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Photochemical Transformations of Cyclic Acetal Radical Cations in Freon Matrices at 77 K

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Abstract—The efficiency of photochemical reactions of radical cations of cyclic acetals (1,3-dioxolane, 1,3-dioxane) is measured in different Freon matrices at 77 K and the influence of the latter on the reaction path is discovered. The possible nature of the paramagnetic complexes that form in photochemical reactions of cyclic acetal radical cations in Freon-11 is suggested.

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Radical cations (RCs) in the condensed phase are intermediates in radiation-chemical, electrochemical, photochemical, catalytic, etc., processes. In the past years, chemical transformations of RCs of organic compounds (alkanes, ethers, esters, acetals, amides, carboxylic acids, etc.) in the ground and excited states [1–3] have been studied with the use of stabilization of RCs in Freon matrices at low temperatures [4]. Using matrices other than Freon, in particular, sulfur hexafluoride SF_6, whose ionization potential noticeably exceeds the ionization potential of Freons, made it possible to reveal photochemical reactions of RCs previously not observed in Freon matrices [3, 5]. In particular, the study of phototransformations of 1,3-dioxolane RCs [6, 7] in the SF_6 matrix showed that the primary act involves the formation of the distonic RC.

This work is a continuation of studies of photochemical reactions of electronically excited RCs of cyclic acetals stabilized at low temperatures in Freon matrices. The study is aimed at elucidating the mechanism of reactions of electronically excited 1,3-dioxane and 1,3-dioxolane RCs and quantifying their reactivity in Freon matrices and comparing it with the reactivity of RCs of cyclic ethers.

EXPERIMENTAL

$CFCl_3$ (Freon-11, ~99%, Aldrich), $CFCl_2CF_2Cl$ (Freon-113, 99.99%), CF_3CCl_3 (Freon-113a, 99%, Aldrich), CF_2Cl_2 (Freon-12, 99.7%), and SF_6 (~99.5%) were used as matrices. In some cases, Freons were additionally purified by common procedures. 1,3-Dioxolane (99%, Lancaster), 1,3-dioxane (97%, Aldrich), and 1,4-dioxane (99% Aldrich) were used as purchased.

Solutions (0.1–0.5 mol %) of these compounds in Freon matrices were placed in quartz or SK-4B glass ampoules, pumped out to a pressure of ~0.1 Pa, and irradiated at 77 K to a dose of 2–4 kGy; the source of radiation was a 5BKhV6-W X-ray tube (50 kV, 80, mA).

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-3 radiospectrometer, permitting the recording of a spectrum in digital form. The concentration of paramagnetic centers in a sample was determined by comparing to the reference, a single crystal of $CuCl_2 \cdot 2H_2O$ with a known number of paramagnetic Cu^{2+} ions. The absolute error in determination of the concentration of paramagnetic particles in experimental samples was no more than ±20%. EPR spectra were simulated using the common PEST WinSim and Simfonia programs.

Optical absorption spectra at 77 K were recorded on a Specord M-40 spectrophotometer; flat quartz cells with an optical path length of ~0.1 cm were used for recording spectra. The oscillator strength of an electronic transition was determined by the equation $f \cong 4.32 \times 10^{-9} \varepsilon_{max} \Delta H_{1/2}$, where ε_{max} is the molar absorption coefficient at an absorption band maximum and $\Delta H_{1/2}$ is the half-width of an absorption band.

A DRSh-250 high-pressure mercury lamp either with cutoff glass filters ($\lambda = 436$ nm (the maximal transmission $T_{max} = 27\%$, the half-width of the transmission band $\Delta\nu_{1/2} = 2400$ cm^{-1}), $\lambda = 546$ nm ($T_{max} = 58\%$, $\Delta\nu_{1/2} = 900$ cm^{-1}), $\lambda = 578$ nm ($T_{max} = 45\%$, $\Delta\nu_{1/2} = 1700$ cm^{-1})) or with an interference filter for cutting off light at 700 nm was used as a light source. The absolute light intensity determined by ferrioxalate actinometry

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† Deceased.

