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Study of the electron-transfer initiated reaction of *N,N*-dichloro-5-iodo-3-oxa-octafluoropentane sulfonyl amide and carbomethoxydifluoromethane sulfonyl azide with 2-methyl-2-nitrosopropane

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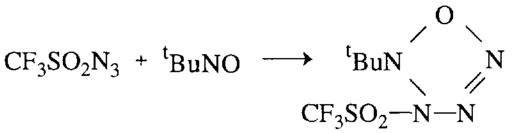
Abstract

The reactions of *N,N*-dichloro-5-iodo-3-oxa-octafluoropentane sulfonyl amide (**1**) and carbomethoxydifluoromethane sulfonyl azide (**2**) with 2-methyl-2-nitrosopropane (**3**) have been studied by EPR spectroscopy. Our results suggest that these reactions are initiated by electron transfer (ET) between the perfluoroalkane sulfonyl compounds and the donor **3**. The reaction of the dichloroamide **1** with **3** yields either one of two products, i.e., the unsymmetrical nitroxide **4** or the symmetrical nitroxide **5**, depending on the nature of the solvent and the amount of **1** used. Possible mechanistic paths are discussed.

Keywords: EPR spectroscopy; Electron-transfer initiated reaction; Dichloroiodooxa-octafluoropentane sulfonyl amide; Carbomethoxydifluoromethane sulfonyl azide; Methylnitrosopropane

1. Introduction

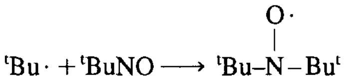
N,N-Dichloroperfluoroalkane sulfonyl amides, $R_FSO_2NCl_2$, perfluoroalkane sulfonyl azides, $R_FSO_2N_3$, and their reactions have rarely been studied. *N,N*-Dichlorotrifluoromethane sulfonyl amide was first prepared in 1974 by Yagupolskii and coworkers [1], and more recently they also reported its reaction with diphenyl sulfide and trifluoromethylphenyl sulfide [2,3]. Recently, Kamigata et al. [4] have reported their study on the reaction of trifluoromethane sulfonyl azide with nitroso compounds and suggested that the reaction follows the cycloaddition path shown below:



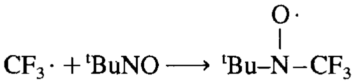
$$\xrightarrow{-N_2O} {}^tBuN{=}NSO_2CF_3 \longrightarrow {}^tBuN{=}N\cdot + CF_3SO_2\cdot$$

$${}^tBuN{=}N\cdot \longrightarrow {}^tBu\cdot + N_2$$

$$CF_3SO_2\cdot \longrightarrow CF_3\cdot + SO_2$$



$${}^tBu\cdot + {}^tBuNO \longrightarrow {}^tBu{-}\overset{O\cdot}{N}{-}Bu^t$$



$$CF_3\cdot + {}^tBuNO \longrightarrow {}^tBu{-}\overset{O\cdot}{N}{-}CF_3$$

The present paper reports EPR studies on the reactions of *N,N*-dichloro-5-iodo-3-oxa-octafluoropentane sulfonyl amide [$ICF_2CF_2OCF_2CF_2SO_2NCl_2$, (**1**)] and carbomethoxydifluoromethane sulfonyl azide [$MeO_2CF_2SO_2N_3$, (**2**)] with 2-methyl-2-nitrosopropane [${}^tBuNO$, (**3**)]. Our results suggest that these reactions are initiated by electron transfer (ET) and do not seem to proceed by the mechanism suggested by Kamigata et al.

2. Experimental details

2.1. Preparation of the title compounds, solvents and reagents

N,N-Dichloro-5-iodo-3-oxa-octafluoropentane sulfonyl amide (**1**), carbomethoxydifluoromethane sulfonyl azide (**2**), 5-iodo-3-oxa-octafluoropentane sulfonyl fluoride and 2-iodo-1-chlorotetrafluoroethane were prepared according to

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procedures described in Ref. [5]. 1,1,2-Trichlorotrifluoroethane (F-113) was purified by fractional distillation (b.p. 47–48 °C). 2-Methyl-2-nitrosopropane (**3**) was purchased from the Sigma Chemical Company. All other solvents, e.g., dichloromethane, benzene, chloroform, tetrachloromethane and $NaNO_2$, were of analytical grade.

