

Phototransformations of Methylsubstituted Oxiranes' Radical Cations in Freonic Matrices at 77 K¹

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Abstract—It has been established that, upon X-ray irradiation of various methyloxiranes in freonic matrices at 77 K, both open and cyclic (with the elongated C–C bond) forms of radical cations are stabilized. It has been shown that observed reversible photoinduced transformations of 2,3-dimethyloxirane and methyloxirane radical cations are related to the conversion between the open and cyclic forms of the radical cations with high quantum yields (0.02–0.39, depending on the oxirane and the matrix). For the trimethyloxirane radical cation the action of light on the *trans*-isomer of the open form results in its photoinduced transformation into a C-centered radical with low quantum efficiency ($\sim 4 \times 10^{-3}$). Tetramethyloxirane radical cations, stabilized in their open form, are resistant to the action of light. Probable causes of the observed effects are discussed. Upon the X-ray irradiation of 2,2-dimethyloxirane in freonic matrices at 77 K, a cyclic form of the radical cation is stabilized (presumably, as part of a complex with matrix molecules) which transforms into a distonic C-centered radical cation under the action of light with the quantum yield of $\sim 10^{-3}$.

Keywords: methyloxiranes, X-ray irradiation, freons, cation-radicals, photochemical reactions, mechanism, effectiveness.

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INTRODUCTION

The structure and photochemistry of radical cations (RCs) originating from small heterocycles are of significant interest since those species exhibit high lability and diversity among their reaction pathways. The authors [1–4] believed that in freonic matrices at 77 K oxirane RC's were stabilized in their open forms, formed upon the C–C bond cleavage. Stabilization of the oxirane RC's cyclic forms was deemed feasible at lower temperatures (4.2 K) in Freon-11, with open forms yielded at temperatures of 40 K and higher [3]—however, the authors did not provide any attributes (magnetic resonance parameters, optical absorption spectra) of paramagnetic centers observed at temperatures lower than 40 K. It has been discovered [4] that under the action of light in the region of 400–600 nm upon the irradiated solutions of methyloxirane and *cis*-2,3-dimethyloxirane in Freon-11 at 77 K, reversible changes in the EPR and optical absorption spectra take place, which the authors attributed to *cis-trans*-isomerization of the oxirane RCs' open forms [1–4].

The aim of our research was to investigate the nature of paramagnetic species stabilized upon the X-ray irradiation of methylsubstituted oxiranes dissolved in various freons at 77 K and to describe the mechanism of their photoinduced transformations.

EXPERIMENTAL

CFCl₃ (Freon-11, ~99%, Aldrich), CF₃CCl₃ (Freon-113a, >99% according to NMR data, synthesized from 99% Aldrich Freon-113 using a known technique [5]) were used as matrices; in certain cases freons were purified using standard procedures. Methyl-, *cis*- and *trans*-2,3-dimethyl-, 2,2-dimethyl-, trimethyl- and tetramethyloxirane (97%, Aldrich) were used as received.

The methylsubstituted oxirane/freon solutions (0.3–0.5 mol %) were inserted into quartz or SK-4B glass tubes, evacuated to ~ 0.1 Pa and irradiated at 77 K to doses of 2–4 kGy; a 5BHV6-W X-ray source (33 kVA, 80 mA) was used.

The EPR spectra of resulting paramagnetic species were recorded on a Varian E-3² spectrometer in conditions that prevented saturation and modulation broadening. The EPR spectra were simulated with the use of the PEST WinSim and Simfonia standard software packages [6], as well as the ESRCOM² package. The amount of paramagnetic centers in the samples was derived by using a CuCl₂ · 2H₂O monocrystal as a standard. The stability of detection conditions in the EPR spectrometer's resonator was controlled by a detection of an internal standard's spectrum's compo-

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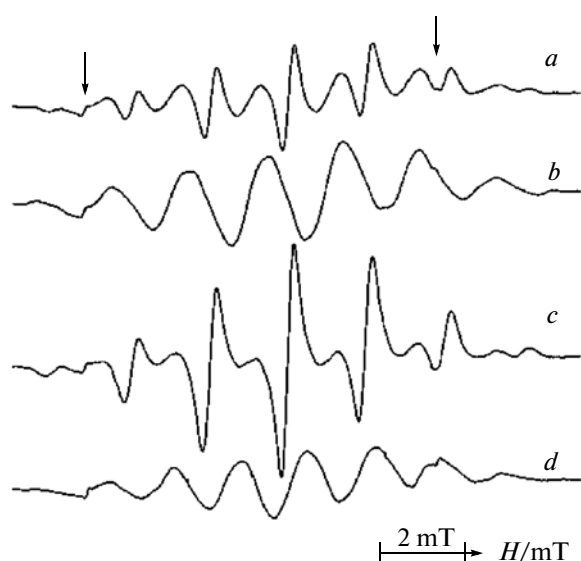


Fig. 1. EPR spectra detected in irradiated 2,3-DMO/Freon-113a solutions immediately after X-ray irradiation at 77 K (a), after the action of light with $\lambda = 578$ nm upon the irradiated sample at 77 K (b), after the action of light with $\lambda = 436$ nm upon sample b (c), after warming the samples b and c to 111 K (d). * Here and in the further EPR spectra arrows point to the second and fifth components of the hyperfine structure of the additional Mn^{2+} ions in MgO powder.

ment, simultaneously with the spectra of the studied samples (with an Al_2O_3 monocrystal, doped with Cr^{3+} ions, acting as the standard). The optical absorption spectra were measured on a Specord M-40 spectrophotometer at 77 K using flat quartz tubes with an optical path length of ~ 0.1 cm. Oscillator strength values were calculated using the following equation:

$$f \approx 4.32 \times 10^{-9} \varepsilon_{\max} \Delta\nu_{1/2},$$

where ε_{\max} is the molar absorption coefficient in the maximum of the absorption band, $\text{M}^{-1} \text{cm}^{-1}$, while $\Delta\nu_{1/2}$ is the half-width of the absorption band, cm^{-1} [7].

A high-pressure mercury lamp (DRSh-250) was used as a light source. For the extraction of the 436 nm band in the mercury spectrum, a glass filter was used ($T_{\max} = 27\%$, $\Delta\nu_{1/2} = 2400 \text{ cm}^{-1}$). For the extraction of the 546 and 578 bands, interference filters were used ($T_{\max} = 37\%$, $\Delta\nu_{1/2} = 390 \text{ cm}^{-1}$; $T_{\max} = 30\%$, $\Delta\nu_{1/2} = 297 \text{ cm}^{-1}$). The intensity of light for the bands employed constituted: 1.2×10^{-9} to 1.1×10^{-8} (436 nm), 6.0×10^{-9} (546 nm) and 2.2×10^{-9} (578 nm) Einstein $\text{cm}^{-3} \text{ s}^{-1}$. Quantum yields in photochemical reactions were derived from the decrease in the number of initial RC or the increase in the number of resulting paramagnetic species versus the light dose absorbed by the RCs. The absolute uncertainty for the determination of the intermediates' absorption coefficients and for the quantum yields of their transformations did not exceed 30%.

The density functional (DFT) quantum chemistry calculations were carried out using a PBE0 approximation [8, 9]. Expansion of the exchange-correlation density on an auxiliary basis set was used to boost the computations [10]. Valency-correlation L2 basis was used in the computations [11]. The accuracy of the self-consistency amounted to 10^{-7} atomic units (a.u.), the accuracy of the exchange-correlation density integration amounted to 10^{-9} a.u. per atom, while the geometries were optimized up to the 10^{-5} a.u. gradient norm. The computation for the charge and spin populations on atoms was carried out by representing the calculated wave function in a minimal atomic basis of a special type, orthogonalized in comply with the requirement of zero dipoles on bonds [12]. The isotropic hyperfine coupling (hfc) constants were calculated with the use of Fermi formula [13]. The PRIRODA software package was employed for all of the computations [14].