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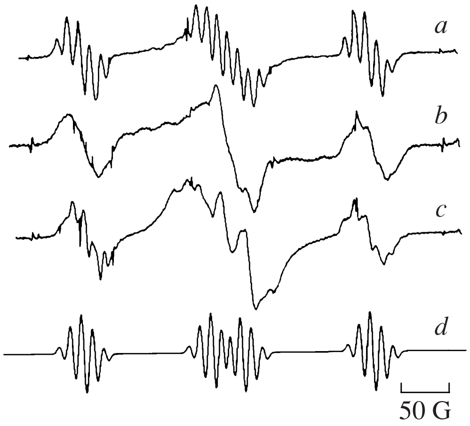


Fig. 1. EPR spectra of X-irradiated 0.1 mol % solutions of 1,3-dioxolane in (*a*) Freon-11, (*b*) Freon-113, and (*c*) Freon-113a at 77 K and (*d*) the model EPR spectrum of 1,3-dioxolane RCs with a_1(1H) = 137 G, a_2(1H) = 168 G, and a_3(4H) = 11.5 G.

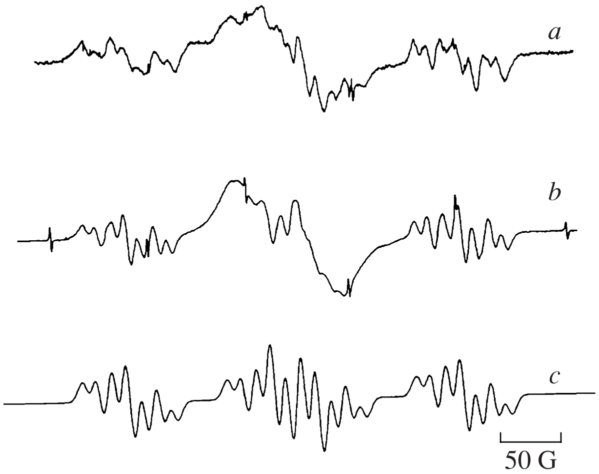


Fig. 2. EPR spectra of X-irradiated 0.1 mol % solutions of 1,3-dioxane in (*a*) Freon-113a at 77 K and (*b*) Freon-11 with mechanical pulverization of the sample, and (*c*) the model EPR spectrum of the 1,3-dioxane RCs with a_1(1H) = 122 G, a_2(1H) = 160 G, a_3(2H) = 25 G, and a_4(2H) = 12 G.

(436 nm), Reinicke's salt actinometry (546 and 578 nm), and tetranitromethane–triphenylamine actinometry [8] was 1.2×10^{-5}, 5.8×10^{-5}, 8.2×10^{-7}, and 4.0×10^{-9} einstein cm^{-3} s^{-1} at 436, 546, 578, and 700 nm, respectively. The quantum yield of a photochemical reaction was calculated from the decrease in the RC concentration as a function of the dose absorbed by the RC. The absolute error in determination of quantum yields was no more than ±25%.

RESULTS AND DISCUSSION

Magnetic Resonance Parameters of 1,3-Dioxolane, 1,3-Dioxane, and 1,4-Dioxane RCs

Upon X-ray irradiation of solutions of acetals (1,3-dioxolane and 1,3-dioxane) in Freons at 77 K, not only organic RCs but also paramagnetic centers (PCs) of another nature that form from molecules of Freon and organic additions are stabilized in the matrix, the content of RCs in initial samples in different Freons being, as a rule, no higher than 40%.

A specific feature of the EPR spectra of the cyclic acetal RCs is that the low- and high-field groups of lines of the hyperfine structure (HFS) do not overlap with the signals of other PCs and can be used for determining the RC concentration (Figs. 1*a*–1*c*, 2*a*, 2*b*).

The hyperfine coupling (HFC) constants (a_1(H) = 136.0 G, a_2(H) = 167.5 G, and a_3(4H) = 11.5 G) and the linewidth measured between the points of the maximal slope ($\Delta H_{\max} \approx 4.5$ G) that ensure the best fit of the calculated EPR spectrum (Fig. 1*d*) to the experimental spectrum of the 1,3-dioxolane RC in the Freon-11 matrix are consistent with the data in [9] for the HFC constants of these RCs in the Freon-11 matrix (a_1(1H) = 134.0 G, a_2(1H) = 166.0 G, and a_3(4H) = 11.0 G); however, they noticeably differ from the data in [10] for the same matrix (a_1(2H) = 153.0 G and a_2(4H) = 11.2 G). We found that the EPR spectra of RCs stabilized in the Freon-11 matrix depend on the orientation of a sample with respect to the magnetic induction vector of the external magnetic field. This experimentally established fact creates extra difficulties for simulation of spectra in a matrix.