2.2. Preparation of the reaction samples

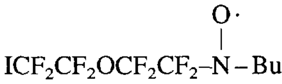
Different measured amounts (25 μl, 100 μl or 150 μl) of the reactant, i.e., **1**, **2**, $ICF_2CF_2OCF_2CF_2SO_2F$ or ICF_2CF_2Cl, were each added to 1 mg of ^tBuNO in 450 μl of different solvents, e.g., F-113, $CHCl_3$, CCl_4, CH_2Cl_2 or benzene. Each reaction mixture was injected into an EPR sample tube. When $NaNO_2$ (1 mg) was reacted with 100 μl of **1** or **2**, the amount of solvent used was also 450 μl. EPR spectra of the above-mentioned reaction mixtures were recorded in 3-mm sample tubes at room temperature.

2.3. Measurement of EPR spectra

All EPR spectra were measured on a Varian E-112 spectrometer with X-band, field modulation 100 kHz, response time 0.25 s and sweep width 10 mT. The magnetic field was determined by a ^1H NMR field meter and the microwave frequency by a frequency meter for super-high frequency. Simulation of the spectra was carried out on a Bruker ER 200 D Aspect 2000 computer.

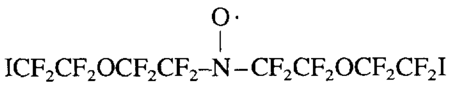
3. Results and discussion

Reaction of amide **1** with **3** mainly yields either one of two products, i.e., the unsymmetrical nitroxide **4** (5-iodo-3-oxa-octafluoropentyl t-butyl nitroxide), or the symmetric nitroxide **5** [bis(5-iodo-3-oxa-octafluoropentyl) nitroxide], depending on the amount of **1** and the nature of the solvent.



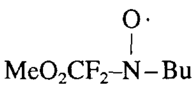
$\mathrm{ICF_2CF_2OCF_2CF_2{-}\overset{\overset{O\cdot}{|}}{N}{-}Bu^t}$

(**4**)



$\mathrm{ICF_2CF_2OCF_2CF_2{-}\overset{\overset{O\cdot}{|}}{N}{-}CF_2CF_2OCF_2CF_2I}$

(**5**)



$\mathrm{MeO_2CF_2{-}\overset{\overset{O\cdot}{|}}{N}{-}Bu^t}$

(**6**)

However, the reaction of $NaNO_2$ with **1** yields only product **5**, when different amounts of **1** were used in various solvents, while reaction of azide **2** yields only the unsymmetrical nitroxide **6** (carbomethoxydifluoromethyl t-butyl nitroxide). Structural assignments of products **4**, **5** and **6** were based on their EPR spectra (see Figs. 1 and 2 and Table 1).

Finally, the iodo compounds $IC_2F_4OC_2F_4SO_2F$ and IC_2F_4Cl have been found to be unreactive with ^tBuNO under similar conditions.

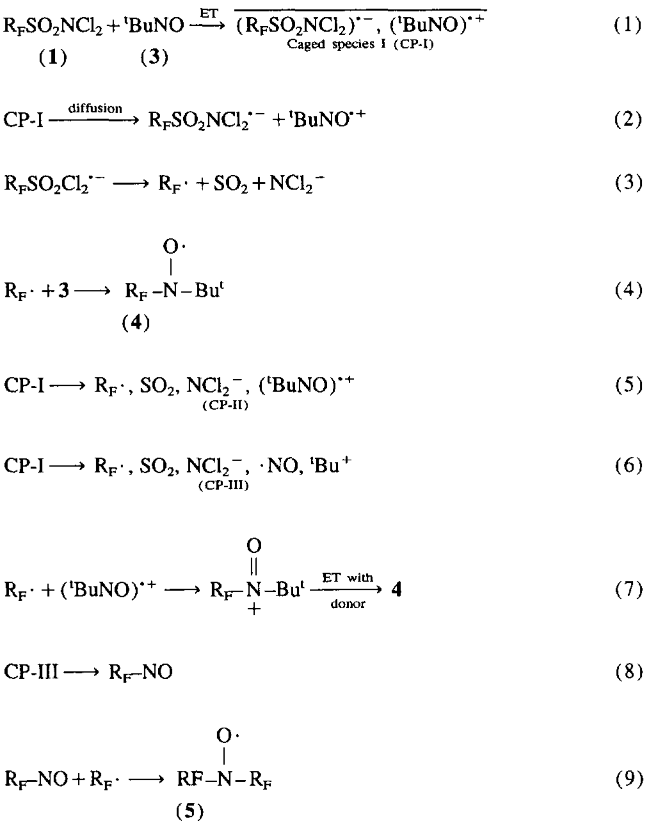
Although it does not seem possible to describe all the reaction paths in full detail, apparently the main features of

