Photochemical reactions of dimethyl ether radical cations in freon matrices and SF_6 at 77 K

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It has been shown for the first time that under the action of light within the absorption band of dimethyl ether radical cations in freon matrices [$\lambda_{max} \cong 436$ nm, $\varepsilon_{max} \cong (2.5\pm0.5)\times10^3$ M^{-1} cm^{-1}], the radical cations decay due to charge transfer to freon molecules, whereas in an SF_6 matrix they undergo deprotonation with quantum yields $\Phi \cong (4–15)\times10^{-2}$ and $\Phi \cong (2–6)\times10^{-4}$, respectively, at 77 K.

Radical cations are among the most important intermediates in many photochemical, radiation and oxidation processes. However, scant data are available on the reactivity of electronically excited radical cations.[1] Recently, the quantum yields of phototransformations of some radical cations in various freon matrices were determined[2–5] and the previously stated opinion on the significance of charge transfer processes from organic radical cations to freon molecules[6] was confirmed. The SF_6 matrix was used previously, *e.g.* for the stabilisation of some radical cations,[7] but the phototransformations in this matrix have not been studied. However, the large difference between the ionisation potentials of SF_6 and those of the majority of organic compounds ($\Delta \geq 5$ eV) permits studies of the phototransformations of radical cations to be carried out in this matrix in the absence of charge transfer to matrix molecules.

The purpose of this study was to obtain data on the mechanism and efficiency of dimethyl ether (DME) radical cations stabilised in freon and SF_6 matrices at 77 K.

In the experiments, DME solutions (0.1–0.5 vol.%) in a freon mixture containing 1:1, v/v, of $CFCl_3$ (freon-11) and CF_2BrCF_2Br (freon-114B2), whose glass transition temperature is 77 K, as well as in freon-11 (0.5 vol.%), freon-114B2 (0.5 vol.%) and SF_6 (0.02–4 vol.%) were evacuated to 10^{-4} Torr and irradiated with X-rays (E = 50 kV); the total absorbed dose was 0.5–2.0 kGr. EPR and optical absorption spectra of the intermediates formed were recorded on an E-3 Varian radio-frequency spectrometer and a Specord M-40 spectrophotometer (optical path 0.3 cm) using the same samples. The absolute error in the determination of the concentration of paramagnetic centres by EPR under the conditions used did not exceed ±20%. A high-pressure mercury lamp with a narrow-band glass filter (λ = 436 nm, $\Delta\nu_{1/2} \cong 3000$ cm^{-1}) was used as the light source. The absolute intensity of light was determined by ferric oxalate actinometry (λ = 436 nm); the light intensity was 1.6×10^{-4} einstein cm^{-3} s^{-1}. The volume of each sample was 0.08–0.13 cm^3.

Since all of the matrices used in our experiments, except freon mixture, were polycrystalline, we used the monomolecular photochemical reaction of di-*p*-cresylnitroxyl (DCN), which was carried out in 10^{-4} M solutions in the same matrices, as a special standard for the evaluation of the effective optical path in these matrices. Assuming that the quantum yields of DCN phototransformation in various frozen freons and SF_6 are nearly the same, we found that the effective optical path in various polycrystalline matrices is 1.5–4.0 times longer than that in glassy samples. The data obtained were in good agreement with the previous estimates[3] made using the photochemical reaction of diphenyldiazomethane as the standard. The extinction coefficients and the quantum yields reported in the present study were obtained in 4 to 6 successive experiments; the error values are given for a confidence limit of 0.95.

Upon exposure of DME solutions in individual freons and in their mixtures to X-ray irradiation at 77 K, their EPR spectra displayed a characteristic signal due to DME radical cations [a(6H) ≈ 43.0 G],[9] which had the best resolution in freon-11.

