift}} \text{n-RN}(O\bullet)COR_F$$

(**3**)

The relative ease with which a 1,2-shift occurs in $R_FC{=}O$ is strongly dependent on the bulk of the R groups [17, 18]. In the present reactions, the n-alkyl groups are not bulky and this allows the 1,2-shift to occur from O to the N atom.

Further studies on the reactivity of nitroxides **3** are being conducted.

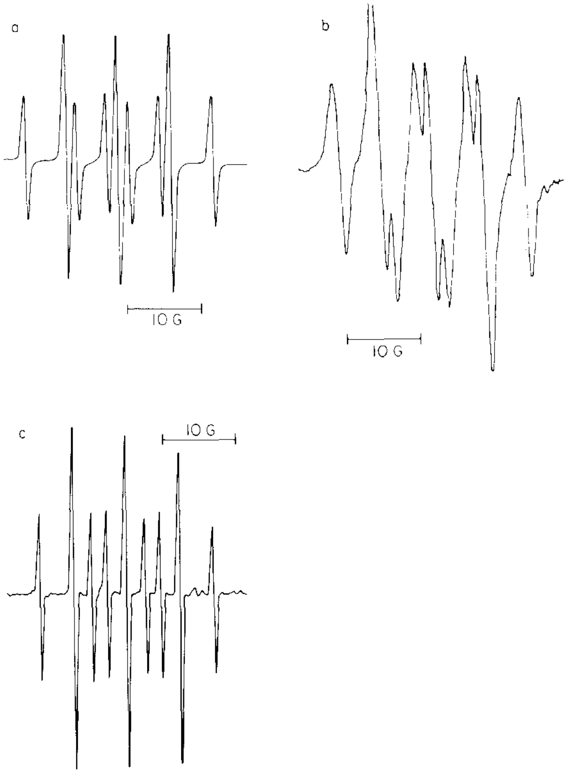


Fig. 1. EPR spectra of some representative n-alkyl perfluoroacyl nitroxides (**3**). (a) $Bu^nN(O\cdot)COC_7F_{15}$-n; (b) $Pr^iCH_2CH_2N(O\cdot)COC_3F_7$-n; and (c) $PhCH_2N(O\cdot)COC_2F_5$.

Experimental

Reagents

Perfluorodiacyl peroxides were prepared from the corresponding acyl chlorides, NaOH and H_2O_2 in F113 at *c.* −8 °C according to the procedure described in our previous report [19].

O-Benzoyl n-alkylhydroxylamines were prepared from benzoyl peroxide and the amines (Bu^nNH_2, $Pr^iCH_2NH_2$) by following the procedure described by Zinner [20]. In a typical preparation, 25 mmol of recrystallized benzoyl peroxide was dissolved in 35 ml dry benzene in an N_2-flushed 100 ml flask fitted with a dropping funnel containing 10 ml of a solution of 50 mmol n-alkylamine in benzene. With magnetic stirring and cooling using an ice–water bath, the amine solution was added over 30 min. The mixture was then warmed up to 40 °C for 30 min, 20 ml ether was added to the mixture, which was filtered, washed with aqueous $FeSO_4$ and acidified several times with H_2SO_4. The solution was then washed with distilled water twice and the solvent removed under vacuum, to give an oily yellow liquid. After chromatographic purification on a silica gel column with petroleum ether/

ether (4:1) eluent, colorless pure liquid was obtained. The pure compound was not stable and had to be dissolved in ether and kept under N_2 in the dark.

EPR experiments

Depending on the reactant ratio, a given volume of $(R_FCO_2)_2$ solution in F113 (0.2 M) was transferred through a stainless-steel syringe into an N_2-flushed EPR tube containing a mixed amount of an F113 solution of the substrate. After mixing with shaking, the EPR tube was inserted in the EPR cavity at room temperature. The spectra were recorded using Varian E112 and JEOL JES-FEIXG EPR spectrometers. The conditions employed were as follows: 100 kHz modulation; frequency, 9.17 GHz (X band); microwave power, 0.5~30 mW; time constant, 0.128~0.5 s. The *g* factors were determined by using a standard Mn^{2+} sample.

Acknowledgement

We thank NFS of China for financial support.

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