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Effect of Freon matrices on the intermediates stabilized in X-ray irradiated 1,7-dioxaspiro[5,5]undecane solutions at 77 K

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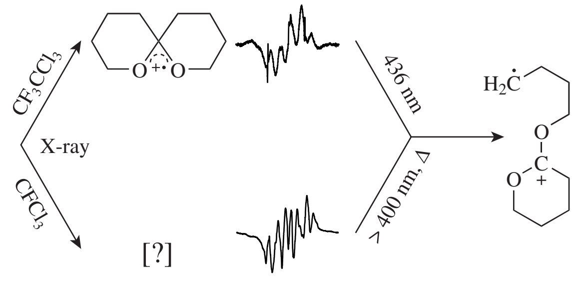
Freon matrices affected the nature of species stabilized upon the X-ray irradiation of frozen 1,7-dioxaspiro[5,5]undecane (DOSU)/CF_3CCl_3 or DOSU/$CFCl_3$ solutions at 77 K. This manifested in the stabilization of a ring-closed DOSU radical cation (RC) with an absorption maximum at ~440 nm in CF_3CCl_3 *versus* a paramagnetic intermediate with no absorption in this spectral region and a notably different EPR spectrum in $CFCl_3$. Interestingly, the ultimate product in a sequence of photochemical and thermally induced transformations was the same in both matrices: a distonic DOSU RC with a terminal alkyl fragment afforded upon C–C bond cleavage at the spiro carbon atom.



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Various matrix effects have been discovered when using Freon matrices to stabilize organic radical cations (RCs) upon indirect low-temperature ionization and study their reactivity at low temperatures. So far, such examples have only been reported for $CFCl_3$ matrices. For instance, σ^* complexes characterized by EPR spectra with notable $a_{||}(Cl)$ lines (due to the interaction between an unpaired electron and a chlorine nucleus in the matrix molecule) were found for RCs derived from methyl formate,[1] trimethyl phosphate,[2] five-, six- and seven-membered lactones,[3] and cyclic acetals (1,3-dioxolane and 1,3-dioxane).[4] As reported by Symons *et al.*,[5] the value of $a_{||}(Cl)$ rises in a direct ratio to difference between the ionization energies of the matrix molecule and the substrate. Furthermore, some curious features in the EPR spectra associated with additional hyperfine coupling (hfc) constants ($\leqslant$ 1.4 mT), which were attributed to the unpaired electron interacting with the fluorine nucleus in the matrix molecule, led to a hypothesis on π^* complexes with the RCs of tetrafluoroethylene[6] and *trans*-hex-3-ene[7] in a $CFCl_3$ matrix.

As of today, the UV-VIS spectra of RC/$CFCl_3$ complexes remain unattested. The same can be said about their thermally induced reactions and phototransformations. This study focuses on the 1,7-dioxaspiro[5,5]undecane (DOSU) RC afforded in Freon matrices ($CFCl_3$ and CF_3CCl_3) at 77 K: their structures, magnetic resonance and other spectroscopic characteristics and presumptive reaction pathways. The DOSU was selected due to the fact that σ^* complexes were earlier reported[4] in a study of the phototransformations of the RC derived from 1,3-dioxolane, a cyclic acetal, in $CFCl_3$. The current studies were additionally complicated by the need to account for multiple conformation states of the RCs. Upon stabilization in frozen Freons, these conformers could notably differ from those predicted by quantum chemical calculations (density functional theory (DFT), molecular dynamics) since we used continuous approximations to account for the solvents. To evaluate the results obtained for $CFCl_3$ and compare them with a point of reference, we chose another Freon, CF_3CCl_3, which is characterized by an almost the same ionization energy (11.77 and 11.78 eV, respectively) and similarly freezes as a polycrystalline matrix. However, their melting points at 1 atm are 162.5 and 250 K for $CFCl_3$ and CF_3CCl_3, respectively. Curiously, even though their solid-state characteristics are largely similar, no complexes formed by organic RCs and CF_3CCl_3 molecules were reported.

DOSU RCs were yielded upon X-ray irradiation of frozen DOSU/CF_3CCl_3 (~0.3 mol%) and DOSU/$CFCl_3$ (~0.5 mol%) solutions[†] at 77 K. The Freon synthesis, sample preparation procedures, irradiation techniques, EPR and UV-VIS spectroscopic measurements,[‡] and photochemical experiments were described in detail earlier.[8] The EPR spectra of radical ionic pairs were modeled using the Orthos program package.[9]

The quantum chemical calculations were performed by the unrestricted DFT method using the ORCA 4.1.1 program package.[10] B3LYP and B2PLYP functionals[11] together with the

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[†] The Freons CF_3CCl_3 (>99% based on NMR data, obtained from ~99% Aldrich $CF_2ClCFCl_2$) and $CFCl_3$ (Aldrich, > 99%) were used as matrices. Substrate DOSU (~98%, Abcr) was used without additional purification.

