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Journal of Fluorine Chemistry 69 (1994) 191–194

JOURNAL OF FLUORINE CHEMISTRY

Short communication

Spin trapping of fluoroalkyl radicals

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Received 19 October 1993; accepted 2 February 1994

Abstract

The formation of fluoroalkyl radicals in liquid chlorofluorocarbons ($CF_2Cl-CFCl_2$, $CFCl_3$, $CFCl_2-CH_3$, $CHF_2-CF_2-CF_2Cl$, $CF_3-CFH-CF_3$ and CCl_4) has been investigated by means of the spin trapping technique and ESR spectroscopy. It is shown that the primary fluoroalkyl radicals which were generated in these compounds by ionising radiation are preferably formed by bond cleavage at carbon atoms attached to one fluorine atom. Besides the liberation of chlorine atoms in chlorine-containing compounds, in $CHF_2-CF_2-CF_2Cl$ and $CF_3-CFH-CF_3$ fluorine atoms were also detected. By comparison of radicals formed from γ-irradiated $CF_2Cl-CFCl_2$ (CFC-113) and from $CF_2Cl-CFClI$ or $CF_2I-CFCl_2$ by zinc reduction, it was demonstrated that in CFC-113 both $\cdot CF_2-CFCl_2$ and $\cdot CFCl-CF_2Cl$ radicals are formed, whereas in iodine-containing homologues the formation of one species is favoured.

Keywords: Spin trapping; Fluoroalkyl radicals; ESR spectroscopy; γ-Irradiation; Zinc reduction; Phenyl-tert-butylnitrone

1. Introduction

Fluoroalkyl radicals are commonly considered to be the intermediates formed during coupling reactions of iodofluoroalkanes in synthetic fluorine chemistry [1–3]. Furthermore, they are generated in the stratospheric depletion of ozone by chlorofluorocarbons (CFCs) and during their application in plasma and nuclear chemistry [4,5].

The aim of the work reported in this paper was the investigation of radical formation in liquid CFCs under the influence of ionising radiation compared with the generation of radicals by UV light and zinc reduction as used in coupling reactions. The work was focused on the widely used chlorofluorocarbon $CF_2Cl-CFCl_2$ (CFC-113) (Aldrich, 99.99% purity) and the iodine-containing homologues $CF_2Cl-CFClI$ and CF_2I-$CFCl_2$. ESR spectroscopic studies of γ-irradiated CFC-113 in the solid state at 77 K [6] indicate that the formation of the $\cdot CFCl-CF_2Cl$ radical by dissociative electron capture is favoured, the radical showing a well-defined anisotropic ESR hyperfine structure. During irradiation at room temperature, a more complex reaction mechanism is expected. This assumption is based on the results of Fukumizu et al. [7], who reported various scavenger products of bromine with radicals formed in γ-irradiated CFC-113 at 293 K.

2. Experimental

In order to elucidate the structure of the radical intermediates in liquid CFCs, the spin trapping technique has been applied to this problem, e.g. short-lived radicals were reacted with a nitrone or a nitroso compound to form stable spin adducts, which are detectable by ESR spectroscopy. In the first set of experiments, spin trapping in γ-irradiated CFC-113 and other CFCs (^{60}Co γ-radiation, 1.25 MeV, 55.6 Gy min^{-1}) was studied, using phenyl tert-butylnitrone (PBN) as a spin trap compound. All experiments were carried out in the absence of oxygen by dissolving the spin trap compounds in a concentration of 0.1 mol l^{-1} in the CFCs ($CFCl_3$, CCl_4: Aldrich; $CFCl_2-CH_3$, $CHF_2-CF_2-CF_2Cl$, $CF_3-CFH-CF_3$: Hoechst; purity >99%).

The ESR spectra of the spin adducts in different CFCs were recorded on a Varian E4 ESR spectrometer immediately after irradiation. The spectrometer settings were: scan range, 100 G; modulation amplitude, 0.1 G; microwave power, 5 mW; time constant, 0.3 s; scan

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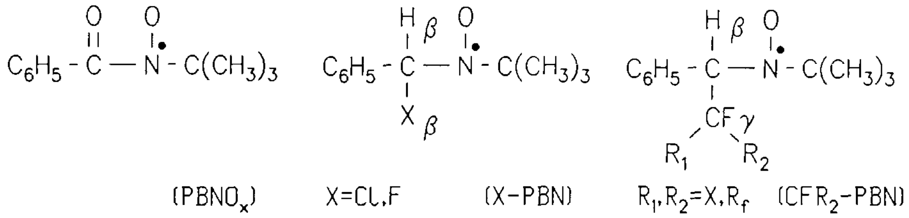
SSDI 0022-1139(94)03118-J

