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Photochemical reactions of trimethylene sulfide radical cations in Freon matrices at 77 K

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Photobleaching (λ = 436 nm) of trimethylene sulfide radical cations ($\lambda_{max} \approx 460$ nm, $\varepsilon_{max} \approx 345$ dm^3 mol^{-1} cm^{-1}) stabilised in different Freon matrices at 77 K results in the formation of distonic radical cations $CH_2CHSHCH_2^{\cdot+}$.

Radical cations (RCs) are primary products of the one-electron oxidation of organic molecules and act as intermediate particles in various radiation-chemical, electrochemical, photochemical and catalytic solid-phase processes.

The investigation of chemical reactions of organic RCs (*i.e.*, alkanes, ethers, esters, acetals, amides, carboxylic acids, *etc.*) in ground and excited states gained notable development in recent years.[1–3] Though new methods of registration of RC in solutions, such as quantum beats spectroscopy,[4] have recently been developed, the method of stabilization of RC in Freon matrices at low temperatures[5] is still the most widely spread one used in the study of structure and activity of RC. It is known that photobleaching of the RC of cyclobutane in Freon 11 at 77 K leads to a transformation into the RC of but-1-ene.[6]

The aim of this work was to study the mechanism and efficiency of photochemical reactions of RCs of cyclic sulfides stabilised in different Freon matrices at 77 K taking the trimethylene sulfide RC as a model.

We used $CFCl_3$ (Freon 11, ~99%, Aldrich), $CFCl_2CF_2Cl$ (Freon 113, 99.9%), CF_3CCl_3 (Freon 113a, 99%, Aldrich) as matrices; in certain cases Freons were additionally purified using standard techniques. Trimethylene sulfide (97%, Aldrich) was used without additional purification.

The solutions of test compounds in Freons (0.1 mol%) evacuated at ~0.1 Pa were sealed in quartz and SK-4B glass tubes and irradiated at 2–4 kGy and 77 K. A 5BKhV6-W X-ray generator (50 kV, 80 mA) was the emitting source.

The EPR spectra of the generated paramagnetic particles were recorded on a Varian E-3 X-band spectrometer. The error of absolute measurements of concentration of paramagnetic particles did not exceed ±20%. Simulations of EPR spectra were carried with the use of the PEST WinSim and WINEPR Simfonia software.[7] Optical spectra were recorded on a Specord M-40 spectrophotometer at 77 K; quartz tubes with 1 mm optical path lengths were used for optical measurements. The oscillator strengths for electronic transitions were obtained as[8] $f \cong 4.32\times10^{-9}\varepsilon_{max}\Delta\nu_{1/2}$, where ε_{max} is the molar absorption coefficient in the maximum of the absorption band, dm^3 mol^{-1} cm^{-1}; $\nu_{1/2}$ is the half-width of the absorption band, cm^{-1}.

A DRSh-250 high-pressure mercury lamp with a glass filter to select mercury spectral lines at λ = 436 nm (T_{max} = 27%, $\Delta\nu_{1/2}$ = 2400 cm^{-1}) was used as a light source. The absolute light intensity measured by ferryoxalate actinometry (λ = 436 nm) was 1.2×10^{-5} Einstein cm^{-3} s^{-1}. Quantum yields were calculated from the decrease of the amount of radical cations and the corresponding increase in the amount of the paramagnetic reaction products as a function of the light dose absorbed; the error of absolute measurements of quantum yields did not exceed 25%.

The calculations by the method of density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) and PBE-1 exchange-correlation functional were carried out using the PRIRODA program package.[9]