RESULTS AND DISCUSSION

2,3-dimethyloxirane. The X-ray irradiation of the frozen 0.3 mol % 2,3-dimethyloxirane (2,3-DMO) / Freon-113a solutions at 77 K results in an EPR spectrum (Fig. 1a) which can be described as a superposition of two signals consisting of nine and eight equidistant lines, respectively. The first of them, characterized by a nearly binomial pattern, may result from an unpaired electron interacting with eight magnetically equivalent protons and is described by the hfc constant of ~ 1.9 mT. According to the data acquired from quantum chemical calculations (Table 1), RCs III and IV (Fig. 2), i.e. *cis-cis-trans*- and *cis-cis-cis*-isomers of the open form, possess hfc constant values that are the closest to experimental ones (upon their averaging for each of the methyl groups)—however, in the case of RC II (Fig. 2), the *cis-trans*-isomer of the open form, the difference between experimental and calculated values is also rather small. The fitting of the second experimental signal (which consists of eight equidistant lines) is optimal with the following values for the hfc constants: a (3H) ≈ 2.1 mT, a (3H) ≈ 1.8 mT, a (1H) ≈ 1.6 mT, a (1H) < 0.1 mT (with the linewidth of ~ 0.6 mT). Those six protons with hfc constant values close to 2.1 and 1.8 mT might be attributed to the two methyl groups, while the proton with a 1.6 mT value could be associated with one of the methine groups. The hfc constant values obtained by fitting are close to those (Table 1) found in the quantum chemical computations for the cyclic *trans*-isomer of the RC with the elongated C–C bond (VI), with the exception of significant variation in the value of the hfc constant on

³ The nature of paramagnetic centers formed upon the irradiation of *cis*- and *trans*-2,3-dimethyloxirane (2,3-DMO) solutions in Freons at 77 K is identical. With regard to this, we will not specify *cis*- or *trans*-isomer further on, bearing the equivalence of the results obtained for those species in mind.

Table 1. Calculated values of the isotropic hfc constant values (mT) for the 2,3-DMO RC

RC	a (H ₆)	a (H ₇)	a (H ₈)	a (H ₉)	a (H ₁₀)	a (H ₁₁)	a (H ₁₂)	a (H ₁₃)
I	1.57	1.57	3.00	0.06	3.00	3.00	0.06	3.00
II	1.50	1.90	0.05	2.52	2.52	2.82	2.82	0.05
III	1.75	1.75	0.74	3.70	0.96	0.73	3.70	0.96
IV	1.75	1.75	0.73	0.96	3.70	0.73	0.96	3.70
V	1.11	1.11	1.56	0.39	3.36	1.56	3.36	0.39
VI	1.16	0.09	1.47	4.19	0.49	1.28	4.39	0.17
VII	2.91	2.91	0.68	0.13	0.05	0.68	0.13	0.05

the methine proton H₆ (Fig. 2). It should be noted that the hfc constant values calculated for the cyclic *cis*-isomer with the elongated C–C bond (V) as well as those calculated for the cyclic *trans*-isomer of the RC with a shortened C–C bond (VII) (Fig. 2) notably diverge from those obtained experimentally.

In the optical absorption spectrum of the samples irradiated at 77 K, induced absorption bands arise in the region of $\lambda > 380$ nm. After standard photobleach-

ing of the ionic products of the matrix's irradiation, for which light with $\lambda > 690$ nm [15] is employed, the action of light with $\lambda = 578$ nm at 77 K leads to an almost complete transformation in the EPR spectrum: the nine-line spectrum is converted into an eight-line spectrum with the total amount of paramagnetic species remaining virtually unchanged (Fig. 1b).

At the same time, an absorption band at 575 nm in the optical spectra disappears, while the intensity of a

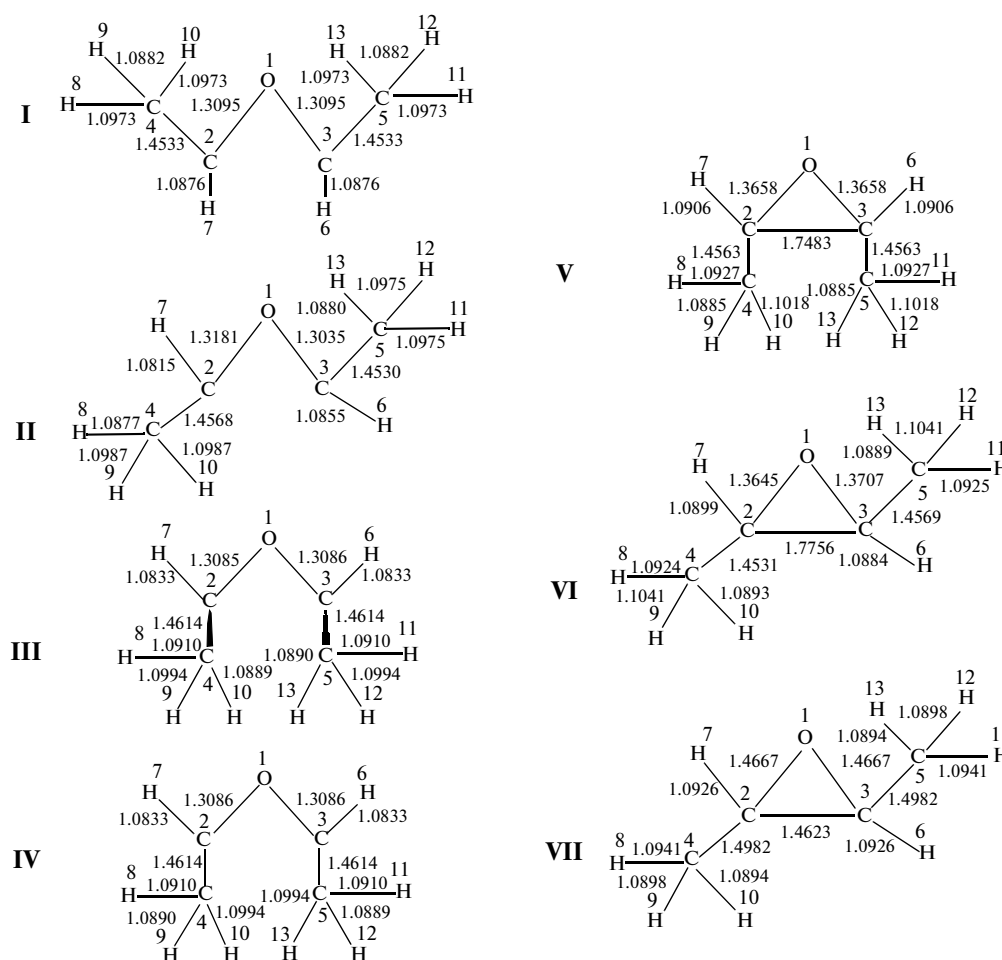


Fig. 2. The structures of the 2,3-DMO RC's cyclic and open form (I–VII) which are yielded in the irradiated 2,3-DMO/freon solutions (the bond lengths are indicated in nm).

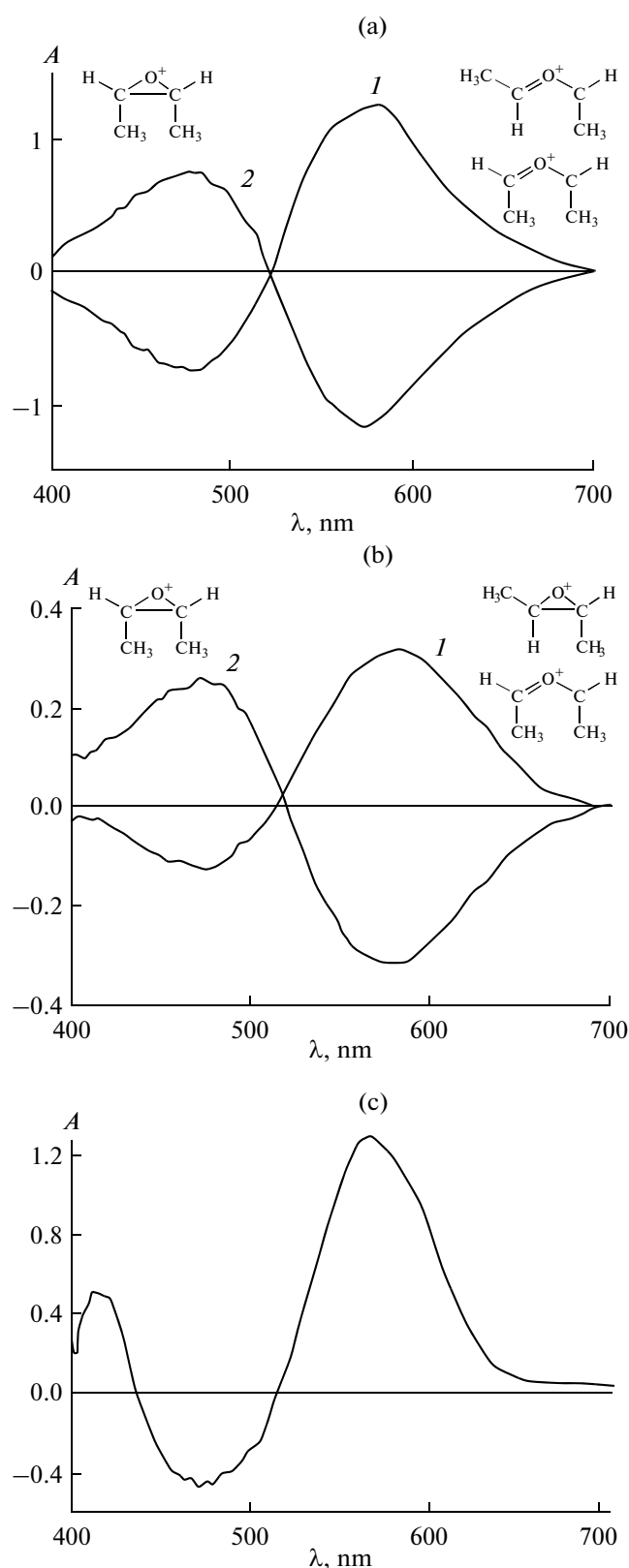


Fig. 3. Difference optical absorption spectra, detected upon the action of light with $\lambda = 578$ (1) and 436 (2) nm upon the irradiated 2,3-DMO/Freon-113a (a) and 2,3-DMO/Freon-11 (b) solutions at 77 K, after the thermally induced transformations of the 2,3-DMO RC's open form in Freon-113a at 111 K (c).

