Journal of Fluorine Chemistry, *43* (1989) 1–14

Received: November 18, 1987; accepted: October 15, 1988

PHYSICOCHEMICAL PROPERTIES OF 1,2-BIS(F-ALKYL)ETHENES STUDIED BY CW-ESR

MICHAEL KUPFER, REINHARD STOESSER, ULLRICH PROESCH

Department of Chemistry, Humboldt-University of Berlin,
1040 Berlin (G. D. R.)

and LOTHAR KOLDITZ

Central Institute of Inorganic Chemistry,Academy of Sciences
of the GDR, 1199 Berlin (G. D. R.)

SUMMARY

1,2-Bis(F-alkyl)ethenes are very useful as model compounds for perfluorocarbons under several headings. The ability of these highly-fluorinated substances to dissolve remarkable quantities of gases such as O_2 , CO_2 etc. as well as the time dependent changes of the partial pressures of these gases was studied using spin probes (TEMPOL) by cw-ESR .

In addition, primary and secondary radicals created by UV/VIS- and ionizing radiation, respectively, were detected by cw-ESR, demonstrating the close relationship of 1,2-bis (F-alkyl)ethenes and perfluorocarbons. The presence of the CH=CH-unit in 1,2-bis(F-alkyl)ethenes is the reason that additional secondary reactions occur and aggregates could be observed.

0022-1139/89/$3.50

INTRODUCTION

Perfluorocarbons (PFCs) differ in their chemical and physical properties from hydrocarbons. For example, they are generally remarkably stable thermally and have the ability to dissolve considerable quantities of gases such as O_2 , CO_2 etc. [1] . Therefore, such compounds have been widely used as gas-carriers in technical and medical applications. Because perfluorocarbons are inert and nontoxic physiologically, emulsified preparations of a number of liquid perfluorocarbons have been applied as blood substitutes [2,3]. To investigate the interactions between PFC and dissolved gases, sophisticated physicochemical methods and techniques have been used [4] .

Unfortunately, perfluorocarbons are very apolar compounds, so that in many cases substances, which could be used spectroscopically for characterizing the PFC are insufficiently soluble.

To investigate the behaviour of PFC by cw-ESR two methods were followed :

(i) investigation of modified fluorinated model substances in which conventional spin probes show sufficient solubility

(ii) application of new modified spin probes soluble in perfluorocarbons.

Because of their close relationship to perfluorocarbons, a promising approach was to choose 1,2-bis(F-alkyl)ethenes as model compounds. Very pure 1,2-bis(F-butyl)ethene <u>1</u> and 1,2-bis(F-hexyl)ethene <u>2</u> can be synthesized in high yield [5] .

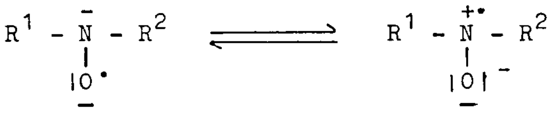
We shall discuss the behaviour of 1,2-bis(F-alkyl)ethenes from two aspects: The application as fluorinated solvents and the chemical reactions induced in them photo-and radiation-chemically.

RESULTS AND DISCUSSION

4-Hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPOL) in 1 and 2

(a) Matrix effects

ESR spectra of nitroxide spin probes are known to be very useful [7] for obtaining information about solvents and their interactions with dissolved substances. To understand the influence of the matrix on 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPOL) ESR spectra, it is necessary to consider the electronic structure of nitroxide radicals as described by canonical formulae [6] :



$$R^1-\underset{|\underline{O}^{\bullet}}{\overset{-}{N}}-R^2 \rightleftharpoons R^1-\underset{|\underline{O}|^{-}}{\overset{+\bullet}{N}}-R^2$$

(I) (II)

The fact that the real electronic structure is the superposition of several limiting structures is the reason that the hyperfine constant A_n of the nitroxide radicals increases with increasing matrix polarity. Change in solvent viscosity restricts molecular movement and broadens lines, especially of the high field transition.