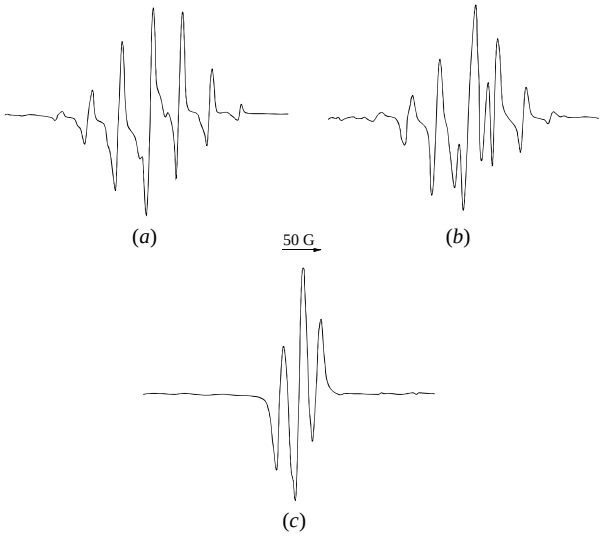

Figure 1 EPR spectra of irradiated solutions of DME in freon-11 (*a*) and SF_6 (0.02 vol.%) (*b*), (*c*), before (*a*), (*b*) and after the action of light with λ = 436 nm, at 77 K.

In freon-11 and freon-114B2, the DME radical cations account for 80% of the overall concentration of paramagnetic centres produced by irradiation. In the optical absorption spectra, the irradiation of DME solutions in freon mixtures at 77 K results in the appearance of absorption bands with $\lambda_{max} \cong 370$ and 590 nm, which can be assigned to radical cations of freons,[8] and an absorption band with $\lambda_{max} \cong 435$ nm. The EPR spectra of irradiated DME solutions in freon mixtures contain a signal due to the DME radical cations and an overlapping signal which appears upon irradiation of pure freon mixture. The intensities of both absorption and EPR spectra of freon radical cations and radicals were comparable to those of DME radical cations. Because in this case the most high-field components of the EPR spectrum of DME radical cations were not distorted by any other overlapping signals, the determination of the concentration of radical cations was carried out using the shape factor of these components obtained in irradiated solutions in freon-114B2 (the shape of the EPR spectrum lines of DME radical cations is most similar to that observed for freon mixtures).

When irradiated solutions of DME in freon mixtures are exposed to light with λ = 436 nm, changes in intensity of the

Table 1 Quantum yields of photochemical reactions of DME radical cations in freon-11, freon-114B2 and SF_6 at 77 K.

Matrix	Φ_1	Φ_2	β^a
Freon-11	0.15±0.03	0.06±0.01	0.4±0.1
Freon-114B2	0.04±0.01	—	—
SF_6	$(6.1\pm0.4)\times10^{-4}$	$(3.4\pm0.4)\times10^{-4}$	0.3±0.05

[a]The proportion of radical cation with a relatively high reactivity Φ_1.

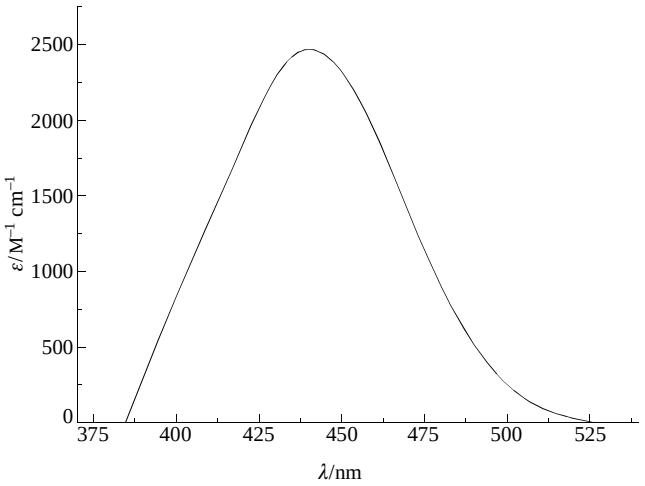

Figure 2 Absorption spectrum of DME radical cations in irradiated solutions of DME (0.4 vol.%) in freon mixtures at 77 K.