The best-fit HFC constants and $\Delta H_{\max}$ values for the 1,3-dioxolane RC in the Freon-113 matrix at 77 K were determined from the EPR spectra (Fig. 1b) to be a_1(1H) = 136.0 G, a_2(1H) = 167.5 G, and a_3(4H) = 11.5 G; $\Delta H_{\max}$ = 11.0 G. These values are identical to the above values for the Freon-11 matrix. However, the experimental EPR spectra show broader lines and the HFC constants a_3(4H) in them are poorly detectable. In interpreting experimental EPR spectra, one should take into account that irradiation of solutions of 1,3-dioxolane in the Freon-113 matrix leads to the formation 1,3-dioxa-cyclopent-2-yl radicals (a^{α}(H) = 21.3 G, g = 2.0032) [10]. The EPR spectrum of irradiated solutions of 1,3-dioxolane shows, in addition to the signals of the RC and 1,3-dioxacyclopent-2-yl radicals, broad lines of the poorly resolved spectrum of $CF_2ClC^{\bullet}FCl$ radicals forming from the matrix molecules (according to [11], the HFC constants measured in thiourea inclusion compounds are $a_{\mathrm{iso}}^{\alpha}$ (F) = 65.0 G and a_{iso}^{β} (Cl) = 8.0 G).

The HFC constants for the 1,3-dioxolane RCs stabilized in the Freon-113a matrix at 77 K that lead to the best fit of the calculated EPR spectrum to the experimental spectrum of the RCs (Fig. 1*c*) are the same as those obtained for these species in other Freon matrices (a_1(1H) = 136.0 G, a_2(1H) = 167.5 G, and a_3(4H) = 11.5 G) but somewhat differ from the values reported in

[12] (a_1(1H) = 137 G, a_2(1H) = 146 G, a_3(2H) = 24.5 G, and a_4(2H) = 10.0 G).

Inasmuch as the spectra in [12] were recorded at 95 K, the differences in HFC constants for the protons of the bridging methylene group of the O–CH$_2$–O moiety can be due to averaging of their values with an increase in temperature. The average of the HFC constants that we obtained for these protons (141 G) is close to the average value (141.5 G) determined in [12–15]. The large HFC constants for the methylene protons of the O–CH$_2$–O moiety in acetal RCs are evidence of efficient π–σ–π spin density delocalization mainly over this moiety. The nonequivalence of the methylene protons indicates that this methylene group is out of the molecule plane. According to [9], the angle between the molecular plane and the direction to the bridging group is about 20°. The close values of a_1(1H) and a_2(1H) for the 1,3-dioxolane RCs stabilized in different Freons demonstrate that the RCs stabilized in the matrices under consideration have nearly the same geometry.

After exposure of 1,3-dioxolane solutions in the Freon-113a matrix at 77 K to X-rays, the EPR spectrum showed, in addition to the signals of PCs formed from Freon-113a molecules and 1,3-dioxane, the signal of the 1,3-dioxane RCs (Fig. 2a). The calculated HFC constants for the 1,3-dioxolane RCs (a_1(1H) = 122.0 G, a_2(1H) = 160.0 G, a_3(2H) = 24.5 G, and a_4(2H) = 10.5 G) that provide the best fit to the experimental spectrum (Fig. 2a) differ form the data in [12] (a_1(1H) = 137 G, a_2(1H) = 146 G, a_3(2H) = 24.5 G, and a_4(2H) = 10.0 G). In the other Freon matrices under study (Freon-11, Freon-113), the EPR spectra of irradiated 1,3-dioxane solutions differ insignificantly from the spectra recorded in Freon-113a. However, in these cases, the interpretation of the EPR spectra of 1,3-dioxane RCs is additionally complicated by the observed angular dependence of the spectrum on the orientation of a sample in the magnetic field of a radiospectrometer when the Freon-11 matrix is used and by large linewidths, which prevents the experimental observation of the smallest of the HFC constant for the protons of the RCs in the Freon-113 matrix. We tried to eliminate the angular dependence of the EPR spectra of 1,3-dioxane RCs in the Freon-11 matrix by mechanical pulverization of samples at 77 K before irradiation (Fig. 2*b*). In this case, the HFC constants that ensure the best fit to the experimental spectrum are the same as the above values for Freon-113a.