band at 465 nm increases (Fig. 3a). The subsequent action of light with $\lambda = 436$ nm at 77 K results in a reverse process, as confirmed by the changes in both EPR (Fig. 1c) and optical absorption spectra (Fig. 3a). These mutual transformations can be carried out repeatedly since the loss in the integral intensity of the EPR spectra and the corresponding decrease of the absorption band intensity in the optical spectra do not exceed 10% within a reaction cycle.

A comparison of the variations in the EPR and optical spectra taking place upon the action of light with $\lambda = 578$ and 436 nm made it possible to estimate the absorption coefficients for the species involved in the transformations: $\varepsilon_{578} \approx 5.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ($f \approx 0.56$) and $\varepsilon_{436} \approx 2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ($f \approx 0.30$), respectively. On the basis of published [4] and our own quantum chemical data, *cis*- and *trans*-isomers of the 2,3-DMO's open form (I–IV) (Fig. 2) should possess similar optical absorption spectra and magnetic resonance parameters (Table 1), which cannot account for the reversible changes in the EPR spectra observed experimentally. That is the reason why we, in contrast to our colleagues [4], do not associate the observed photochemical transformations of the 2,3-DMO RC with the conversion between the *cis*- and *trans*-isomers of the ring-open form.

Obtained experimental data leads us to believe that the nine-line EPR spectrum ($a(8H) = 1.9$ mT) and the 575 nm absorption band are associated with the open form of the 2,3-DMO RC, which is isoelectronic to the allyl radical and results from the C–C bond cleavage. This species may exist both in *cis*- and *trans*-configurations (*cis-cis-cis*-, *cis-cis-trans*- and *cis-trans-trans*-isomers of the RC (Table 1, Fig. 2), characterized by sets of hfc constants close to those required). We associate the eight-line EPR spectrum, characterized by the splitting of 1.9 mT, and the absorption band at 465 nm, with the 2,3-DMO RC in its cyclic form. This interpretation is based on the results of quantum chemical calculations (Table 1), which show that such hfc constants are revealed for the RC's *trans*-isomer (VI) (Fig. 2) with the elongated C–C bond (~ 0.178 nm). We do not regard the difference in the values of the constants, observed for one of the methine protons and amounting to 0.4 mT, as significant.

The feasibility of a cyclic RC's formation upon X-ray irradiation (including the notion of an elongated C–C bond) had been discussed earlier [16]—however, it should be noted that photoinduced cyclization of a ring-open RC originating from a member of oxirane's homologous series was observed here for the first time. The experimental optical absorption spectrum of 2,3-DMO RC's cyclic form's *trans*-isomer was revealed to resemble trimethylene oxide RC's spectrum, detected in freonic matrices at 77 K and exhibiting an absorption maximum at 450 nm [17].

The quantum yields of the open (II–IV) and cyclic (VI) RC's photochemical transformations, derived from the linear initial sections of concentration versus

the light dose absorbed dependencies, were found to be quite high: ~ 0.39 in the case of light with $\lambda = 578$ nm and ~ 0.07 in the case of light with $\lambda = 436$ nm at 77 K.

The warming of the samples with stabilized 2,3-DMO RCs (77–111 K) leads to the conversion of the eight-line EPR spectrum with the splittings of 1.9 mT (Fig. 1b) to a nine-line spectrum with splittings of ~ 1.7 mT (Fig. 1d). Those transformations are reversible upon subsequent lowering of the temperature to 77 K and are, most likely, associated with the dynamics of intramolecular motions in the RC's *trans*-isomer with the elongated C–C bond, which is manifested in the increase of a hfc constant on one of the methine protons. It is curious that warming of the samples with the open form of the 2,3-DMO RC stabilized (77–111 K) also leads to the conversion of the nine-line EPR spectrum with the splittings of 1.9 mT (Fig. 1c) to a nine-line EPR spectrum with splittings of ~ 1.7 mT (Fig. 1d). The lowering of the temperature causes a change that is opposite to the one described above. Since this change is accompanied by an alteration in the sample's optical absorption spectrum, where the band with the maximum at 575 nm perishes (meanwhile, the decay of the band in the region of 380–390 nm is associated with the demise of freonic centers [15, 18]) and the intensity of the 465 nm band rises (Fig. 3c), we conclude that the observed process may be attributed to the cyclization of the 2,3-DMO RC's open form. Thus, an insignificant rise in temperature results in a cyclization reaction taking place for the 2,3-DMO RC in the Freon-113a matrix. It should be noted that even though cyclization reactions are characteristic of allyl radicals, which are isoelectronic to the discussed RC [19–21], upon their photoexcitation, a thermally induced cyclization reaction taking place for RCs seems unusual and requires further investigation. Tentatively, it may be associated with specific solvation of the RC's cyclic form as compared to the open form, which is determined by the difference in their geometry and the change in the spatial localization of the charges (Fig. 2).

The X-ray irradiation of the frozen 0.3 mol % 2,3-DMO/Freon-11 solutions at 77 K results in a complicated EPR spectrum (Fig. 4a), while, in the optical absorption spectrum, an induced absorption band arises in the region of $\lambda > 380$ nm at 77 K. After using the photobleaching procedure mentioned earlier to eliminate the ionic products of matrix irradiation, the action of light with $\lambda = 578$ nm at 77 K results in an almost complete conversion of the signal initially observed in the EPR spectrum to an eight-line spectrum with splittings of ~ 1.9 mT, while the total amount of paramagnetic species remains virtually unchanged (Fig. 4b).

At the same time, an absorption band at 575 nm in the optical spectra disappears, while the intensity of a band at 470 nm increases (Fig. 3b). The subsequent action of light with $\lambda = 436$ nm at 77 K results in a reverse process, as confirmed by the changes in both

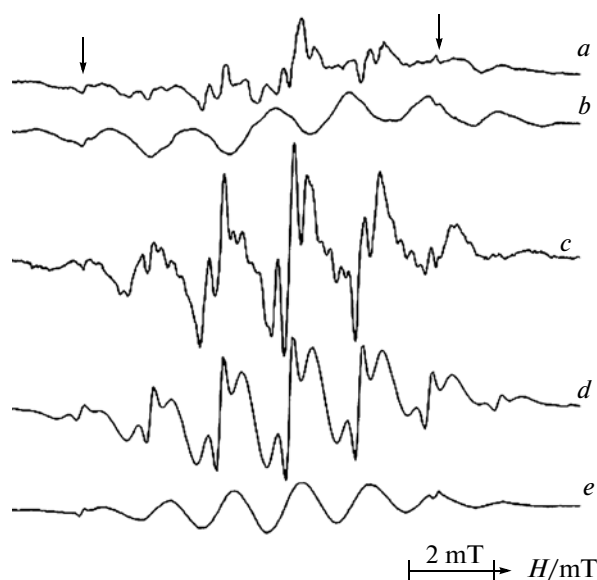


Fig. 4. EPR spectra detected in irradiated 2,3-DMO/Freon-11 solutions immediately after X-ray irradiation at 77 K (a), after the action of light with $\lambda = 578$ nm upon the irradiated sample at 77 K (b), after the action of light with $\lambda = 436$ nm upon sample b (c), fitting results for spectrum c (d), upon heating the samples b and c to 90 K (e).