Perfluorocarbons are extremely hydrophobic and apolar. Therefore, even if the nitroxide spin probe is sufficiently soluble in PFC, the nitrogen splitting constant A_n is small, comparable to that in the hypothetical gas phase, because there are only small electrostatic interactions.

The unusual properties of 1,2-bis(F-alkyl)ethenes result from their being highly-fluorinated whilst containing the CH=CH-unit. It was thus very interesting to characterize the behaviour of such ethenes as matrices. The π^*-value used by Kamlet *et al.* [7] is reliable in describing solvent dipolarity. Calculating from solvatochromic data, we obtained for **1** $\pi^*=0.1$. In comparison to perfluorocarbons which all have negative π^*-numbers [8], 1,2-bis(F-alkyl)ethenes seem to be a little bit more dipolar. But common aprotic, dipolar solvents like dimethylsulfoxide possess π^*-numbers greater than 0.7 [7].

(b) Influence of oxygen

The line width and form of ESR spectra are influenced by paramagnetic species dissolved in the matrix. For instance molecular oxygen affects the spin-spin-relaxation time of free radicals in solution mainly through Heisenberg exchange [9].

Comparing the ESR spectra of TEMPOL in air-saturated water and **1**, respectively, a broadening of the individual lines including a remarkable decrease of the amplitude can be seen in the latter case in Fig. 1.

On saturating the solution with oxygen the ESR spectrum of TEMPOL changes considerably (Figs. 2 and 3). The ESR spectral shape changes with time confirming that solvent **1** by comparison with benzene and F-decalin can accept and donate oxygen rapidly. This fact is very interesting from

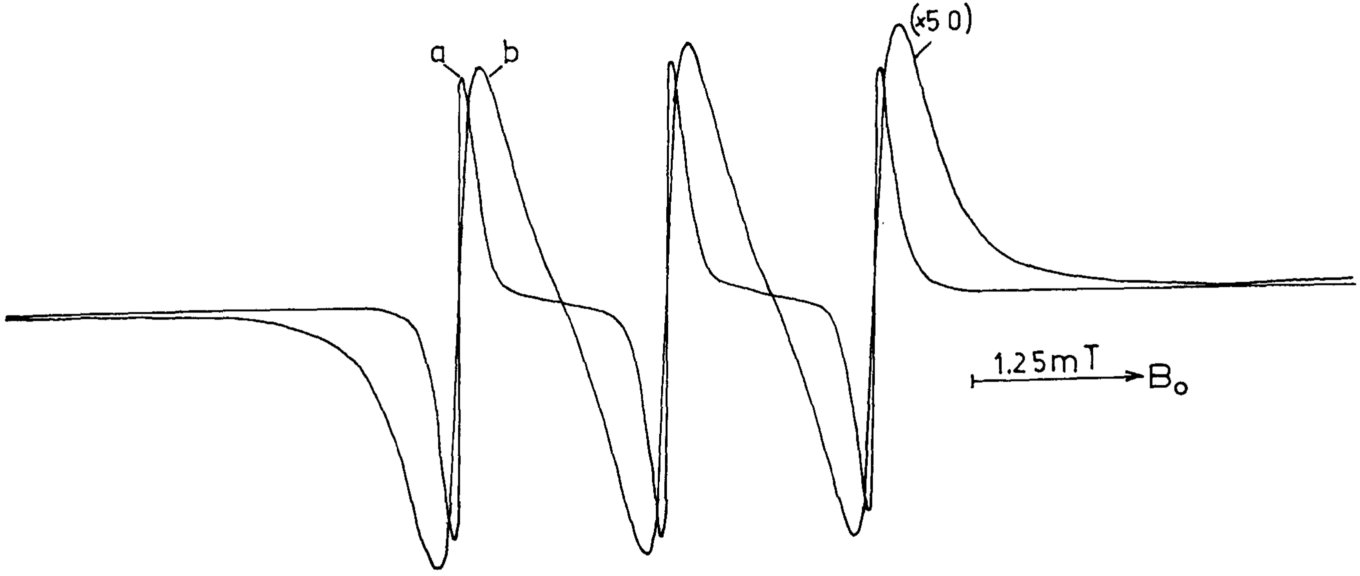


Fig. 1. 4-Hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPOL) a) in N_2-saturated <u>1</u> and b) in air-saturated <u>1</u>.