After irradiation of 1,4-dioxane in the Freon-11 matrix at 77 K, the EPR spectrum showed the signal of 1,4-dioxane RCs (Fig. 3*a*). The HFC constants due to two groups of equivalent protons that provides the best fit of the calculated EPR spectrum to the experimental one (a_1(4H) = 9.0 G and a_2(1H) = 10.5 G, Fig. 3*c*) are nearly the same as in [16]. For the other Freon matrices that we used (Freon-113a, Freon-113), the EPR spectra of irradiated 1,4-dioxane solutions differ in that they show the signals of matrix radicals and different yields of 1,4-dioxan-2-yl radicals.

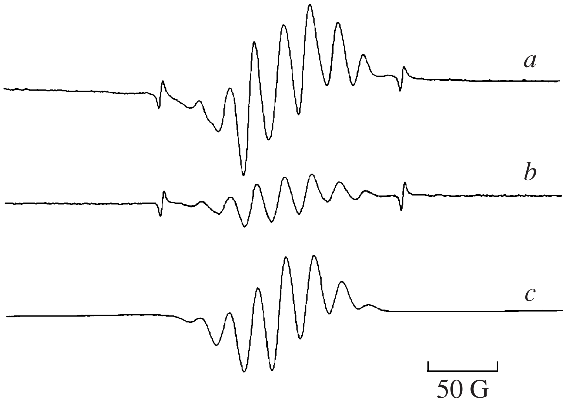


Fig. 3. EPR spectra of X-irradiated 0.2 mol % solutions of 1,4-dioxane (*a*) in Freon-11, (*b*) after exposure to light with λ = 436 nm, and (*c*) the model EPR spectrum of the 1,4-dioxane RCs with parameters a_1(4H) = 9.0 G and a_2(1H) = 10.5 G.

Absorption Spectra of Radical Cations of Cyclic Acetals and Ethers

The absorption spectrum of intermediates—the difference spectrum after exposure of irradiated 1,3-dioxolane solutions in the Freon-11 matrix at 77 K to light with a wavelength of 436, 546, and 578 nm (Fig. 4a)—has a clear maximum at λ = 440 nm and a broad featureless band in a long-wavelength region (λ > 650 nm). An analogous spectrum, with a maximum at λ = 385 ± 5 nm and a broad featureless band in a low-wavelength region (λ > 600 nm), was also obtained for intermediates that vanish upon exposure of irradiated 1,3-dioxane solutions in Freon matrices (Freon-11, Freon-113) to light with a wavelength of 436, 546, and 578 nm (Fig. 4b). Inasmuch as the intensity of the bands with maxima at λ = 440 nm and λ = 385 ± 5 nm changes in parallel with a change in the concentration of 1,3-dioxolane and 1,3-dioxane RCs detected by EPR, we assign these bands to absorption of the corresponding RCs of cyclic acetals. Gaussian decomposition in the long-wavelength region of the difference absorption spectra allows us to distinguish two bands with maxima at λ = 580 ± 10 nm and λ = 700 ± 10 nm. According to [17], the absorption band at 580 ± 10 nm can arise from ion pairs $F^{+\bullet}/Cl^-$, where $F^{+\bullet}$ stands for the RCs of matrix molecules; we believe that the long-wavelength band at 700 ± 10 nm is due to the presence of cyclic acetal RCs in the samples under consideration. It is worth noting that two absorption bands at 450 and 730 nm were observed in [19] for the RCs of 2,4-dioxapentane (methylal) at 77 K. Comparison of changes in the concentration of 1,3-dioxolane and 1,3-dioxane RCs measured by EPR and the intensity of their absorption bands at 77 K makes it possible to estimate the extinc-