Table 1
EPR parameters of spin adducts

Entry No.	Product	Conditions employed	a_N (mT)	$a_F{}^\alpha$ (mT)	$a_F{}^\beta$ (mT)	g	Other solvents used
1	**4**	**3** + 25 or 100 μl of **1** in F-113	1.175	2.100		2.0054	$CHCl_3$, CCl_4
2	**5**	**3** + 150 μl of **1** in F-113	0.884	0.996	0.100	2.0056	$CHCl_3$, CCl_4
3	**5**	**3** + 100 or 150 μl of **1** in PhH	0.896	1.170	0.125	2.0058	
4	**4** [a]	**3** + 25 μl of **1** in PhH	1.161	2.001	0.099	2.0053	
5	**5**	**3** + 100 or 150 μl of **1** in CH_2Cl_2	0.896	1.195	0.125	2.0058	
6	**4** [a]	**3** + 25 μl of **1** in CH_2Cl_2	1.161	2.099	0.074	2.0052	
7	**5**	$NaNO_2$ + 100 or 150 μl of **1** in F-113	0.872	1.170	0.125	2.0055	CH_2Cl_2, CCl_4
8	**6**	**3** + 100 μl of **2** in CH_2Cl_2	1.141	2.182		2.0056	

[a] A small 1:2:1 triplet from β-CF_2 appeared in solvents PhH and CH_2Cl_2, but not in F-113.

the above-mentioned results may be delineated or rationalized via the mechanistic propositions given in Scheme 1 [6].



$$\underset{(1)}{R_FSO_2NCl_2} + \underset{(3)}{{}^tBuNO} \xrightarrow{ET} \underset{\text{Caged species I (CP-I)}}{\overline{(R_FSO_2NCl_2)^{\bullet -},\ ({}^tBuNO)^{\bullet +}}} \qquad (1)$$

$$\text{CP-I} \xrightarrow{\text{diffusion}} R_FSO_2NCl_2^{\bullet -} + {}^tBuNO^{\bullet +} \qquad (2)$$

$$R_FSO_2Cl_2^{\bullet -} \longrightarrow R_F\cdot + SO_2 + NCl_2^- \qquad (3)$$

$$R_F\cdot + 3 \longrightarrow \underset{(4)}{R_F\text{-}\overset{\overset{\displaystyle O\cdot}{|}}{N}\text{-}Bu^t} \qquad (4)$$

$$\text{CP-I} \longrightarrow \underset{\text{(CP-II)}}{R_F\cdot,\ SO_2,\ NCl_2^-,\ ({}^tBuNO)^{\bullet +}} \qquad (5)$$

$$\text{CP-I} \longrightarrow \underset{\text{(CP-III)}}{R_F\cdot,\ SO_2,\ NCl_2^-,\ \cdot NO,\ {}^tBu^+} \qquad (6)$$

$$R_F\cdot + ({}^tBuNO)^{\bullet +} \longrightarrow R_F\text{–}\underset{+}{\overset{\overset{\displaystyle O}{\|}}{N}}\text{–}Bu^t \xrightarrow[\text{donor}]{\text{ET with}} 4 \qquad (7)$$

$$\text{CP-III} \longrightarrow R_F\text{–}NO \qquad (8)$$

$$R_F\text{–}NO + R_F\cdot \longrightarrow \underset{(5)}{RF\text{–}\overset{\overset{\displaystyle O\cdot}{|}}{N}\text{–}R_F} \qquad (9)$$

Scheme 1.

The reaction is most likely initiated by an electron transfer (ET) between acceptor **1** and donor **3**, giving rise to a caged species I (CP-I), which is composed of a radical anion $R_FSO_2NCl_2^{\bullet -}$ and a radical cation ${}^tBuNO^{\bullet +}$ [Eq. (1)]. What happens next seems to depend on the relative life-span of CP-I. In halocarbon-type solvents, i.e., F-113, $CHCl_3$ and CCl_4, the life-span seems to be shorter because the halogenated radical anion can diffuse more quickly into the bulk of the solvent [Eq. (2)]. Consequently, respectable amounts of the perfluoroalkyl radicals $R_F\cdot$ are formed in the bulk solution [Eq. (3)]. They will be easily trapped by reagent **3** to yield the unsymmetrical nitroxide **4** (entry 1 and Fig. 1), as indicated by Eq. (4) [6]. Naturally, diffusion is not the only possible pathway. When the life-span of CP-I becomes longer in nonpolar solvents such as benzene and CH_2Cl_2, considerable amounts of CP-I might be transformed into both CP-II [Eq. (5)] and CP-III [Eq. (6)]. CP-II may follow a radical–cation radical coupling reaction [Eq. (7)] [7] which will eventually yield detectable amounts of the product **4** after ET from a donor (e.g. **3**) when the concentration of $R_F^\bullet$ in the bulk is low (entries 4 and 6, Table 1). However, CP-I may also lead to CP-III [Eq. (6)] which can yield R_F–NO according to Eq. (8). When the concentration of $R_F^\bullet$ in the bulk becomes higher because more **1** has been used (entries 3 and 5, Table 1), then detectable amounts of the symmetrical