EPR (Fig. 4c) and optical absorption spectra (Fig. 3b). Those mutual transformations can be carried out repeatedly, as in the case of the Freon-113a matrix mentioned above. We should note that, in contrast to the Freon-113a matrix, in the Freon-11 matrix the eight-line signal with ~ 1.9 mT splittings transforms into a spectrum (Fig. 4c) that can be successfully fitted as a superposition of two signals. The former, while characterized by a linewidth of ~ 0.55 mT and hfc constant values of a $(8H) \approx 1.7$ mT, exhibits additional interaction with a nucleus possessing a spin of 0.5 and a hfc constant of ~ 0.7 mT (around 90% of integral intensity); in the latter, hfc constants amount to a $(8H) \approx 1.7$ mT and the linewidth is ~ 0.2 mT (approximately 10% of integral intensity) (Fig. 4d). Since it is acknowledged [22] that small additional splittings on fluorine atoms (0.5–1.0 mT) can be observed for the matrices of freons in EPR spectra, accounting for the RC-matrix molecule interactions, we can attribute the additional splitting in the first signal to that effect. We ascribe the second signal to the RC that exhibit weak interactions with the matrix and are, most probably, located in the defective regions of the polycrystalline Freon-11 matrix. The absorption spectrum of the yielded paramagnetic species (Fig. 3b, absorption band with maximum at 575 nm) leaves no doubts about ascribing it to the ring-open form of the 2,3-DMO RC.

A comparison of the variations in the EPR and optical spectra taking place upon the action of light with $\lambda = 578$ and 436 nm made it possible to estimate the absorption coefficients for the species involved in the transformations: $\epsilon_{578} \approx 6.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and

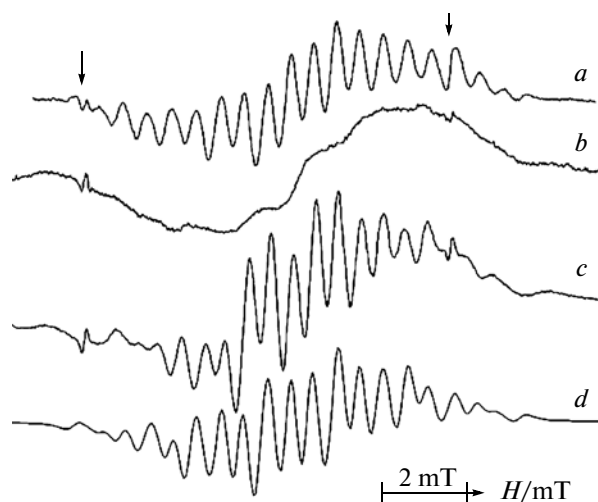


Fig. 5. EPR spectra* detected in irradiated 2,2-DMO/Freon-11 solutions at 77 K (a), in 2,2-DMO/Freon-113a solutions at 77 K (b), upon warming to 140 K (c), fitting results ($a(4H) = 1.63$ mT, $a(3H) = 1.13$ mT, $a(F) = 0.67$ mT) for the spectrum observed in Freon-11 at 77 K (d). *Spectra presented after the deduction of EPR signals pertaining to the matrix radicals.

$\epsilon_{436} \approx 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which is close to the values revealed for the Freon-113a matrix.

As in the case of the Freon-113a matrix, we ascribed the observed EPR and optical absorption spectra to the open and cyclic forms of the 2,3-DMO RC. The warming of the samples with the open form of the 2,3-DMO RCs stabilized in the freonic matrix (77–90 K) leads to a transformation of the corresponding EPR spectrum (Fig. 4c) into a nine-line signal with a $(8H) = 1.7$ mT (Fig. 4e). The lowering of the temperature to 77 K results in the conversion of the nine-line EPR spectrum with splittings of ~ 1.7 mT into an eight-line spectrum with a splitting of 1.9 mT (Fig. 4b), as described above. The changes that proceed in the EPR spectra and correlate with temperature changes may be explained by specific dynamics of intramolecular motions, as in the case of Freon-113a.

2,2-dimethyloxirane. The X-ray irradiation of the frozen 0.5 mol % 2,2-dimethyloxirane (2,2-DMO)/Freon-11 solutions at 77 K results in a well-resolved multiplet signal (Fig. 5a) with at least 20 practically equidistant lines in the EPR spectrum (the splitting amounts to 0.65–0.7 mT). In the sample's optical absorption

spectrum, a wide absorption band with the maximum located at $\lambda = 435\text{--}440$ nm ($\epsilon_{436} \approx 7.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, $f \approx 0.19$) arises (Fig. 6a)—which is characteristic of ether RCs, including cyclic ones ($\lambda_{\text{max}} \approx 430\text{--}450$ nm, $f \approx 0.1$) [17, 23, 24]. In irradiated 2,2-DMO/Freon-113a solutions at 77 K, an absorption band also arises, with its maximum located in the region of 425 nm ($\epsilon_{436} \approx 1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $f \approx 0.25$). However, only a poorly resolved signal is detected in the EPR spectrum in this case (Fig. 5b), while warming the sample to 111 K reveals hyperfine structure—which proves to be of multiplet nature at 140 K, closely resembling the one detected in the Freon-11 matrix: we observed practically equidistant lines with the splitting of ~ 0.6 mT (Fig. 5c). Those transformations are reversed upon subsequent cooling to 77 K. These experimental observations lead us to conclude that the paramagnetic species yielded upon irradiation in studied freons are identical.

As the analysis of computations shows (Table 2), such EPR spectra cannot be accounted for by the ring-open form of the 2,2-DMO RC **VIII** (Fig. 7), formed upon C–C bond cleavage. The C–O bond cleavage would have led to an RO-type radical; such species are characterized by large hfc constants with β -protons (more than 5 mT [25, 26]), which, obviously, do not agree with the experimental EPR spectrum as well. Meanwhile, cyclic form **IX** (Fig. 7) with the elongated C–C bond (~ 0.179 nm), assuming averaging for hfc constants with protons in every methyl group, possesses the following set of constants (Table 2): a $(4H) \approx 1.6$ mT, a $(3H) \approx 1.2$ mT, a $(1H) < 0.1$ mT. This set can be used as a starting point in the fitting of the experimental spectrum, but only if we assume an additional splitting (~ 0.6 mT) on one of the methylene group's protons: a $(4H) \approx 1.6$ mT, a $(3H) \approx 1.1$ mT, a $(1H) = 0.6$ mT (Fig. 5d). As computations showed (Table 2), a slight deviation of the optimal calculated geometry **IX** to form **IXa** (namely, the methylene's group rotation of ~ 8 degrees with the corresponding change in energy amounting to no more than 0.8 kJ/mol) results in the increase of up to 0.7 mT for the second methylene proton hfc constant, while the other hfc constants change insignificantly. A small change in energy upon the distortion of geometry allows us to suggest stabilization of the deformed cyclic RC by means of RC-matrix interaction.

Alternatively, the matrix effect may be associated with the formation of a π -complex, yielded by form **IX**

Table 2. Calculated values of the isotropic hfc constant values (mT) for the 2,2-DMO RC

RC	$a(H_0)$	$a(H_7)$	$a(H_8)$	$a(H_9)$	$a(H_{10})$	$a(H_{11})$	$a(H_{12})$	$a(H_{13})$
VIII	2.22	2.32	0.02	1.09	1.09	1.89	0.03	1.89
IX	0.08	1.57	1.02	0.52	3.22	0.84	2.81	0.03
IXa	0.68	1.58	0.96	0.49	3.36	1.08	3.26	0.03
X	3.89	3.89	0.84	0.10	0.08	0.84	0.08	0.10