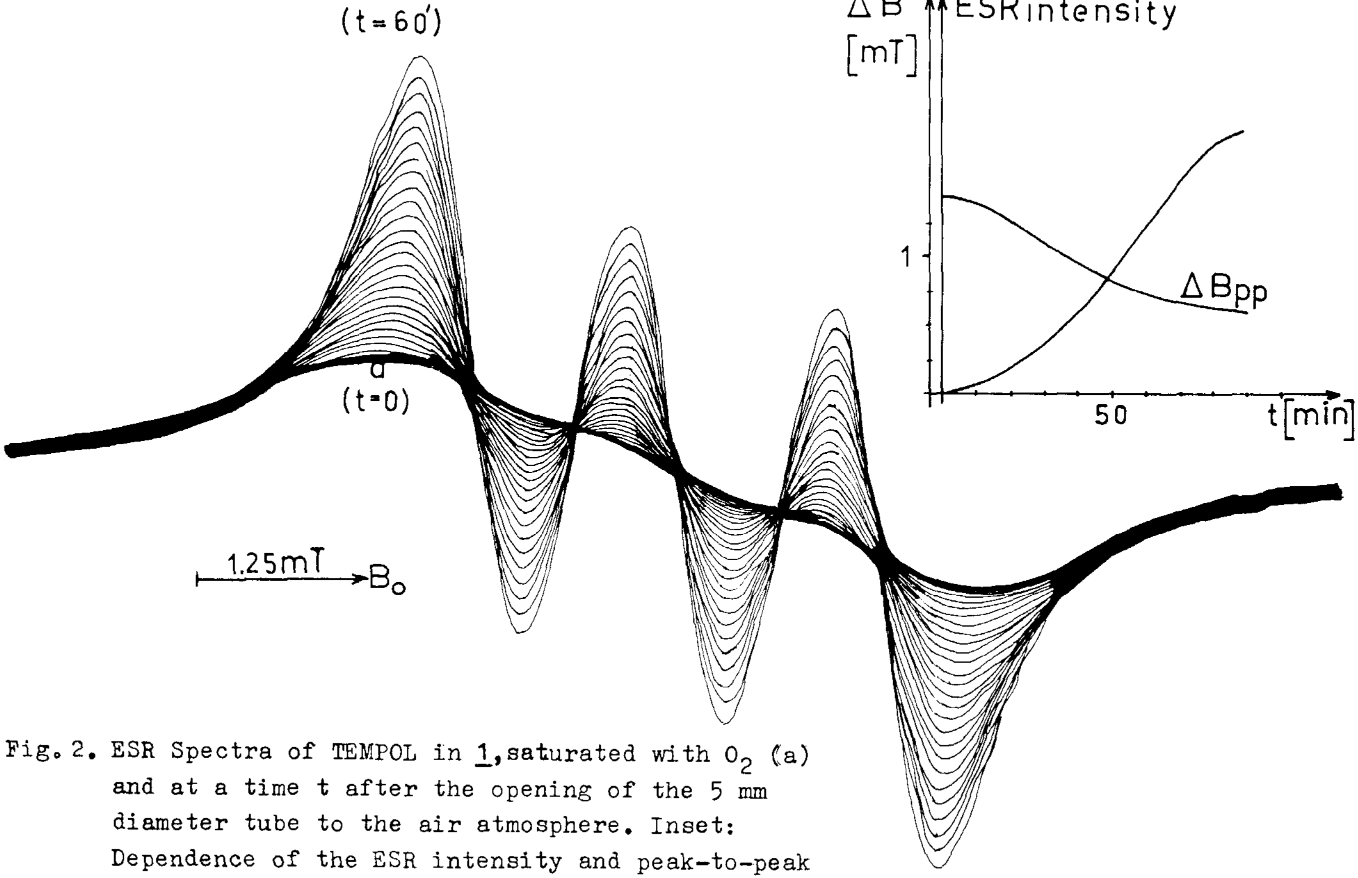


Fig. 2. ESR Spectra of TEMPOL in 1, saturated with O_2 (a) and at a time t after the opening of the 5 mm diameter tube to the air atmosphere. Inset: Dependence of the ESR intensity and peak-to-peak width ΔB from t.