Table 1
ESR hyperfine coupling constants of PBN spin adducts obtained in chlorofluorocarbons after γ-irradiation together with their assignments

Halocarbon	g	a_N (G)	$a_{\beta\text{-H}}$ (G)	$a_{\beta\text{-}^{35}\text{Cl}}$ (G)	$a_{\beta\text{-F}}$ (G)	$a_{\gamma\text{-F}}$ (G)	Assignment
CCl_4	2.0061	7.75	–	–	–	–	$PBNO_x$
	2.0068	11.69	0.88	6.13	–	–	Cl–PBN
	2.0056	13.5	1.5	–	–	–	CCl_3–PBN
$CF_2Cl-CFCl_2$	2.0061	7.69	–	–	–	–	$PBNO_x$
(CFC-113)	2.0068	12.01	0.74	6.13	–	–	Cl–PBN
	2.0056	13.78	1.22	–	–	1.22	CF_2Cl–CFCl–PBN
$CFCl_3$	2.0061	7.69	–	–	–	–	$PBNO_x$
(CFC-11)	2.0068	12.00	0.88	6.00	–	–	Cl–PBN
	2.0056	13.51	1.08	–	–	1.46	$CFCl_2$–PBN
$CFCl_2-CH_3$	2.0061	7.69	–	–	–	–	$PBNO_x$
(CFC-141b)	2.0069	12.12	1.00	5.88	–	–	Cl–PBN
	2.0056	13.88	1.25	–	–	1.25	CH_3–CFCl–PBN
$CHF_2-CF_2-CF_2Cl$	2.0061	7.69	–	–	–	–	$PBNO_x$
(CFC-226)	2.0069	12.12	1.00	5.88	–	–	Cl–PBN
	2.0059	12.00	–	–	42.62	–	F–PBN
	2.0056	13.78	1.85	–	–	1.19	CFR_2–PBN
$CF_3-CFH-CF_3$	2.0059	12.75	1.38	–	43.25	–	F–PBN
(CFC-227)	2.0056	13.06	1.5	–	–	–	R–PBN



Scheme 1.

rate, 6.5 G min^{-1}. Using PBN as a spin trap compound, the hyperfine coupling constants of the spin adducts were obtained as summarised in Table 1. The structure of the spin adducts and the assignment of coupling constants are shown in Scheme 1.

3. Results and discussion

This technique allows detection and identification of both halogen and alkyl radicals simultaneously. In chlorine-containing chlorofluorocarbons, the absorption of the Cl–PBN spin adduct was observed as the dominant signal in accordance with the low C–Cl bond strength. The coupling constants of the nitroxyl nitrogen atom in Cl–PBN varied from 11.69 G in the spin adduct derived from CCl_4 to 12.12 G in that from $CHF_2-CF_2-CF_2Cl$ (CFC-226), corresponding to the increased solvent polarity. The Cl–PBN adduct is unstable and undergoes disproportionation to a diamagnetic species and an unsubstituted nitroxide $PBNO_x$ ($a_N = 7.7$ G). Hence the signal of Cl–PBN decays rapidly and the absorption of the more stable chlorofluoroalkyl–PBN adduct remains observable. This shows a characteristic set of coupling constants which disclose the individual structure of the trapped fluoroalkyl radical. For alkyl radicals from CFC-113, CFC-11, CFC-141b and CFC-226, a γ-fluorine coupling was observed resulting from a fluorine atom which is directly attached to the carbon atom of the trapped alkyl radical species. During the radiolysis of CFC-227 in the presence of PBN, the alkyl–PBN adduct formed showed no further splitting by a γ-fluorine atom, indicating a $\cdot C(CF_3)_3$ structure for the trapped radical.

In addition to these findings it was shown that C–F bond cleavage becomes more likely with increasing chain length of the chlorofluorocarbons, and F–PBN adducts were observed in CFC-226 and CFC-227 which exhibited a characteristic large coupling constant (42 G) for the β-fluorine atom. The application of this technique to iodine-containing CFCs yielded no stable PBN adducts because the liberated iodine oxidised the spin adducts rapidly to diamagnetic compounds.