[‡] The EPR spectra were measured with Varian E-3 and Bruker EMXPlus X-band spectrometers.

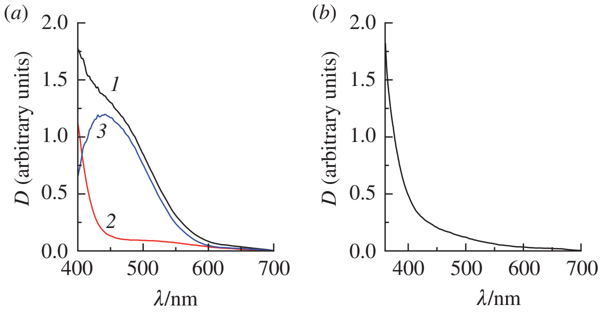


Figure 1 (*a*) UV-VIS spectra of X-ray irradiated 0.3 mol% DOSU/CF_3CCl_3 solutions at 77 K: (*1*) initial and (*2*) after the action of light with λ = 436 nm; (*3*) difference UV-VIS spectrum of X-ray irradiated 0.3 mol% DOSU/CF_3CCl_3 solutions at 77 K. (*b*) UV-VIS spectrum of X-ray irradiated 0.5 mol% DOSU/$CFCl_3$ solutions at 77 K.

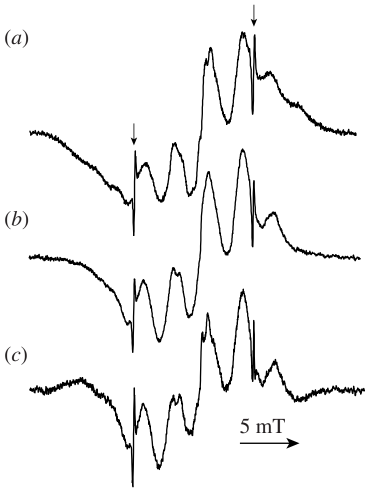
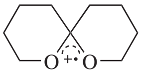


Figure 2 EPR spectra detected in X-ray irradiated 0.3 mol% DOSU/CF_3CCl_3 solutions at 77 K (*a*) before and (*b*) after the action of light with λ = 436 nm and (*c*) the difference EPR spectrum of the species perishing upon photolysis. The arrows indicate the hyperfine structure components belonging to Mn^{2+} impurities in powdered MgO, which was used as an internal standard.

full-electron def2-TZVP basis set[12] were used to calculate the geometry of potential energy surface (PES) minima. Geometries at minima were additionally checked for the presence of imaginary vibration frequencies. The spin-Hamiltonian parameters were calculated using the B3LYP functional together with the full-electron N07D basis set.[13] The influence of a solvent was accounted for with the COSMO model.[14] The electronic transitions and corresponding oscillator strengths were calculated by the time-dependent density functional theory (TD DFT).

The structural formulas of the intermediates discussed in this work are given below:



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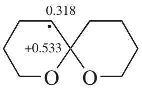

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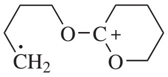

3

The results of the DFT, B3LYP/N07D calculations revealed that the prospective DOSU RC conformers are characterized by Mulliken spin populations predominantly localized symmetrically on the oxygen atoms of O–C–O fragments with values of 0.2–0.4. In this regard, the DOSU RC resembles the previously investigated 1,3-dioxolane RC,[4] where the reported Mulliken spin populations calculated for the oxygen atoms were ~0.3.