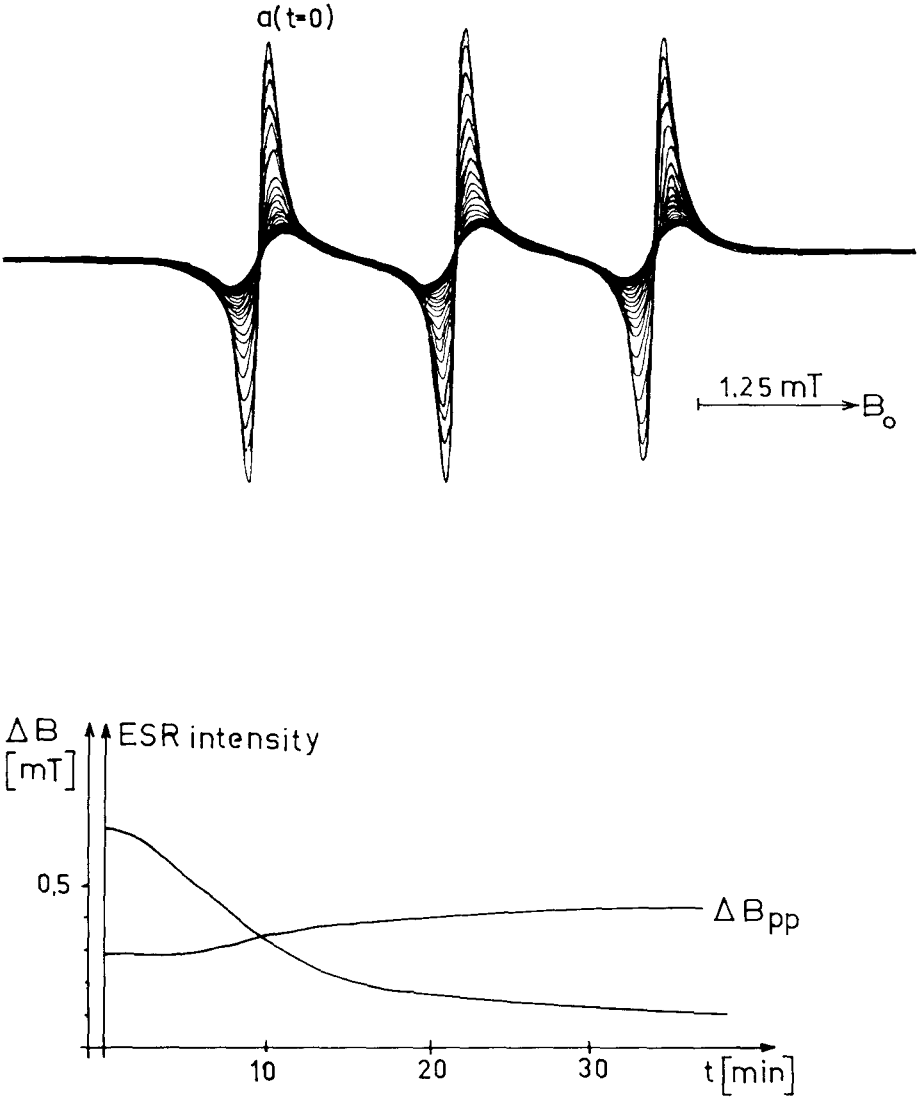


Fig. 3. ESR Spectra of TEMPOL in **1**, saturated with N_2 (a); t: the time dependence as in Fig. 2 for the diffusion of O_2 from air.

a physiological viewpoint. Quantitative evaluation of TEMPOL ESR spectra confirm the higher oxygen solubility in 1 (50.3 % v/v [2]) than in benzene (20 % v/v [2]) at 278 K (Fig. 4).

In contrast to the results published by Lai et al. [9] , who investigated TEMPOL-laurate, a water-insoluble nitroxide free radical derivate of lauric acid, the solvent systems chosen in this paper enable the direct use of one spin probe to determine oxygen partial pressures in different solvents.