In order to obtain further information about the radicals formed in γ-irradiated CFC-113 compared with radicals generated from $CF_2Cl-CFClI$ and

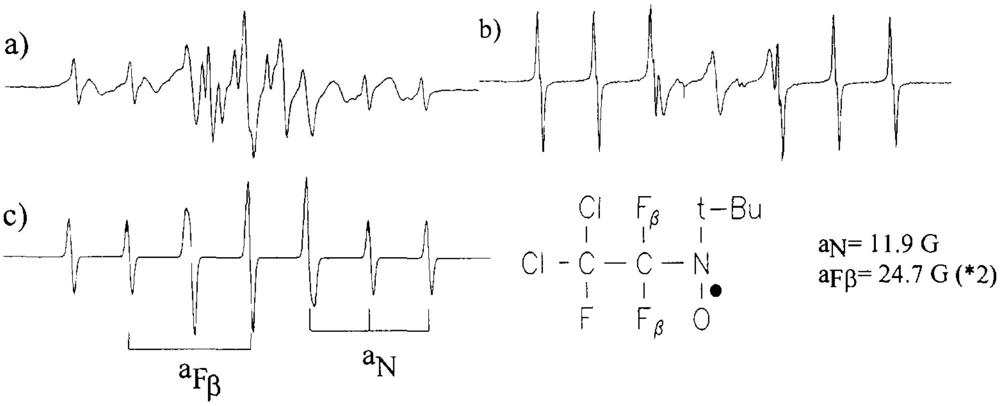
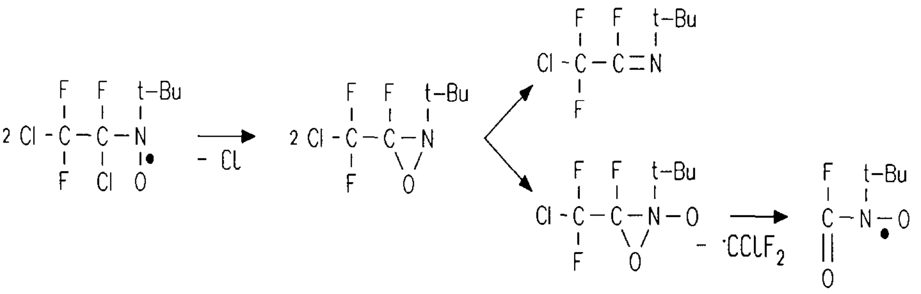


Fig. 1. ESR spectra of the $CFCl_2-CF_2-MNP$ adduct and assignment of coupling constants: (a) generated from CFC-113 at 20 °C by ionising radiation; (b) generated from $CF_2I-CFCl_2$ by UV photolysis at −20 °C; (c) simulated for room temperature.



Scheme 2.

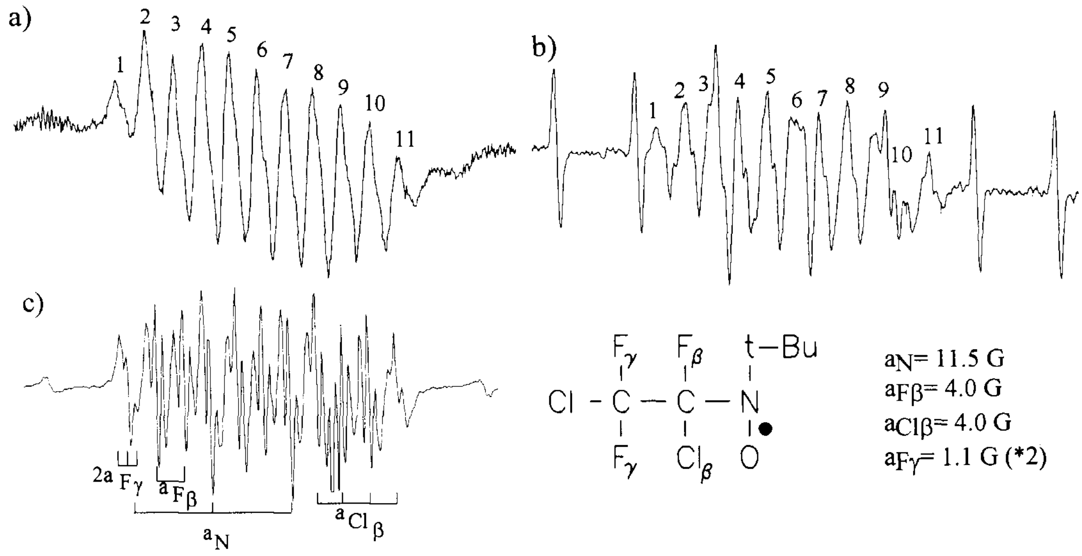


Fig. 2. ESR spectra of the $CF_2Cl-CFCl-MNP$ adduct and assignment of coupling constants: (a) generated from CFC-113 at −60 °C by ionising radiation; (b) generated from $CF_2Cl-CFClI$ by zinc reduction at 20 °C; (c) generated from a gaseous CFC-113/MNP mixture at 20 °C.