The X-ray irradiation of frozen (77 K) 0.1 mol% solutions of trimethylene sulfide in Freon 11 results in the appearance of a signal in the EPR spectrum, which is characterised by axially anisotropic *g*-tensor ($g_{\parallel} > g_{\perp}$) and hyperfine interaction of four magnetically equivalent protons and also one proton with a noticeably smaller hyperfine splitting constant [Figure 1(*a*)]. The hyperfine couplings equal to $a_1^{H}(4H_{\beta})$ = 3.2 mT, $a_2^{H}(1H_{\gamma})$ = = 1.2 mT, and $\Delta g = g_{\parallel} - g_{\perp} = 0.022$, $g_{iso} \approx 2.019$ [Figure 1(*d*)] provide the best simulation of the experimental spectra of these paramagnetic particles. As we have indicated, the annealing of X-ray irradiated 0.1 mol% solutions of trimethylene sulfide in Freon 11 to 150 K results in the disappearance of additional γ-proton hyperfine coupling and appearance of an EPR signal close to the one observed in the literature[10] [Figure 1(*b*)]. Hence, comparing our results and previously reported data[10] allows us to attribute the observed EPR spectrum to the trimethylene sulfide RC. Note that we did not observe the formation of dimeric trimethylene sulfide RCs [a(8H) = 0.9 mT[11]] in the range of the trimethylene sulfide concentrations used in all of the test Freons.

Along with the signal from the RC of trimethylene sulfide, additional signals were observed in the EPR spectrum from other radical products formed from Freon and trimethylene sulfide molecules under X-ray irradiation. Though these intermediates have broadened components of hyperfine structure, they still have an influence on the overall form of the EPR spectra observed in various irradiated Freons.

The irradiation of trimethylene sulfide solutions in Freon 11 at 77 K generates coloured products, which are characterised by the UV-VIS electronic absorption spectrum consisting of two bands at 370 and 460 nm, which could be resolved by Gaussian two-peak approximation. The consequent photobleaching (436 nm) leads to the disappearance of this originally generated UV-Vis absorption spectrum. It is known that dimethyl sulfide and tetrahydrothiophene RCs stabilised in 2-butyl chloride at 77 K[12] have absorption maxima at 375 and 465 nm. We estimate the molar absorption coefficient at 460 nm as $\varepsilon_{max} \approx 3.4\times10^2$ dm^3 mol^{-1} cm^{-1}. It was estimated by comparison of the values of concentration changes of trimethylene sulfide RC, measured by EPR method, with the corresponding absorbances obtained. The oscillator strength for this electron transition is $f = 7.3\times10^{-3}$. The molar absorption coefficient and oscillator strength are rather low for the RC of trimethylene sulfide due to low symmetry of this electron transition.

Photobleaching at 436 nm leads to the disappearance of the trimethylene sulfide RC and formation of new paramagnetic species [Figure 1(*c*)] in all of the Freon matrices. These species have a triplet EPR spectrum with a binominal intensity distribution due to interaction with two magnetically equivalent protons. The hyperfine splitting constant is $a(2\text{H}) = 2.2$ mT, $g_{\text{iso}} \approx 2.003$. Some trimethylene sulfide RCs disappear after photobleaching at 436 nm and 77 K in Freon matrices without formation of paramagnetic species as the total quantity of paramagnetic species in the frozen solution decreases. Thus, only 30% trimethylene sulfide RCs react in a Freon 11 matrix, and about 50% in a Freon 113 and Freon 113a. This indicates that the two processes, namely, the photoinduced charge transfer, which leads to a decrease of the integral intensity of the EPR spectra, and the formation of the new paramagnetic species, have similar quantum yields.

$$\text{cyclo-C}_3\text{H}_6\text{S}^{+\bullet} \rightarrow \text{H}_2\text{CS}^{+\bullet} \quad (1)$$

$$\text{cyclo-C}_3\text{H}_6\text{S}^{+\bullet} \rightarrow [\text{H}_2\text{CS}^{+\bullet}\cdots\text{H}_2\text{C=CH}_2] \quad (2)$$

$$\text{cyclo-C}_3\text{H}_6\text{S}^{+\bullet} \rightarrow [\text{cyclo-C}_2\text{H}_3\text{S–Me}]^{+\bullet} \quad (3)$$

$$\text{cyclo-C}_3\text{H}_6\text{S}^{+\bullet} \rightarrow \text{CH}_2\text{CHSH}^+\text{CH}_2^{\bullet} \quad (4)$$