Paramagnetic species by gamma-irradiation of 1 and 2

Compounds 1 and 2 are chemically inert under thermal excitation. However, primary radicals giving rise to consecutive reactions can be generated by gamma-irradiation of 1 and 2 at 77 K (Fig. 5). Depending on the chosen conditions (O_2-presence, temperature), radical reactions have been found which are comparable to those of perfluorocarbons, e.g. F-alkanes [10] . Primary radicals involved in such radical reactions are $CF_3^\bullet$ and $C_2F_5^\bullet$.

Due to the CH=CH-unit in 1,2-bis(F-alkyl)ethenes, gamma-irradiation of 1 and 2 produces further radicals, and ions e.g. $C_4F_9CH{=}CHCF_2^{(+)\bullet}$, which have previously been observed by mass-spectroscopy [11] . On raising the temperature ($T \geqslant 140$ K) in the presence of oxygen, these particles react to more stable peroxyradicals recognizable by their well-known ESR spectra (Fig. 5). The shape of the ESR spectra changes with temperature; such temperature dependence is connected with the motion of the peroxyradicals [9] .

There should be an effect from the radical-induced polymerization process in olefinic systems 1 and 2. The formation of the intermediate paramagnetic species with enlarged molecular mass and viscosity restricts the movement and therefore the shape of the ESR spectrum [12] .