$CF_2I-CFCl_2$ by photolysis and zinc reduction, the spin trap compound 2-methyl-2-nitroso-propane (MNP) was used. The compounds $CF_2Cl-CFClI$ and $CF_2I-CFCl_2$ were synthesised by the addition of ICl to $CF_2=CFCl$ according to Barr et al. [8] and two fractions were separated by trap-to-trap distillation at 1 mmHg pressure. The fractions were analysed by ^{19}F NMR spectroscopy using an 80 MHz FT-NMR spectrometer (Tesla BS 587 A) and $CFCl_3$ as internal reference ($CF^AF^BCl-CF^CClI$: purity ~80%; $\delta_A = -62.07$ ppm, $\delta_B = -64.94$ ppm, $\delta_C = -72.80$ ppm [$J_{AB} = 162.5$ Hz, $J_{AC} = 15.4$ Hz, $J_{BC} = 15.4$ Hz] and $CF_2{}^DI-CF^ECl_2$: purity ~70%; $\delta_D = -55.51$ ppm, $\delta_E = -67.40$ ppm [$J_{DE} = 14.3$ Hz]).

The halogen–MNP spin adducts were not observable because they undergo fast disproportionation. However for trapped fluoroalkyl radicals, the ESR spectra of the spin adducts yield more detailed information on the molecular structure because the trapped species is directly attached to the NO group of the nitroxyl radical. After γ-irradiation of liquid CFC-113 in the presence of MNP, complex ESR spectra were observed. At 20 °C, the spectrum [Fig. 1(a)] is dominated by seven equally spaced absorption lines which are superimposed by weaker signals. The line distance of this signal is ca. 12 G. On generating radicals from $CF_2I-CFCl_2$ with MNP added at -20 °C by UV photolysis (low-pressure Hg lamp), the spectrum in Fig. 1(b) was obtained. It consists of nine lines including three broadened centre lines. This selective broadening effect decreased at higher temperature and at room temperature an equal spaced septet was formed. The independent generation and trapping of the $\cdot CF_2-CFCl_2$ radical in two different systems gave final experimental proof for the signal assignment to the structure in Fig. 1. The observed coupling constants were confirmed by the spectra simulation shown in Fig. 1(c).

Corresponding experiments were carried out for $CF_2Cl-CFClI$ to allow a comparison to CFC-113. On irradiating CFC-113 with MNP added at -60 °C, the ESR spectrum shown in Fig. 2(a) was observed at the same temperature. It consists of 11 equally spaced lines, having a line distance of 4 G. Enhanced resolution was not possible on increasing the temperature, since the spin adduct disproportionated rapidly to diamagnetic compounds and a COF–MNP adduct ($a_N = 6.6$ G, $a_F = 3.3$ G) at higher temperatures (Scheme 2).

By analogy to the coupling reactions, a $CF_2Cl-CFClI$/MNP solution was treated with zinc dust at 20 °C and the ESR spectra recorded in situ (Fig. 2(b)). In addition to a signal arising from $CFCl_2-CF_2-$MNP impurities an 11-line signal corresponding to that in Fig. 2(a) was obtained. ESR spectra with enhanced resolution (Fig. 2(c)) were recorded after evaporation of a CFC-113/MNP mixture, allowing the gas stream to pass through a UV reactor and dissolving the reaction products in liquid CFC-113 located in the cavity of the ESR spectrometer. Computer analysis of the complex ESR spectrum allowed coupling constants to be attributed to the structure of $CF_2Cl-CFCl-$MNP as in Fig. 2, thus enabling correction of the values reported by Belevskii and Westfahl [9], who observed no coupling of γ-fluorine atoms in the $CF_2Cl-CFCl-$MNP adduct.

These results indicate that depletion of liquid and gaseous CFCs, and especially of CFC-113, by ionising radiation proceeds via a more complex set of reaction products than expected from solid-state studies. By application of the spin trapping technique and a comparison of radiation experiments with the coupling reactions of iodine-containing analogues, it has been shown that the primary radicals formed in irradiated CFC-113 are identical with those generated from their corresponding iodine-containing homologues.

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