The UV-VIS spectra of X-ray irradiated 0.3 mol% DOSU/CF_3CCl_3 solutions at 77 K exhibited an absorption band at 400–600 nm with λ_{max} = 440 nm [Figure 1(*a*), curve *1*]. We attributed this band to DOSU RC **1** where spin and positive charge are predominantly delocalized throughout the O–C–O fragment. Correspondingly, the X-ray irradiated samples at 77 K exhibited a five-line EPR spectrum [Figure 2(*a*)]. The subsequent action of light (λ = 436 nm) on the X-ray irradiated samples at 77 K resulted in the complete decay of an absorption band in the UV-VIS spectra [Figure 1(*a*), curve *2*]. At the same time, a five-line EPR spectrum slightly different from the initial one [Figure 2(*b*)] was detected upon photolysis. The intensity ratio of the components was ~1 : 4 : 6 : 4 : 1 [a(4H) ~2.38 mT], while the integral intensity was ~80% of that in the EPR spectra detected before photolysis. These measurements allowed us to plot a difference absorption spectrum of DOSU RC **1** [Figure 1(*a*), curve *3*], which resembled the absorption spectrum of 1,3-dioxolane RCs in $CFCl_3$.[4] By juxtaposing the measured spectrum with the EPR spectroscopic data, we estimated the molar absorption coefficient for DOSU RC **1** in its absorption maximum: $\varepsilon \sim 5.0\times10^3$ dm^3 mol^{-1} cm^{-1} (for the 1,3-dioxolane RC,[4] this coefficient is 6.5×10^3 dm^3 mol^{-1} cm^{-1}). The EPR spectrum of DOSU RC **1** obtained by subtracting the spectrum of the photolysis product from the initial spectrum detected upon radiolysis was also a five-line spectrum with the intensity ratio of ~1 : 2 : 2 : 2 : 1. It can be satisfactorily fitted with the effective hfc constants: a_1(2H) = 2.44 mT and a_2(1H) = 4.61 mT [Figure 2(*c*)]. This spectrum can be attributed to interactions between an unpaired electron and three hydrogen nuclei of the two methylene groups adjacent to the oxygen atoms in the tetrahydropyran rings. In this case, another hfc constant associated with the fourth hydrogen nucleus in the methylene groups can be smaller than the line width in the spectrum (therefore, the constant does not manifest in the EPR spectra). In our opinion, the phototransformation of DOSU RC **1** affords distonic DOSU RC **3**. Characteristically, this structure possesses a terminal alkyl fragment, resulting from C–C bond cleavage at the spiro carbon atom in the tetrahydropyran ring. DOSU RC **3**, with its charge localized on the tertiary carbon atom and its spin localized on the terminal carbon atom, is the most energetically stable DOSU RC structure according to our quantum chemical calculations (out of both ring-closed and ring-open ones). Previously, we suggested a distonic RC with a terminal alkyl fragment as a product in the phototransformations of the 1,3-dioxolane RCs.[4,15] However, in that case, C–O bond cleavage was posited. We estimated the efficiencies of photodissociation and charge-transfer processes for DOSU RC **1** (this reaction, with the matrix acting as a charge acceptor, is responsible for the overall decay in paramagnetic species during the photolysis) at 0.05 and 0.01, respectively. Warming the samples containing DOSU RC **3**, the photolysis product, to 145 K and subsequently cooling them to 77 K barely affected the EPR spectra.

The X-ray irradiation of 0.5 mol% DOSU/$CFCl_3$ solutions at 77 K afforded a different UV-VIS spectrum with no bands at $\lambda_{max} \geqslant$ 360 nm [Figure 1(*b*)]. The multiplet EPR spectrum [Figure 3(*a*)] significantly differed from those found in the CF_3CCl_3 matrix. The DOSU RC conformers and their combinations afforded by the quantum chemical calculations cannot provide magnetic resonance parameters suitable for attributing this EPR spectrum. Interestingly, the EPR spectrum cannot be attributed to complexes formed by organic RCs and $CFCl_3$ molecules[1–5] due to the impossibility of complex formation *via* coordination between the matrix molecules and DOSU RCs (confirmed by DFT calculations and the lack of certain typical features in the experimental EPR spectra). Our attempts to attribute the experimental EPR spectrum to a triplet radical ionic pair were also fruitless since we were unable to detect a signal ascribed to a restricted ΔM_S = 2 transition. Furthermore, the DFT calculations showed that it was impossible to stabilize a pair formed by a DOSU RC and a matrix-derived radical anion: the radical anion is unstable and undergoes dissociation. On the other hand, the calculations of