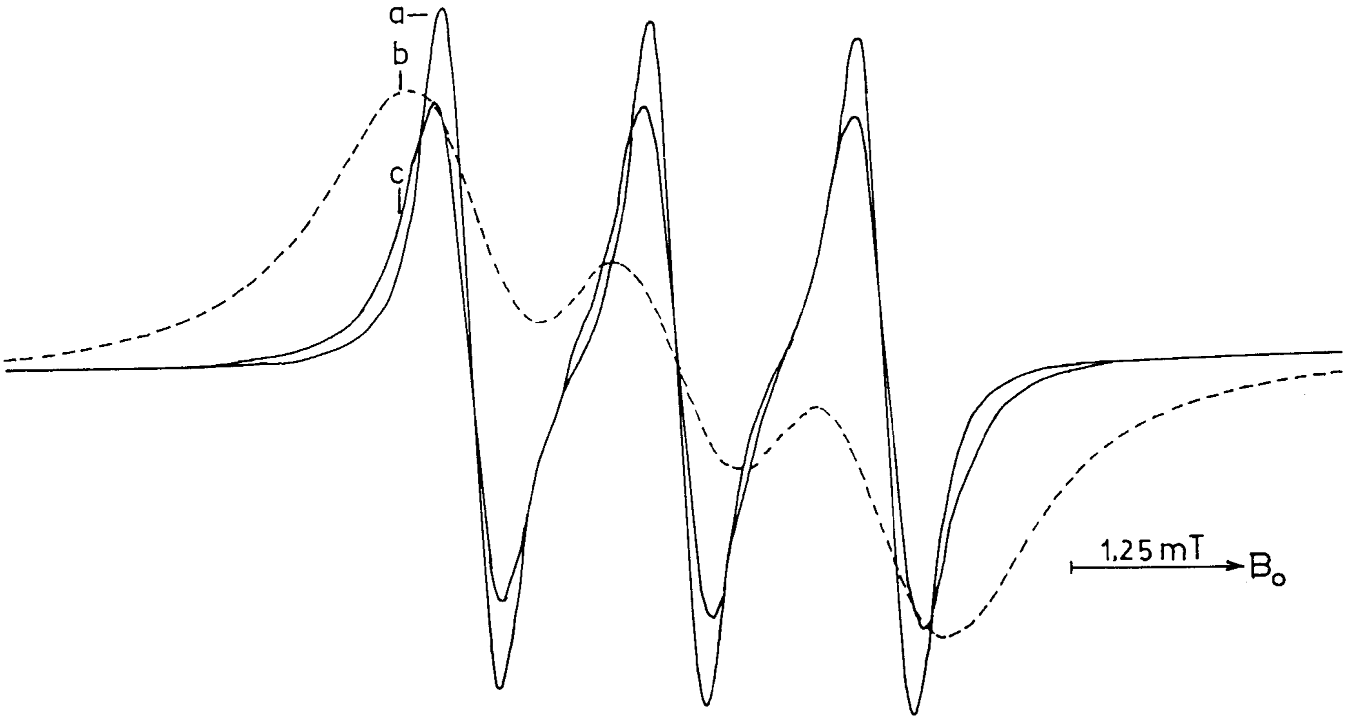


Fig. 4. ESR Spectra of TEMPOL in a) benzene, air-saturated; b) as in a) but O_2 saturated; c) for comparison in 1.

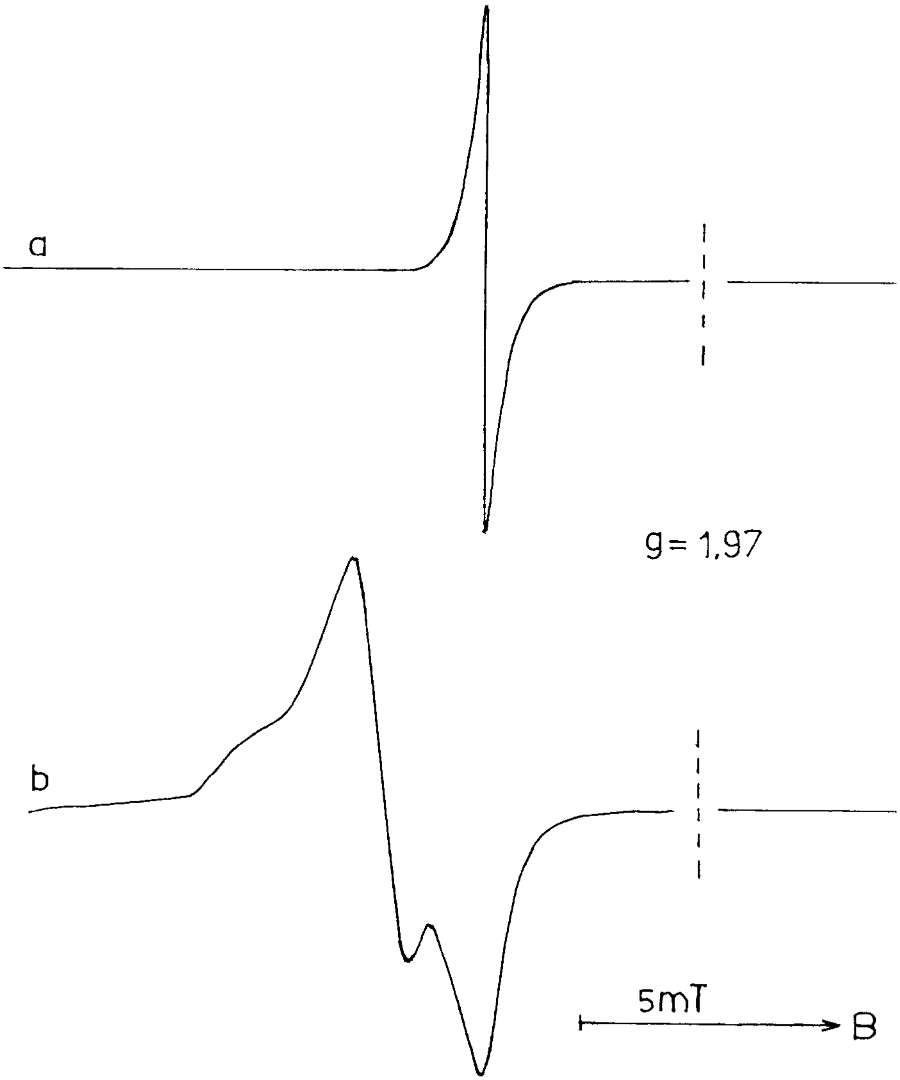


Fig. 5. ESR Spectra of $\underline{1}$ (a) and $\underline{2}$ (b) after γ -irradiation (dose ≈ 10 kGy) at 77 K and recording the spectra at 295 K.