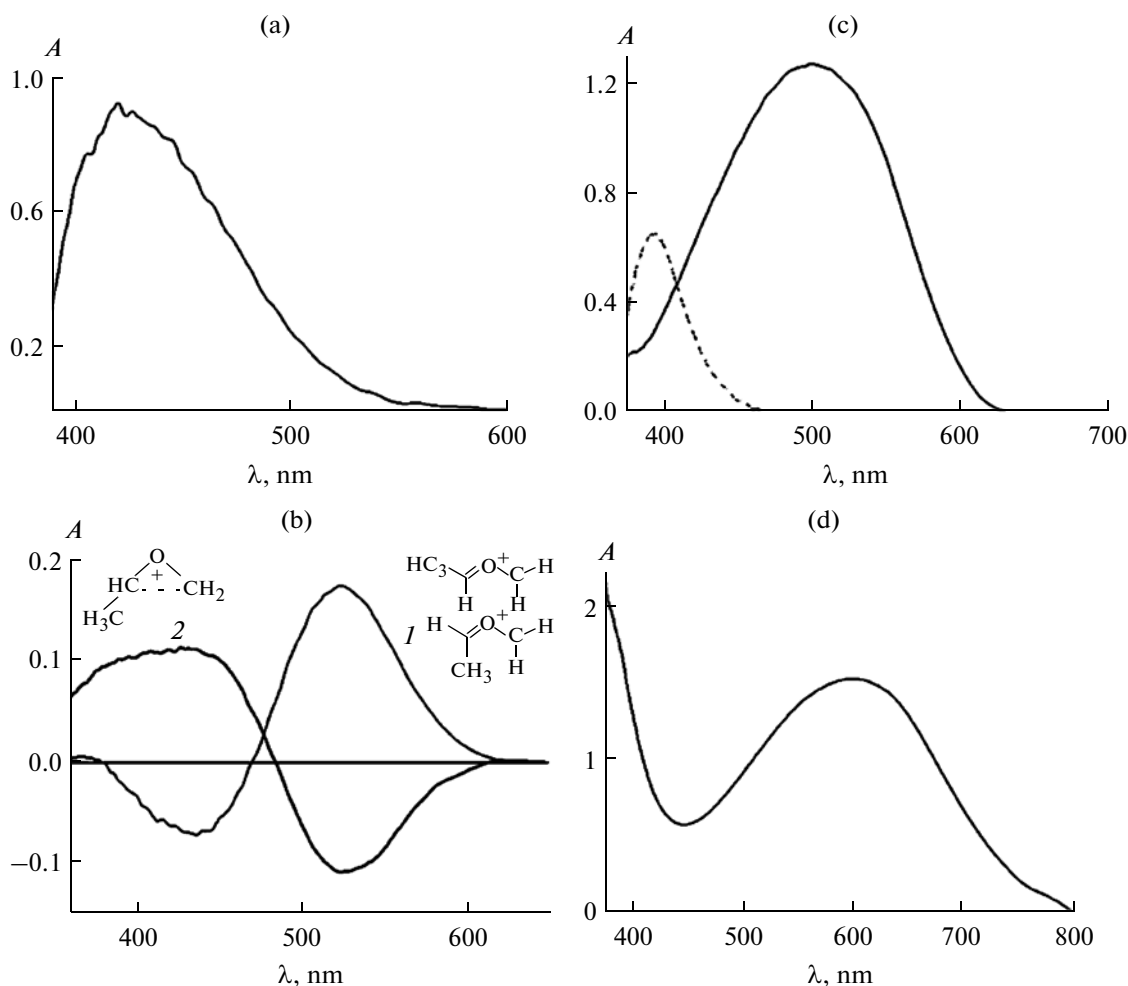


Fig. 6. Difference optical absorption spectra, detected at 77 K after the action of light with $\lambda = 436$ nm upon the irradiated 2,2-DMO/Freon-113a solutions (a), after the action of light with $\lambda = 546$ (1) and 436 (2) nm upon the irradiated MO/Freon-11 solutions (b), for trimethyloxirane/Freon-113a solutions (c), the band attributed to freonic centers and perishing upon warming the samples to 111 K shown with a dotted line, and the induced absorption spectra arising after the irradiation of tetramethyloxirane/Freon-113a solutions (d).

(Fig. 7) and a Freon-11 molecule, which results in additional hyperfine interaction with a fluorine nucleus. As mentioned above, the formation of such complexes, characterized by relatively small hfc constants on fluorine nuclei, had been reported earlier [22]. We have no grounds for making an unequivocal choice between those two attributions—however, we should emphasize that, in both cases, we are dealing with a cyclic form of the RC with the elongated C–C bond. Further on, when discussing the transformations of the 2,2-DMO RC in freons, we will employ this term alluding to any of the two possible variants for the stabilization of the RC's cyclic form with the elongated C–C bond. As for the EPR spectrum observed in irradiated 2,2-DMO/Freon-113a solutions, poorly resolved at 77 K, it can also be attributed to a π -complex with a matrix molecule. However, in this instance, a significant broadening of the spectral lines (Fig. 5b) has to be taken into account—which,

presumably, can be associated with variations in the RC dynamics for different freonic matrices.

A comparison of calculated sets of hfc constants (Table 2) to those obtained by fitting the experimental EPR spectra of the irradiated 2,2-DMO/freon solutions leads us to conclude that there are no signals in the experimental spectra that can be ascribed to the cyclic RC form X with a shortened C–C bond (Fig. 7).

The maximum in the absorption spectrum of 2,2-DMO's primary radiolysis products in Freon-113a (Fig. 6a) is somewhat blue-shifted, as compared to that of the cyclic form of the 2,3-DMO RC in the same matrix. ($\lambda_{\text{max}} = 425\text{--}440$ nm for the 2,2-DMO RC and 465 nm in the case of the 2,3-DMO RC).

The action of light with $\lambda = 436$ nm at 77 K in Freon-11 and -113a results in the 2,2-DMO RC's transformation into a paramagnetic species characterized in the EPR spectrum by a triplet of septets: a (6H) ≈ 0.6 mT and a (2H) ≈ 1.9 mT (Fig. 8a). The best-fit sim-

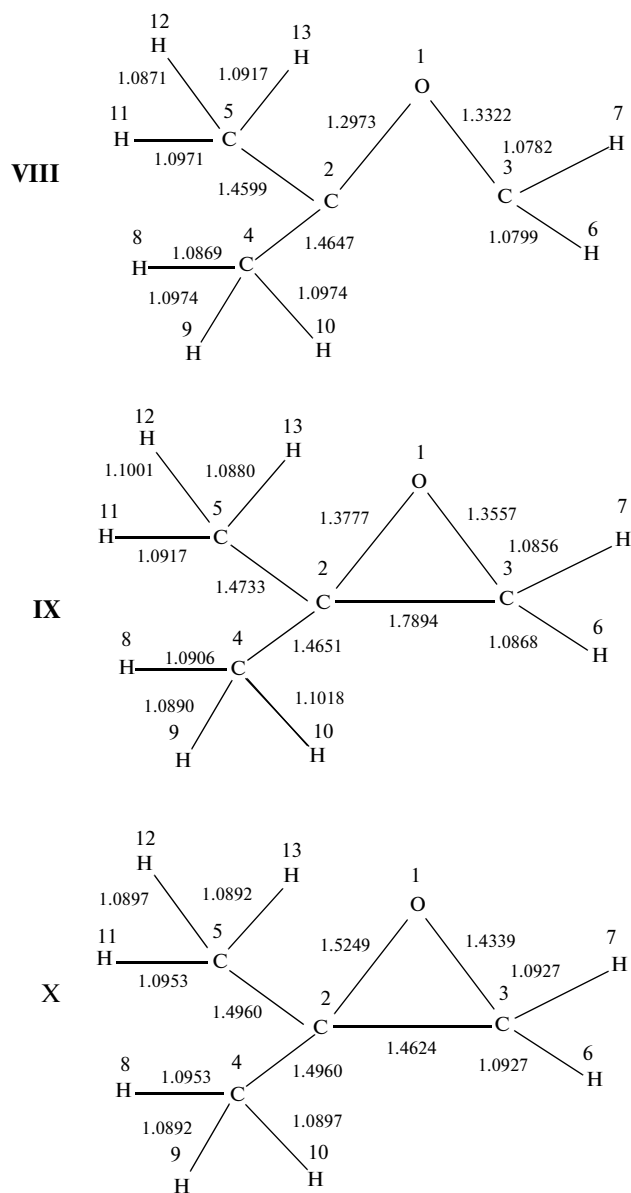


Fig. 7. The structures of the 2,2-DMO RC (VIII–X) which are yielded in the irradiated 2,2-DMO/Freon solutions (the bond lengths are indicated in nm).

ulation for the experimental EPR spectrum (Fig. 8b) suggests the following set of hfc constants: a (6H) = 0.58 mT, a (1H) = 1.85 mT, a (1H) = 1.96 mT.

Correspondingly, the action of light leads to the decay of radiolytically induced optical absorption in the region of $\lambda > 380$ nm (namely, the band with the maximum in the region of $\lambda = 425$ – 440 nm). Photolytically yielded paramagnetic species do not undergo any transformations upon warming, up until their perishing. Experimental data suggest that the photolysis product is a C-centered radical, with both of its methyl groups notably intact. We conclude that this species is a distonic RC, yielded from a cyclic 2,2-DMO RC with the elongated C–C bond. Unfortu-

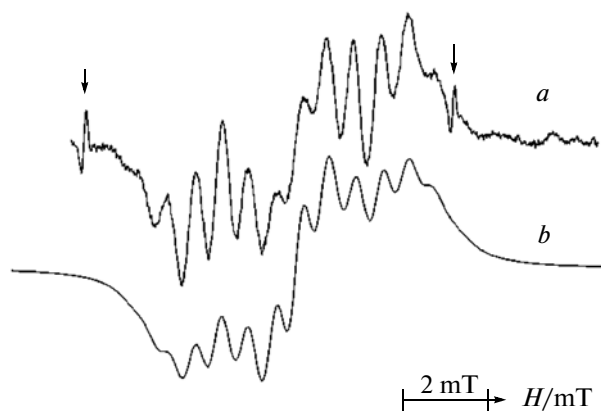


Fig. 8. EPR spectra detected in irradiated 2,2-DMO/freon solutions after photolysis ($\lambda = 436$ nm) at 77 K (a) and the fitting result (the parameters are quoted in the text) for the photolysis product's EPR spectrum (b).

nately, the EPR spectrum corresponding to the photolysis product cannot be fitted adequately with the use of hfc constants obtained for the ring-open RC form VIII (Table 2), since the calculated values for one of the methyl group's protons appear to be significantly higher than needed. This may be ascribed either to overestimation of the spin density delocalization in the DFT computations or to structural distortions owing to strong interactions with the matrix.