Several reaction paths for photobleaching of trimethylene sulfide RC are feasible. The first is accompanied by the formation of thioformaldehyde RC and molecule of ethylene. In this case, either RCs of thioformaldehyde (1) or their complexes with ethylene molecules (2) could be stabilised. Quantum chemical calculations by the DFT method give the hyperfine splitting constant $a(2\text{H}) = 5.4$ mT for thioformaldehyde RC, which is not consistent with one observed experimentally. The quantum-chemical calculations show that such a structure of complex RC of thioformaldehyde with ethylene molecules could be realised for which $a_{\text{iso}}(2\text{H}) \approx 2.3$–$2.4$ mT. Another path of trimethylene sulfide RC transformation could be connected with an isomerization into propylene sulfide RC (3). However, the experimental EPR spectrum of propylene sulfide RC [$a(3\text{H}) = 1.6$ mT, $a^{\text{Me}}(\text{H}) \leq 0.3$ mT] [Figure 1(*c*)] differs from that observed after photobleaching the trimethylene sulfide RC. The last possible pathway of trimethylene sulfide RC transformation is linked with the formation of the distonic RC $\text{CH}_2\text{CHSH}^+\text{CH}_2^{\bullet}$, where a positive charge is localised on the sulfur atom, whereas spin density is localised on the methylene group. DFT calculations give the values of hyperfine splittings on two protons $a(2\text{H}) = 2.1$–2.4 mT, that is in accordance with the one observed experimentally [Figure 1(*c*)]. Thus, the results of quantum chemical calculations show that thioformaldehyde RC complexes with ethylene molecules (2) or the distonic RC $\text{CH}_2\text{CHSH}^+\text{CH}_2^{\bullet}$ could be formed (4), considering hyperfine splitting constants.

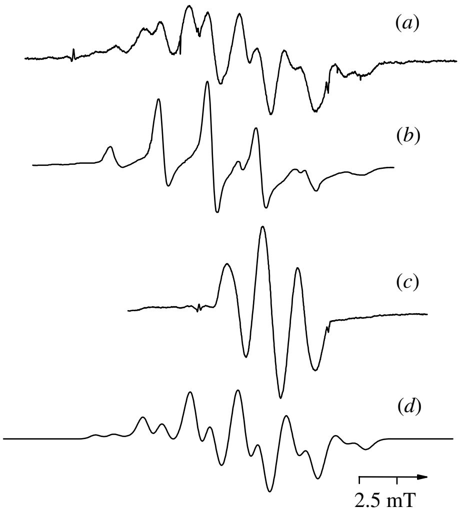

Figure 1 EPR spectra of trimethylene sulfide in Freon 11 (*a*) X-ray irradiated frozen 0.1 mol% solutions at 77 K, (*b*) solution (*a*) after annealing to 150 K, (*c*) solution of trimethylene sulfide RC after photobleaching with $\lambda = 436$ nm at 77 K, (*d*) spectrum (*a*) simulated with the following parameters: $a(4\text{H}_\beta) = 3.2$ mT, $a(1\text{H}_\gamma) = 1.2$ mT, $g_\parallel > g_\perp$ and $\Delta g = 0.022$.

Table 1 Quantum yields (φ) of photochemical reactions of the trimethylene sulfide RC in Freon matrices.

Matrix	φ_{436}	φ_1/φ_2^{a}
Freon 11	0.023±0.007	1/2
Freon 113a	0.022±0.007	1/1
Freon 113	0.010±0.003	1/1

$^a\varphi_1$ is the quantum yield of charge transfer reaction, φ_2 is the quantum yield of formation of distonic RC.

The quantum yields of trimethylene sulfide RC transformation in the Freon matrices are low (Table 1). The variation in the nature of the Freon matrix has little influence on the efficiency and products of the photochemical reactions of the trimethylene sulfide RC.

The fact that we have not observed the formation of the complexes of thioformaldehyde RC with ethylene molecules from non-relaxed RC ($\Delta I_{\text{p}} \approx 3.2$ eV) immediately after X-ray irradiation and that we also have not observed any influence of the Freon matrix nature on the quantum yields (φ_2) of the photochemical reactions allowed us to consider reaction (4) the most probable to occur [reaction (2) in contrast to reaction (4) has $\Delta V^{\neq} \geq 0$ and its efficiency should depend on the free volume, which differs for different matrices]. Furthermore, the value of $g_{\text{iso}} \approx 2.003$ for the product of the reaction is near to the value of g_{iso} for alkyl radicals and is in marked contrast with the values characteristic of complexes of sulfur-containing RCs with neutral molecules, for example, $g_{\text{iso}} \approx 2.013$ for complexes with arenes.[13]

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