absorption band with $\lambda_{max} \cong 435$ nm correlate with changes in the concentration of DME radical cations determined by EPR. This allowed us to assign this absorption band to DME radical cations and to determine their extinction coefficient [$\varepsilon_{max} \cong (2.5 \pm 0.5) \times 10^3$ M^{-1} cm^{-1}] and the oscillator strength in the corresponding electron transition ($f \approx 0.07$) (Figure 2).

In all freon matrices used, the action of light with $\lambda = 436$ nm at 77 K results in the decay of DME radical cations without the formation of any paramagnetic particles. This process has the same spectral dependence as the absorption spectrum of DME radical cations. Since the energy of a photon with $\lambda = 436$ nm is higher than the difference between the ionisation potentials of freons and DME, it is natural to relate the changes observed to the photo-induced charge transfer from DME radical cations to matrix molecules. The dependence of the photo-induced decay kinetics of DME radical cations in a freon-11 matrix on the absorbed light dose has a bimodal shape, as in the cases reported previously;[2,4,5] this may suggest a kinetic non-equivalence of reacting particles in the solid phase (Table 1).

To eliminate the possibility of charge transfer to matrix molecules, we studied the photo-transformation of DME radical cations in an SF_6 matrix. The EPR spectrum of irradiated solutions of DME in SF_6 at 77 K displays a superposition of a well resolved signal of DME radical cations [a(6H) ≈ 43.0 G] and a signal due to $\cdot CH_2OCH_3$ radicals [a(2H) ≈ 18.0 G] [Figure 2(*b*)].† Computer simulation of experimental EPR spectra shows that a 200-fold increase in the concentration of DME in SF_6 results in an increase in the relative yield of neutral radicals from just 0.4 to 0.6. This implies that at the concentration of DME in SF_6 used for photochemical experiments (0.02 vol.%), the accumulation of $\cdot CH_2OCH_3$ radicals under X-ray irradiation is due to the decomposition of the DME radical cations which have not undergone relaxation, rather than to ion-molecular reactions in associates. The action of light with $\lambda = 436$ nm on irradiated DME solutions (0.02 vol.%) results in a decrease in intensity of the EPR signal of radical cations and a synchronous increase in the signal of $\cdot CH_2OCH_3$ radicals, while the total concentration of paramagnetic particles remains unchanged [Figure 1(*c*)]. The dependence of the photo-transformation kinetics of DME radical cations in SF_6 on the absorbed light dose also has a bimodal shape (Table 1). The quantitative conversion of DME radical cations to $\cdot CH_2OCH_3$ radicals under the action of light could be interpreted with reasonable reliability as a result of photo-induced deprotonation of DME radical cations:

$$CH_3OCH_3^{+\cdot} \longrightarrow \cdot CH_2OCH_3 + H^+$$

† At high amplifications, the EPR spectra of irradiated Me_2O solutions at 77 K display components of the SF_6^- radical spectrum;[10] on increasing the temperature of the samples to 135 K, the individual spectrum of SF_5 radicals is observed.[11]

The small quantum yield of this process explains why we were unable to detect it in freon matrices where it cannot compete with the highly efficient charge transfer to matrix molecules.

Along with the conversion of DME radical cations, we observe that the intensity of the EPR signal assigned to SF_6^- changes. We assume that these changes may be due to the reaction:

$$H^+ + SF_6^- \longrightarrow HF + SF_5$$

Unfortunately, the wide extent of the EPR spectrum of SF_6^- prevents us from making a quantitative comparison of DME and SF_6 radical cations. It is important to note that the action of light with $\lambda = 436$ nm on irradiated, pure SF_6 does not cause such changes in the EPR spectra.

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