The quantum yield of the reaction occurring upon photolysis at $\lambda = 436$ nm is estimated at around 0.001. This value is notably lower than those estimated for the phototransformations of the 2,3-dimethyloxirane RC's cyclic form occurring in the same spectral region (~ 0.07 in the Freon-113a matrix and ~ 0.03 in the Freon-11 matrix), as well as for the transformations of the cyclic trimethylene oxide RC [17], where it amounts to ~ 0.4 – 0.5 .

Methyloxirane. The X-ray irradiation of the frozen 0.3 mol % methyloxirane (MO)/Freon-113a solutions at 77 K results in a poorly resolved EPR spectrum (Fig. 9a). Correspondingly, in the samples' optical absorption spectrum, induced absorption bands arise in the region of $\lambda > 380$ nm. After the elimination of ionic products yielded by the irradiation of the matrix, the subsequent action of light with $\lambda = 546$ nm at 77 K results in an almost complete transformation of the poorly resolved signal into a doublet of quintets in the EPR spectrum with the total amount of paramagnetic species in the sample remaining virtually unchanged (Fig. 9b).

At the same time, in the optical absorption spectra, the intensity of the band with its maximum at 530 nm decreases, while the intensity of the band with its maximum at 435 nm increases (Fig. 6b, I). We mentioned earlier that the bands with maxima in the range of 420–480 nm are typical for ether RCs. That is the reason why we can suggest that the species associated with such an EPR spectrum, as well as an absorption band

with its maximum at 435 nm, is one of the RC's cyclic forms. When employing the calculated hfc constant set (Table 3) of the cyclic RC form **XIII** with the elongated C–C bond (Fig. 10) as initial parameters for fitting the experimental spectrum optimally (assuming the absence of averaging for the hfc constants on the methyl group protons), the best agreement between the experimental (Fig. 9b) and best-fit (Fig. 9c) EPR spectra is achieved with the use of the following set: methyl group—a (1H) \approx 2.91, a (1H) \approx 2.14, a (1H) \approx 0.28 mT; methine group—a (1H) \approx 1.26 mT; methylene group—a (1H) \approx 1.00 and a (1H) \approx 1.15 mT. The values for the optimized hfc constants that we associate with the methylene group protons are lower than those obtained in computations by 0.4–0.6 mT—but this kind of disparity, as we have already mentioned, is not critical in evaluations of this type. The employment of the hfc constant set that characterizes the cyclic RC form **XIV** with the shortened C–C in the cycle (Fig. 10) does not allow us to fit the experimental EPR spectrum.

The subsequent action of light with $\lambda = 436$ nm at 77 K provokes a reverse process, detected by changes in the EPR spectra (Fig. 9d), as well as in optical absorption spectra (Fig. 6b, 2). Those mutual transformations are reproducible, as in the case of the 2,3-DMO RC. By comparing the changes taking place under the action of light with $\lambda = 546$ and 436 nm in the EPR and optical absorption spectra, we estimated the absorption coefficients of the mutually transforming species which amounted to $\epsilon_{546} \approx 3.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{436} \approx 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The species formed upon the photolysis employing light with $\lambda = 436$ nm possesses a band with a maximum at 530 nm. Similarly to the 2,3-DMO RC, the position of the maximum in the absorption band lets us assume that this species may be represented by one of the isomers of the MO RC's open form. The employment of the hfc constant sets, calculated for the open form of the MO RC, to optimally fit the EPR spectrum leads to the best agreement between the experimental (Fig. 9d) and fitted (Fig. 9e) EPR spectra with the following values for the hfc constants on protons: a (3H) \approx 1.07, a (1H) \approx 2.17, a (1H) \approx 1.29, a (1H) \approx 1.76 mT. The comparison of the fitting data and quantum chemical calculations shows that, with great likelihood, this signal can be ascribed to the *cis*-isomer of the RC's open form **XII** (Table 3, Fig. 10). The employment of hfc constant values, calculated for the MO RC's open form's *trans*-isomer **XI** (Fig. 10) demonstrates that its EPR spectrum has some notable differences as compared to the *cis*-isomer's spectrum. This allows us to at least hypothesize about the prevalent formation of the MO RC's open form's *cis*-isomer (**XII**) upon the photolysis of the RC's cyclic form with the elongated C–C bond (**XIII**).

The EPR spectrum detected after the action of light with $\lambda = 436$ nm upon MO RC in their cyclic form is better resolved in comparison to the spectrum

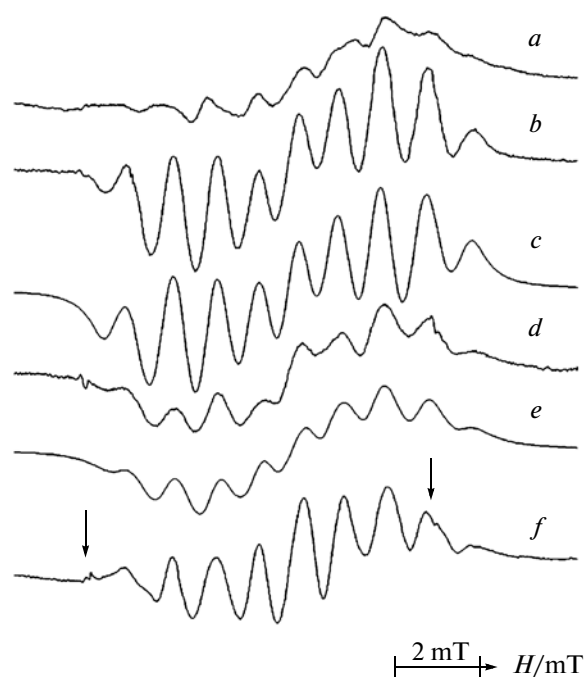


Fig. 9. EPR spectra detected in irradiated methyloxirane/Freon-113a solutions immediately after X-ray irradiation at 77 K (a), after the action of light with $\lambda = 546$ nm upon the irradiated sample at 77 K (b), the fitting result (the parameters are quoted in the text) for spectrum b (c), after the action of light with $\lambda = 436$ nm upon sample b (d), the fitting results (the parameters are quoted in the text) for spectrum d (e), upon warming sample d to 111 K (f).

detected immediately after the action of ionizing radiation (Fig. 9c)—supposedly due to the signal that we attributed to the cyclic form of RC **XIII** being present in it to a lesser degree.

The processes taking place upon the action of light with 546 and 436 nm on the MO RCs stabilized in the matrix of Freon-11 are analogous to those discussed above for the matrix of Freon-113a. The difference for the EPR spectra observed in this matrix (in contrast to the Freon-113a matrix) is the far higher resolution—both after the X-ray irradiation and upon subsequent action of light on the cyclic form of the MO RC.