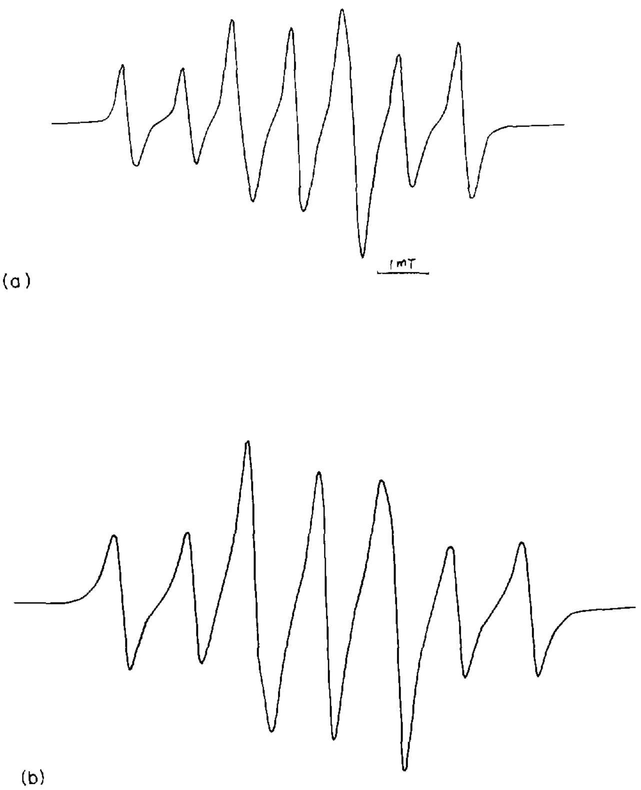


Fig. 1. (a) EPR spectrum of the reaction of $ICF_2CF_2OCF_2CF_2SO_2NCl_2$ (100 μl) and ${}^tBuNO$ in F-113. (b) Simulated spectrum.

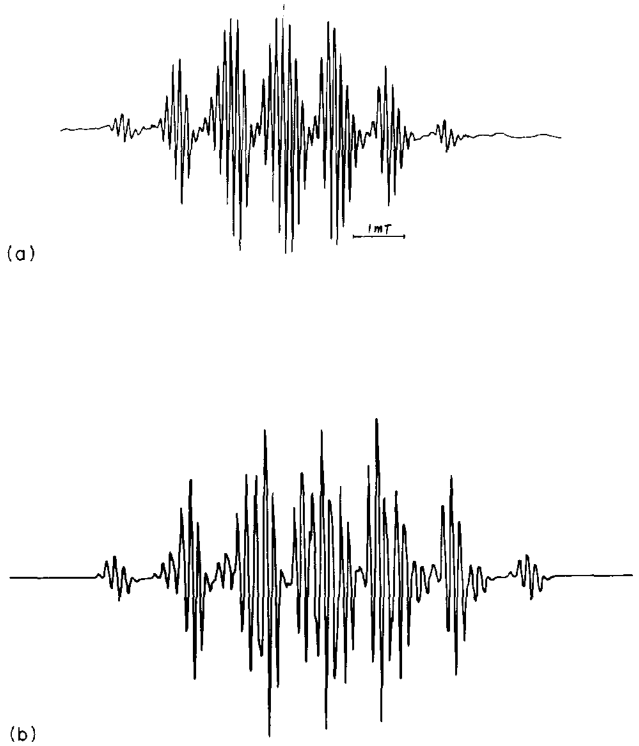


Fig. 2. (a) EPR spectrum of the reaction of $ICF_2CF_2OCF_2CF_2SO_2NCl_2$ (100 μl) and ${}^tBuNO$ in benzene. (b) Simulated spectrum.

nitroxide **5** (Fig. 2) will be formed from the combination of $R_F\cdot$ and R_F–NO according to Eq. (9).