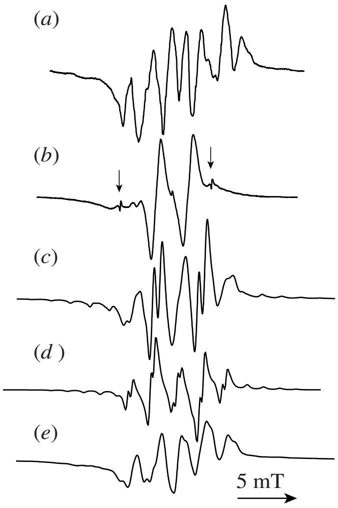

Figure 3 EPR spectra detected in X-ray irradiated 0.5 mol% DOSU/$\mathrm{CFCl_3}$ solutions (*a*) upon X-ray irradiation at 77 K, (*b*) upon the subsequent action of light with $\lambda \geqslant 400$ nm at 77 K, (*c*) upon the subsequent warming of samples (*b*) to 145 K; (*d*) the sum of model EPR spectra of $^{\bullet}\mathrm{CFCl_2}$ radicals and the ring-open form of the DOSU RC in a 2 : 1 ratio; and (*e*) EPR spectra detected upon the subsequent cooling of samples (*c*) to 90 K. The arrows indicate the hyperfine structure components belonging to $\mathrm{Mn^{2+}}$ impurities in powdered MgO, which was used as an internal standard.

the [DOSU RC···$^{\bullet}\mathrm{CFCl_2}$] pair revealed a typical $\Delta M_\mathrm{S} = 1$ transition of radical pairs. The calculated parameters were $D = 0.0154\ \mathrm{cm^{-1}}$ and $E = 0.00027\ \mathrm{cm^{-1}}$ (with $d = 5.6$ Å). These have nothing to do with the experimentally measured EPR spectrum of the radiolysis product in DOSU/$\mathrm{CFCl_3}$ solutions.

Surprisingly, even though the UV-VIS spectra of X-ray irradiated DOSU/$\mathrm{CFCl_3}$ solutions at 77 K had no absorption bands at $\lambda \geqslant 360$ nm [see Figure 1(*b*)], the action of light with $\lambda \geqslant 400$ nm led to significant changes in the EPR spectra of the samples [Figure 3(*b*)]. The multiplet signal measured upon irradiation irreversibly perished and a doublet signal with the hfc constant a(1H) ~ 3.1 mT appeared. Moreover, widened components detected at 77 K were attributed to the EPR spectrum of the $^{\bullet}\mathrm{CFCl_2}$[16] radical. The quantum chemical calculations of hfc constants for various DOSU RC conformers proved that only the ring-closed RC with its tetrahydropyran rings in the chair–chair conformation (namely, **2**) can provide an EPR spectrum close to the experimental one: a(1H) = 3.93 mT, and all the hfc constants for the other hydrogen nuclei were < 1 mT (these hfc constants contributed to the significant widening of doublet components in the spectrum). As opposed to all the other ring-closed DOSU RC conformers, the quantum chemical calculations indicated that the charge and spin distributions in DOSU RC **2** gave it a slight distonic character, which can clear up the nature of its stability towards the action of light with $\lambda \geqslant 400$ nm.

Another thing the quantum chemical calculations revealed is that various conformers of the same oxygen-containing heterocyclic RC can be characterized by different electron transition energies and, even more importantly, radically different molar absorption coefficients in the bands that correspond to these transitions in the UV-VIS spectra (as reported earlier for the cyclopentene oxide RCs[17,18]). The quantum chemical data suggest that this ratio of discrepancy can exceed 30–40 times in the spectral region of 400–500 nm analyzed in terms of a comparison between the ring-closed DOSU RC conformers, which act as intense chromophores, and DOSU RC **2** employed to interpret the spectra of the photolysis product (poorly absorbing at $\lambda \geqslant 360$ nm). This can be an additional explanation for the stability of DOSU RC **2** upon the action of light.