Trimethyloxirane. In the optical absorption spectra, induced upon the irradiation of 0.3% trimethyloxirane (3MO)/Freon-113a solutions at 77 K, two bands with maxima at 500 and \sim 390 nm can be singled out

Table 3. Calculated values of the isotropic hfc constant values (mT) for the MO RC

RC	a (H ₅)	a (H ₆)	a (H ₇)	a (H ₈)	a (H ₉)	a (H ₁₀)
XI	2.27	2.38	0.04	2.38	1.12	2.08
XII	2.11	0.03	1.92	1.92	1.49	1.99
XIII	1.26	3.23	0.28	2.00	1.78	1.40
XIV	4.38	1.16	0.03	0.1	3.29	2.69

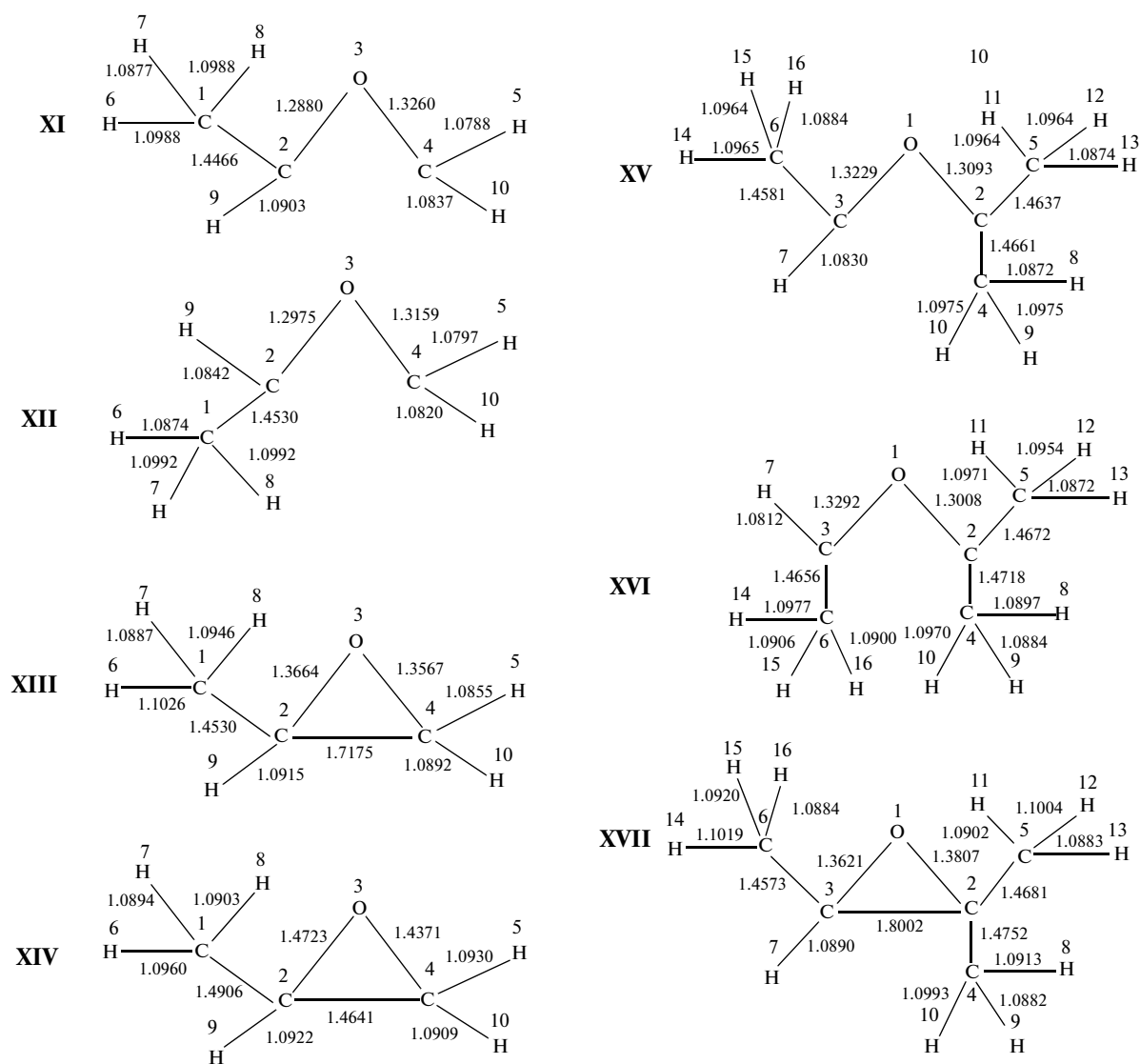


Fig. 10. The structures of the methyloxirane RC (XI–XIV) and trimethyloxirane RC (XV–XVII), which are yielded in the irradiated solutions of methyl- and trimethyloxirane in freons (the bond lengths are indicated in nm).

(Fig. 6c). The band with the maximum at ~ 390 nm perishes upon warming the sample to 111 K, while the EPR spectrum remains virtually intact. Based on that knowledge, the disappearing band may be ascribed to the freonic centers, stabilized in that matrix upon radiolysis and characterized by an absorption maximum in the region of 365–390 nm [15, 18]. The absorption band with the maximum at 500 nm, by analogy to the exam-

ples of the MO and 2,3-DMO RC discussed earlier, was attributed to the ring-open form of the 3MO RC.

The X-ray irradiation of frozen 0.3 mol % 3MO/Freon-113a solutions at 77 K results in an even signal in the EPR spectrum, composed of no less than twelve lines (Fig. 11a)—which, upon warming to 111 K, transforms into an odd signal composed of no less than 17 lines (Fig. 11c) with smaller splittings (while the

Table 4. Calculated values of the isotropic hfc constant values (mT) for the trimethyloxirane RC

RC	a (H ₇)	a (H ₈)	a (H ₉)	a (H ₁₀)	a (H ₁₁)	a (H ₁₂)	a (H ₁₃)	a (H ₁₄)	a (H ₁₅)	a (H ₁₆)
XV	1.84	0.03	1.54	1.54	2.35	2.35	0.05	3.27	3.27	0.07
XVI	2.08	0.37	0.69	2.32	2.32	1.74	0.07	4.23	0.67	1.47
XVII	0.27	0.84	0.02	2.94	0.91	3.18	0.51	3.44	1.41	0.39

total width of the spectrum stays the same). Upon cooling from 111 to 77 K the original structure of the spectrum is restored. The observed reversibility of the changes in the EPR spectra upon changes in temperature lets us attribute them to the internal motion dynamics in the 3MO RC. The results of the quantum chemical computations (Fig. 10, Table 4) show that, among the hfc constants calculated for *trans*- and *cis*-isomers of the RC's open form (XV and XVI, respectively), only the set for the *trans*-isomer ensures satisfactory agreement with the sets describing the optimized fitted spectra—which allow to characterize this species' experimental spectra (Fig. 11a, c) at various temperatures: 77 K, “restrained” motion of the methyl groups— $a(1H) = 1.27$ mT, $a(2H) = 3.45$ mT, $a(2H) = 2.24$ mT, $a(2H) = 1.27$ mT (Fig. 11b); 111 K, free rotation of the methyl groups— $a(1H) = 1.46$ mT, $a(3H) = 2.23$ mT, $a(3H) = 1.46$ mT, $a(3H) = 0.79$ mT (Fig. 11d). The calculations of the hfc constants as well as the low-temperature UV-spectroscopy data allow us to conclude that we cannot detect the cyclic 3MO RC form with the elongated C–C bond (XVII, Fig. 10) immediately after irradiation.

The action of light with $\lambda = 436$ nm upon the irradiated 3MO/Freon-113a solutions at 77 K (the samples were kept at 111 K in preparation) results in the optical absorption band with the maximum at 500 nm perishing, while a triplet with a splitting of 2.2–2.3 mT (Fig. 11e) arises in the EPR spectra. The observed hfc constant value and the absence of optical absorption in the region of $\lambda \geq 360$ nm lead us to believe that this signal may be attributed to a C-centered radical. The results of the quantum chemical calculations for the hfc constants of various distonic RCs and radicals which can be hypothetically formed from 3MO show that, with greatest likelihood, the species in question are radicals of the following structure: $(CH_2)C(CH_3)OCHCH_3$ ($a(2H) \approx 2.3$ – 2.4 mT). It is important to note that the action of light with $\lambda \geq 480$ nm, which covers practically the whole absorption band of the trimethyloxirane RC's open form, does not provoke change in the EPR and optical absorption spectra. This experimental result makes us consider the process described above to be photoinduced, as compared to direct photochemical reactions observed for the previously discussed RCs of methyloxiranes. Most likely, it proceeds to form a non-relaxed RC state which is populated only when photons carrying high energy are used. Comparing the changes taking place under the action of light with $\lambda = 436$ nm in the EPR and optical absorption spectra, we managed to estimate the 3MO RC's open form's absorption coefficient which amounted to $\epsilon_{436} \approx 4 \times 10^3$ M⁻¹ cm⁻¹. The efficiency of this process amounted to ~ 0.004 when related to the light with $\lambda = 436$ nm as absorbed by the trimethyloxirane RC.