The above speculation is also in accord with the results of entry 2 because a larger amount of **1** will lead to the formation of respectable amounts of CP-III [Eq. (6)]. This will lead to the existence of both R_F–NO and $R_F^{\bullet}$ in the bulk, and eventually to the formation of **5** [Eq. (9)]. The above-mentioned mechanistic speculations are also supported by the following two types of experiments (entries 7 and 8). Firstly, use of $NaNO_2$ as the ET donor [6] instead of the spin trap ^{t}BuNO (**3**) means that the reaction leading to the formation of **4** [Eq. (4)] can no longer occur and **5** becomes the only product [Eq. (9)].

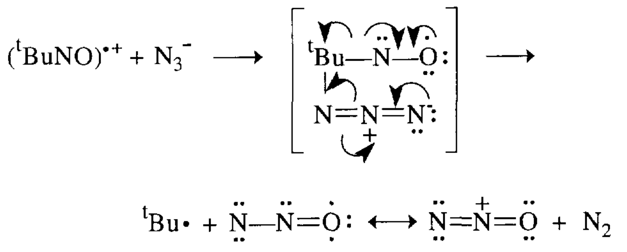
Notably, in this reaction system, R_F–NO can be derived not only from CP-III, as shown in Eq. (8), but also by a series of previously described reactions [Eqs. (23)–(27) in Ref. [6]]. Secondly (entry 8), another type of ET acceptor, i.e., azide **2**, has been found to yield nitroxide **6** (entry 8). Possibly, the azide ion is such a good leaving group [8] that $R_F\cdot$ is formed almost immediately after the ET process, as shown by Eq. (10):

$$\underset{(\mathbf{2})}{R_FSO_2N_3} + {}^tBuNO \longrightarrow R_F\cdot + SO_2 + N_3^- + ({}^tBuNO)^{\bullet +} \qquad (10)$$

The $R_F\cdot$ radicals are, of course, readily picked up by ^{t}BuNO or (^{t}BuNO)$^{\bullet+}$ to form **4** according to Eqs. (4) and (7). It is also worthy of note that azide **2** does not react with $NaNO_2$, perhaps because **2** is a weaker acceptor than dichloroamide **1**.

One may argue that the C–I bonds in **1** are involved in the ET processes. This possibility may be dismissed by (a) that neither $ICF_2CF_2OCF_2SO_2F$ nor ICF_2CF_2Cl react with ^{t}BuNO under similar conditions and (b) that substrate **2**, which does not possess a C–I bond, reacts with ^{t}BuNO (entry 8). The $-CF_2SO_2NCl_2$ or $-CF_2SO_2N_3$ moiety, therefore, is a more powerful ET acceptor than the $-CF_2I$ moiety, even though the latter type of functional group is known to participate in other ET processes [9].

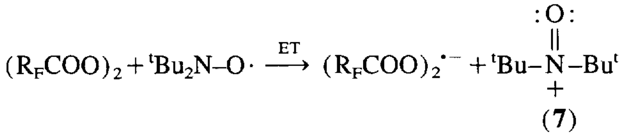
Finally, we suggest that the results of Kamigata et al. are open to an alternative interpretation in terms of ET initiation. Their $CF_3(NO)Bu^t$ product could have been formed in a similar manner to that of our unsymmetrical nitroxide **4**, but the formation of their ^{t}Bu(NO)Bu^t product would require the presence of the ^{t}Bu· radical which might have been formed and reacted according to the following scheme:



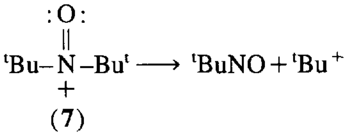
(11)

$$^tBu\cdot + {}^tBuNO \longrightarrow {}^tBu(NO)Bu^t \qquad (12)$$

Furthermore, our previously reported radical-induced homolysis [10] of polyfluorodiacyl peroxides might also have been initiated by an ET process between $(F_FCOO)_2$ and ^{t}Bu(NO)Bu^t. As shown by Eq. (13) and Eq. (14), cation **7** thus produced will lead to the formation of ^{t}BuNO and isobutene (from the deprotonation of ^{t}Bu$^+$):



$$(R_FCOO)_2 + {}^tBu_2N\text{–}O\cdot \xrightarrow{ET} (R_FCOO)_2^{\bullet -} + \underset{(\mathbf{7})}{{}^tBu\text{–}\overset{\overset{:O:}{\|}}{\underset{+}{N}}\text{–}Bu^t} \qquad (13)$$



$$\underset{(\mathbf{7})}{{}^tBu\text{–}\overset{\overset{:O:}{\|}}{\underset{+}{N}}\text{–}Bu^t} \longrightarrow {}^tBuNO + {}^tBu^+ \qquad (14)$$

Acknowledgement

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