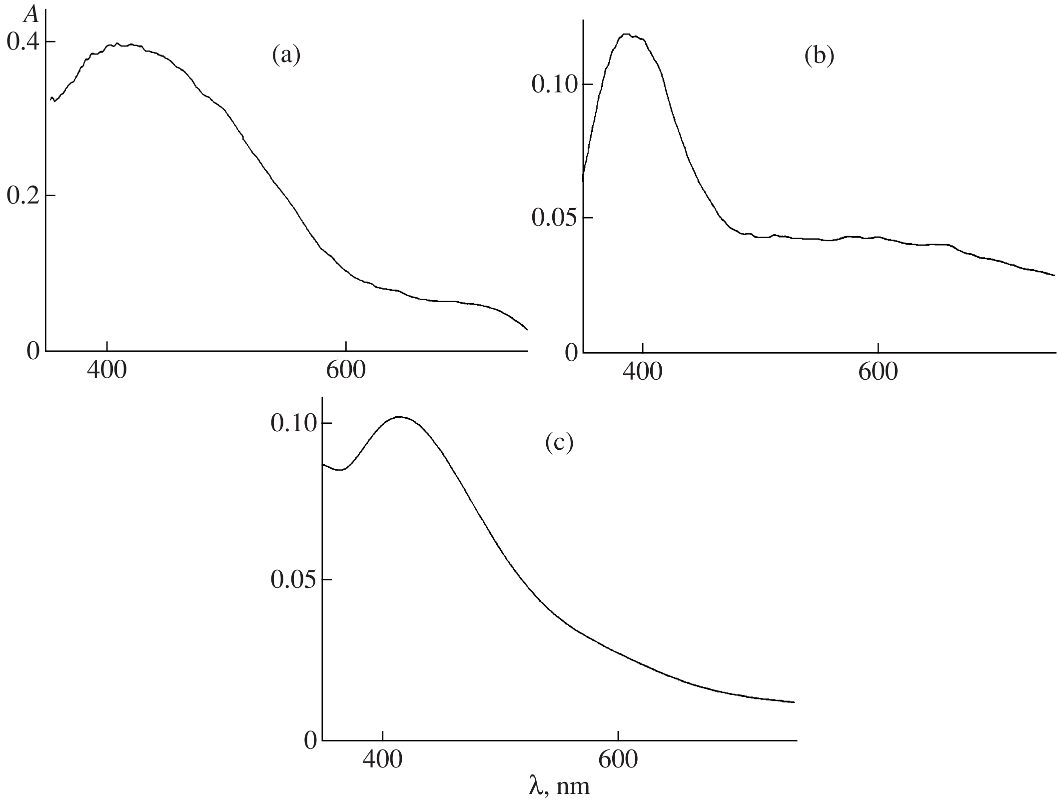


Fig. 4. Optical absorption spectra of (a) 1,3-dioxolane RCs, (b) 1,3-dioxane RCs, and (c) 1,4-dioxane in the Freon-11 matrix at 77 K.

tion coefficients (ε) and oscillator strength (*f*) for electronic transitions (Table 1) in comparison with the known values for RCs of cyclic acetals and ethers. The extinction coefficients and oscillator strength for cyclic acetal RCs noticeably increase on going from 1,3-dioxolane to 1,3-dioxane and 1,3,5-trioxane. It is likely that distortion of the 1,3-dioxane and 1,3,5-trioxane RC structure in Freon matrices reduces the symmetry forbiddenness and causes such a buildup for an $n \longrightarrow \pi^*$ transition.

The absorption spectrum of 1,4-dioxane RCs in the Freon-11 matrix at 77 K—the difference spectrum after exposure of the irradiated sample to light with a wavelength of 365 nm—has a clear maximum at $\lambda = 430$ nm (Fig. 4c). The extinction coefficient and oscillator strength for this electronic transitions were estimated at $\varepsilon \approx 2 \times 10^3$ M^{-1} cm^{-1} and $f \approx 0.08$, which is close to the values typical of ether RCs (Table 1).