Warming the sample containing DOSU RC **2**, the photolysis product, to ~145 K not only notably changed the EPR spectra but also provided a much better resolution in the spectra [Figure 3(*c*)]. This allowed us to isolate a well-resolved signal belonging to the $^{\bullet}\mathrm{CFCl_2}$ radical with the anisotropic hfc constants $a_\perp(\mathrm{F}) = 5.6$ and $a_\parallel(\mathrm{F}) = 16.2$ mT for the fluorine nucleus and $a_\perp(2\mathrm{Cl}) = 0.2$ and $a_\parallel$ (2Cl) = 1.8 mT for the chlorine nuclei (these are close to those reported earlier[16]). Additionally, the following signal components with isotropic hfc constants were isolated: $a_1(2\mathrm{H}) = 2.5$, $a_2(1\mathrm{H}) = 5.4$ and a_3(1H) ~ 0.5 mT. The EPR spectra simulated with these assumptions [Figure 3(*d*)] provided a satisfactory agreement with the experimental spectrum of the sample warmed to ~145 K [see Figure 3(*c*)]. Upon further cooling to 90 K, a five-line signal was detected in the EPR spectra with an intensity ratio of ~1 : 2 : 2 : 2 : 1 and a distance of ~2.5 mT between the lines [Figure 3(*e*)]. Despite formal resemblance between this spectrum and the difference EPR spectrum of the low-temperature radiolysis product in DOSU/$\mathrm{CF_3CCl_3}$ solutions assigned to DOSU RC **1** [see Figure 2(*c*)], we cannot assert that these spectra correspond to the same form of the DOSU RC (mainly, due to the fact that the samples containing the photolysis product in $\mathrm{CFCl_3}$ do not display a characteristic color change associated with the appearance of DOSU RC **1** upon their warming and subsequent cooling). We hypothesize that, even though the intensity ratios of their components were different for the two five-line EPR spectra detected in Freon matrices upon photolysis or photolysis plus thermally induced reaction (1 : 4 : 6 : 4 : 1 for $\mathrm{CF_3CCl_3}$ and 1 : 2 : 2 : 2 : 1 for $\mathrm{CFCl_3}$), both of the signals corresponded to the same species, the DOSU RC conformer with a terminal alkyl fragment afforded upon C–C bond cleavage at the spiro carbon atom (DOSU RC **3**). The disparities in the shapes of the EPR spectra can be attributed to varied geometries in the $-\mathrm{CH_2CH_2^{\bullet}}$ terminal alkyl groups in the RCs upon stabilization in different Freon matrices.

Thus, we can make the following conclusions on the intermediates stabilized in X-ray irradiated frozen DOSU/$\mathrm{CF_3CCl_3}$ and DOSU/$\mathrm{CFCl_3}$ solutions and their transformations. In the irradiated DOSU/$\mathrm{CF_3CCl_3}$ solutions, DOSU RC **1** was stabilized, in which spin and charge were predominantly delocalized throughout the O–C–O fragment; the UV-VIS spectra of the RC were almost identical to those of the RC derived from 1,3-dioxolane, a cyclic acetal containing an O–C–O fragment.[4] We propose distonic DOSU RC **3** with a terminal alkyl fragment as the final transformation product of DOSU RC **1** in $\mathrm{CF_3CCl_3}$. This pathway is similar to that discovered for the phototransformation of the 1,3-dioxolane RC.[4] In the irradiated DOSU/$\mathrm{CFCl_3}$ solutions, neither an absorption band in the UV-VIS spectra nor an EPR spectrum attributed to an individual ring-closed DOSU RC can be detected. We were unable to identify the intermediate formed in this process, having eliminated a series of potential candidates based on our experimental and DFT findings: namely, radical ionic pairs, DOSU RC/$\mathrm{CFCl_3}$ complexes, any available individual DOSU RC conformers and their combinations.

The DOSU RC formed upon the phototransformation of the initial irradiation product in $\mathrm{CFCl_3}$ was structurally different from DOSU RC **1** stabilized upon the irradiation of frozen DOSU/$\mathrm{CF_3CCl_3}$ solutions. Supposedly, this may have something to do with structural peculiarities in solid $\mathrm{CFCl_3}$ (however, no such data exists for $\mathrm{CF_3CCl_3}$).[19] It is likely that the phototransformation product in $\mathrm{CFCl_3}$ at 77 K is one of the ring-closed DOSU RC conformers characterized by weak absorption in the visible part of the spectrum ($\lambda \geqslant 360$ nm). DOSU RC **2** with its tetrahydropyran rings in the chair–chair conformation is the most likely candidate. In the course of an irreversible thermally induced reaction (warming and subsequent cooling), we were able to isolate the signal belonging to the $^{\bullet}\mathrm{CFCl_2}$ radical. Correspondingly, the signal associated with DOSU RC **2** transformed into the signal of distonic DOSU RC **3** with a terminal alkyl fragment identical in its structure to the photolysis product afforded by DOSU RC **1** in the CF_3CCl_3 matrix.

Thus, despite differences in the stabilization mechanisms of the paramagnetic species afforded upon irradiation and subsequent photolysis with visible light, we found that the ultimate products were identical in the two sequences of photochemical and thermally induced transformations in both matrices. Note that the final product formed upon the C–C bond cleavage at the spiro atom in the ring-closed DOSU RC was described by quantum chemical data as the most energetically stable.

The discovered matrix effect necessitates further investigation requiring the study of structurally similar heterocyclic RCs. The obtained data may suggest that traditional continuous solvent approximations in DFT calculations are unable to adequately predict the disparities in the behavior of DOSU RCs in these rather similar Freon matrices.

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