Paramagnetic species generated in 1 and 2 by photoinduction

Major photoreactions have not previously been found in PFC [13] or in 1,2-bis(F-alkyl)ethenes in the absence of photoexcitable substances even under extreme conditions.

Using carbene precursors, e.g. diazofluorene, and radical initiators e.g. dibenzoylperoxide, tetrabromomethane, photoexcitation of 1 and 2 give well-known intermediates such as $\geq$C:, CBr_4, $^{\bullet}CBr_3$ etc. at 77 K. Analogously to the radiation-induced reactions, peroxy radicals were observed when probes containing oxygen were warmed up. As an example of ESR spectrum changes attributed to the temperature increase, the system dibenzoylperoxide and solvent 1 is shown in Fig. 6. Depending on the wavelength of the radiation applied, several photoinduced reactions have been studied at 300 K. Under stationary optical excitation of precursors in 1 or 2, only small radical concentrations were found by ESR spectroscopy. The parameters of ESR spectra obtained in the presence and absence of oxygen seem to indicate that $R-O-O^{\bullet}$ and consecutive radicals of the same type as in experiments with ionizing radiation are formed ($\Delta g=2.0045 \longrightarrow 2.016$).

In the presence of oxygen, consecutive reactions from carbenes and radicals, generated in 1 and 2 by stationary optical excitation, are accompanied by a colour change of the solution to red-violet and the probe becomes turbid, indicating a polymerization process as already considered during the radiation-chemical investigations. The nature of this effect, also observed in the solution of stable radicals like TEMPOL in 1 and 2, is not understood.

EXPERIMENTAL

1,2-Bis(F-alkyl)ethenes have been used without further purification. The spin probe 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPOL) was synthesized according to [14] and purified by column chromatography. Gamma irradiation