The EPR spectrum detected upon the irradiation of 3MO/F-11 solutions at 77 K is characterized by a substantial angular dependence which complicates the analysis. However, the sample's coloration and the

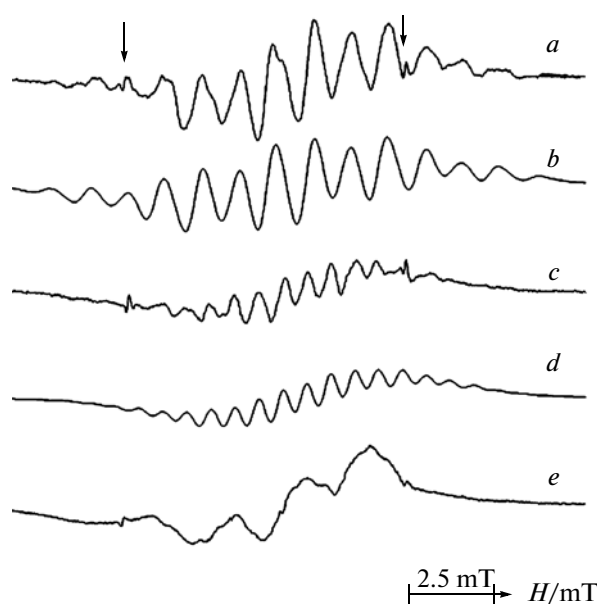


Fig. 11. EPR spectra detected in irradiated trimethyloxirane/Freon-113a solutions after X-ray irradiation and the action of light with $\lambda > 500$ nm at 77 K (a), the fitting results for spectrum a (b), upon warming sample a to 111 K (c), the fitting results for spectrum c (d), after the action of light with $\lambda = 436$ nm upon sample a (e). The fitting parameters are quoted in the text.

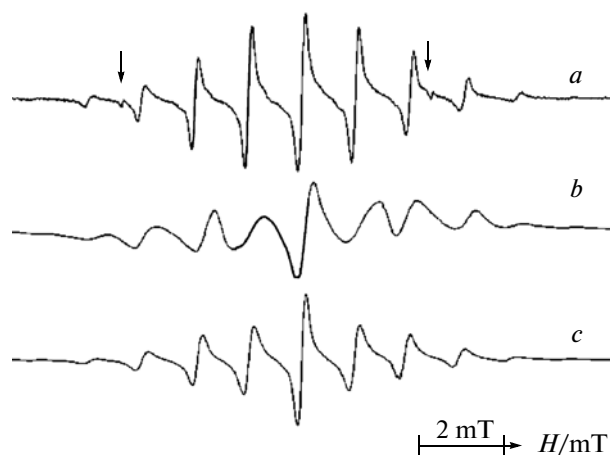


Fig. 12. EPR spectra detected in irradiated tetramethyloxirane solutions immediately after X-ray irradiation in Freon-11 at 77 K (a), in Freon-113a at 77 (b) and 155 K (c).

similar nature of the photoinduced process (the basic splittings in the product's EPR spectrum for Freon-11 are very close to those found for the transformation in Freon-113a) let us conclude that the nature of the RCs stabilized upon irradiation, as well as the nature of their reactions, is identical for those two matrices.

Tetramethyloxirane. The X-ray irradiation of the 0.5 mol % tetramethyloxirane (4MO)/Freon-11 solutions at 77 K results in a well-resolved multiplet signal

Table 5. The position of the maxima in the optical absorption spectra of the open and cyclic forms of RCs originating from methyloxiranes

RC	λ_{\max} , nm		Values for the spin population ρ_Z for the Z atoms of RC*
	Open form	Cyclic form	
Tetramethyloxirane	590	—	XVIII (O ₁ ; C ₂ ; C ₃) -0.122; 0.522; 0.522
2,3-dimethyloxirane	575	465	III (O ₁ ; C ₂ ; C ₃) -0.139; 0.564; 0.564
Methyloxirane	530	435	XII (C ₂ ; O ₃ ; C ₄) 0.396; -0.135; 0.778 XIII (C ₂ ; O ₃ ; C ₄) 0.456; -0.141; 0.733
Trimethyloxirane	500	—	XVI (O ₁ ; C ₂ ; C ₃) -0.125; 0.435; 0.645 XVII (O ₁ ; C ₂ ; C ₃) -0.122; 0.401; 0.683
2,2-dimethyloxirane	—	435–440	—

* For the allyl radical, values of the spin densities (C₁; C₂; C₃) constitute: 0,58; -0,16; 0,58.

where no less than eleven equidistant lines with splittings of 1.2 mT can be singled out (Fig. 12a). This spectrum may be the result of an unpaired electron interacting with either two groups of equivalent protons, differing in the values of their hfc constants (the results of the quantum chemical calculations provide us with slightly overestimated values which lead to an eleven-line spectrum: a (6H) = 1.46 mT and a (6H) = 1.68 mT), or with twelve equivalent protons. Both in the former and in the latter cases we, similarly to our colleagues [3], attribute the observed EPR spectrum to the RC's open form. Correspondingly, a wide absorption band with a maximum at 590 nm arises in the sample's optical absorption spectrum (Fig. 6d). It had been reported [27] that, upon the irradiation of 4MO/Freon-11 and 4MO/Freon-113 solutions at 77 K, a wide band with a maximum at ~560 nm was observed.

However, the shape of the EPR spectrum (Fig. 12b) detected upon the irradiation of the 4MO/Freon-113a solution at 77 K differs from the one discussed earlier for the Freon-11 matrix. Nevertheless, upon warming the sample to 155 K, the shape of the EPR spectrum (Fig. 12c) in this matrix starts to resemble the one observed in the matrix of Freon-11 at 77 K (Fig. 12a), while, at the same time, a multiplet signal of matrix radicals (CF₃C'Cl₂) appears. Cooling the sample to 77 K restores the initial EPR spectrum. We attribute the shape of the spectrum detected at this temperature to dynamic effects, associated with inhibited rotation of methyl groups in the RC's open form. The relation of the induced optical density's value to the RC's concentration let us estimate their absorption coefficient: $\varepsilon_{590} \approx 8.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. It is worth noting that the action of light with $\lambda > 400 \text{ nm}$ does not cause any changes in the radiolytically induced absorption or the initial EPR spectra, observed after irradiation—i.e., tetramethyloxirane RC exhibit high photostability.

CONCLUSIONS

The data on the positions of maxima in the optical absorption spectra of the oxirane RC studied (both open and cyclic forms) is quoted in Table 5. In general, the experimental and computational data revealed shows that the photochemical reactions of 2,3-DMO and methyloxirane RCs in freons are associated with transitions between open and cyclic forms, rather than with those between *cis*- and *trans*-isomers of the RCs' open forms. This conclusion is supported by both EPR (see above) and optical absorption spectroscopic data (the experimental shift in the absorption maxima, observed in the course of photochemical reactions, reaches 110 nm).

The comparison of the absorption maxima of RC originating from various methyloxiranes to the values of atoms' spin population (ρ_Z) demonstrates that, in the cases of 4MO and 2,3-DMO RC, symmetrical distribution of spin population on carbon atoms connected to the oxygen atom is typical—while absorption in the long-wave region of the spectrum (575–590 nm) is also typical. As for the MO and 3MO RC, characterized by asymmetrical distribution of spin population, the absorption maxima are somewhat blue-shifted (by 45–90 nm).

The obtained experimental data reveals that no cyclic forms of the methylsubstituted oxiranes' RCs are observed at 77 K when the number of methyl substituents exceeds two.

The photochemical reactions of the 2,3-DMO and MO RCs' open forms (under the action of light with $\lambda = 578$ and 546 nm, respectively) in the absorption bands of the RCs' open forms (regardless of the type of isomers stabilized) result in the formation of the cyclic forms of the RCs with the elongated C–C bond. This reaction, proceeding for the species isoelectronic to the allyl radicals, is analogous to the photoinduced cyclization yielding the corresponding β -substituted cyclopropyl radicals [19–21], well-known for allyl radicals. If the terminal group is geminal, than the cyclization process in the solid phase becomes highly

unlikely due to sterical hindrances. This may provide an explanation for the photostability of the 4MO RC's open form as well as the absence of a direct reaction for the 3MO RC. In the latter case, we observed photoinduced transformation of the RC's open form into a C-centered radical upon the action of a proton characterized by energy exceeding a certain threshold (~ 2.75 eV or ~ 265 kJ/Einstein). We believe that, in this case, a dissociation of a non-relaxed RC takes place. Such transformation may, presumably, be related to the presence of acidic protons (methine and methyl ones) in the RC. We assume that the first stage of the process may involve the transfer of one of the protons to the oxygen atom's lone electron pair: the lower acidity of the methyl groups' protons, as compared to the methine proton, might be compensated by the gain in energy for the 1,3-transfer (as compared to the 1,2-transfer). For example, the results of the quantum chemical computations for the di-*n*-propyl ether let us estimate the difference in activation energy for the processes of this type (~ 50 kJ/mol [28]). The subsequent effective spontaneous deprotonation of the yielded thermalized distonic RC (the full charge on the hydrogen atom may correspondingly rise to 0.3) is what leads to the formation of the C-centered radical.

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