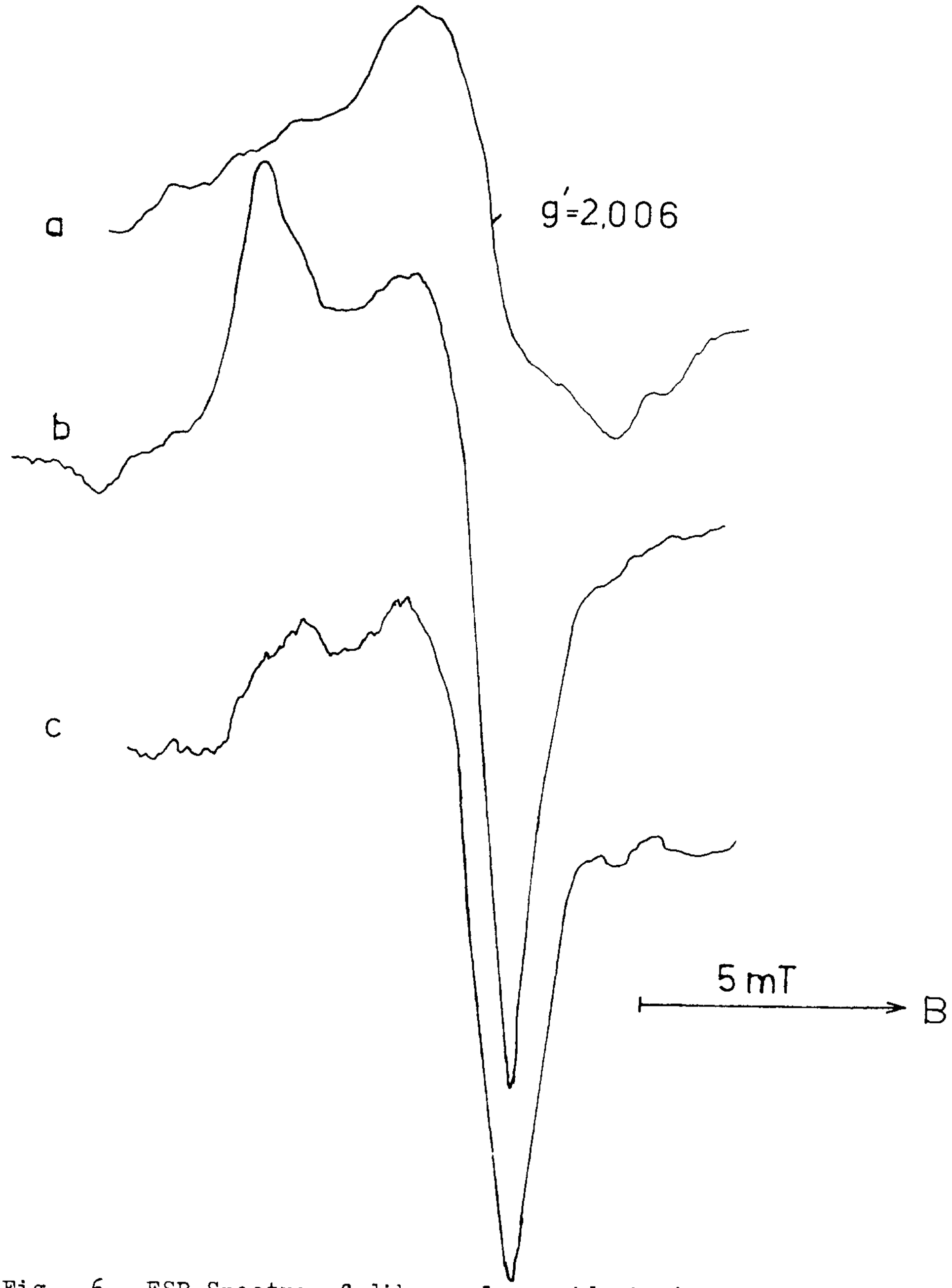


Fig. 6. ESR Spectra of dibenzoylperoxide in **1**, photoexcited with a 500 W Hg-lamp at 77 K. Spectra are recorded at T = 77 K (a) and in warming up the sample (b,c).

experiments were carried out in a ^{60}Co-irradiation facility MRCH GAMMA 100 at 77 K. High-pressure mercury lamp HBO 500 (VEB NARVA, Berlin) and metallic interference filters to select wavelength were used. The cw-ESR spectra were recorded with a VARIAN E 4 X-band spectrometer.

ACKNOWLEDGEMENT

The authors are greatly indebted to Prof. A. Cambon (University Nice, France) for inspiring discussions and his generous support with examples of 1,2-bis(F-alkyl)ethenes.

REFERENCES

1 G. Serratrice, J.-J. Delpuech and R. Diguet, Nouv. J. Chim., 6 (1982) 489.

2 F. Jeanneaux, M. Le Blanc, J. Riess and K. Koyama, Nouv. J. Chim., 8 (1984) 251.

3 J. Riess and M. Le Blanc, Pure Appl. Chem., 54 (1982) 2383.

4 P. Parhami and B.M. Fung, J. Phys. Chem., 87 (1983) 1928.

5 G. Santini, M. Le Blanc and J. Riess, Tetrahedron, 29 (1974) 2411.

6 B. R. Knauer and J. J. Napier, J. Am. Chem. Soc., 98 (1976) 4395.

7 M. J. Kamlet, J. L. Abboud and R. W. Taft, Prog. Phys. Org. Chem., 13 (1981) 485.

8 J. E. Brady and P. W. Carr, J. Phys. Chem., 86 (1982) 3055.

9 C. - S. Lai, S. J. Stair, H. Miziorko and J. S. Hyde, J. Magn. Reson., 57 (1984) 447; 63 (1985) 306.

10 V. I. Goldanskii and I.M. Barkalov, Radiat. Phys. Chem., 28 (1986) 189.

11 A. Chauvin, J. Greiner, R. Pastor and A. Cambon,
J. Fluorine Chem., 27 (1985) 385.

12 R. Stoesser, M. Kupfer and H. Meinert,
J. Fluorine Chem., 29 (1985) 206.

13 H. Mauser and R. Kretschmer,
Z.Phys. Chem. (NF) 80 (1972) 21.

14 G. Sosnovsky and M. Konieczny,
Z. Naturforsch. 31 (B) (1976) 1376.