Light-Induced Transformations of 1,3-Dioxolane, 1,3-Dioxane, and 1,4-Dioxane Radical Cations

Exposure to light with wavelengths of 436, 546, 578, and 700 nm at 77 K leads to the loss of 1,3-diox-

Table 1. Spectral characteristics of RCs of cyclic acetals and ethers

Compound	Matrix	Wavelength λ_{max}, nm	Extinction coefficient ε, M^{-1} cm^{-1} (*f*)	Reference
1,3-Dioxolane	Freon-11	440, >650	–	[7]
		410, >650	6.5×10^3 (0.28)	*
1,3-Dioxane	Freon-11, Freon-113	385 ± 5, 700 ± 10	1.8×10^4 (0.45)	*
1,3,5-Trioxane	Freon-11	430	1.6×10^4 (0.4)	[18]
2,4-Dioxapentane	Freon-11	450, 730	–	[19]
1,4-Dioxane	Freon-11	430	2×10^3 (0.08)	*
Dimethyl ether	Freon-11	435	$(2.5 \pm 0.5) \times 10^3$ (0.07)	[5]
Tetrahydrofuran	Freon-11	430	$(2.1 \pm 0.5) \times 10^3$ (0.07)	[20]

* This work.

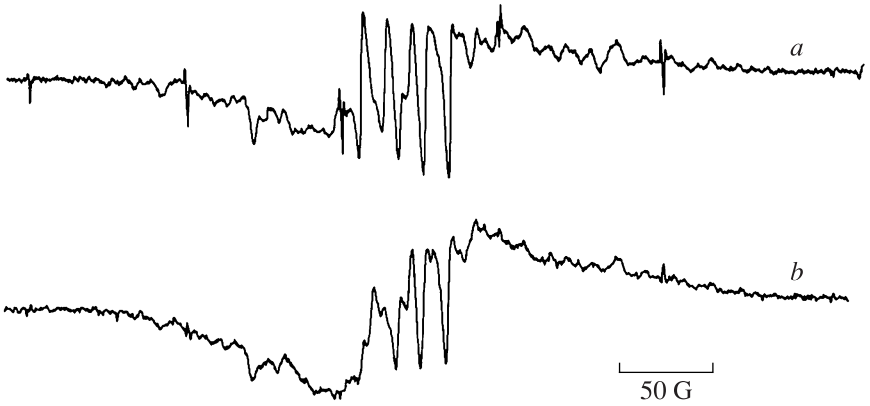


Fig. 5. EPR spectra observed at 77 K in the Freon-11 matrix upon illumination at $\lambda = 546$ nm of (*a*) 1,3-dioxolane RCs and (*b*) 1,3-dioxane RCs.

olane RCs in the Freon-11 matrix and the appearance an EPR signal (Fig. 5*a*) typical of particles with spin density localized on the Cl atom of a Freon molecule (the HFC constants due to the chlorine atom can be determined from the experimental spectrum: $a_{\|}(^{35}Cl) = 65 \pm 1$ G, $\Delta g = g_{\|} - g_{\perp} = 0.003$). Exposure to light with a wavelength of 436 and 546 nm leads to a decrease in the total concentration of PCs, whereas exposure to light at 578 and 700 nm does not affect the PC concentration. To eliminate the angular dependence of EPR spectra of the products of transformation of 1,3-dioxane RCs in the Freon-11 matrix, samples were mechanically pulverized at 77 K before irradiation.

The loss of 1,3-dioxolane RCs exposed to light with a decrease in the PC concentration allows us to assume the occurrence of photoinduced charge transfer to matrix molecules. With allowance for the difference in ionization potential between the molecules of the matrix (11.77 eV) and organic additive (9.9–10.0 eV), this process is possible at a photon energy in the wavelength range used ($\lambda = 436$–578 nm). The quantum yields of the reactions of charge transfer and formation of particles with spin density localized at the Cl atom for 1,3-dioxolane RCs exposed to light of various wavelengths are listed in Table 2.

When Freon-12 (ionization potential, 12.2 eV) is used as the matrix, exposure to light with $\lambda = 436$–578 nm at 77 K leads to the loss of 1,3-dioxolane and 1,3-dioxane RCs without formation of paramagnetic centers. Exposure of 1,3-dioxolane RCs in the Freon 113 matrix at 77 K to light with $\lambda = 436$ and 546 nm leads to the loss of RCs; however, the overall concentration of paramagnetic particles remains constant. The paramagnetic phototransformation products are the $O{=}CHOCH_2C^{\bullet}H_2$ radicals ($a^{\alpha}(2H) = 20$ G, $a^{\beta}(1H) = 30$ G), which is consistent with the data in [7]. The quantum yields of the 1,3-dioxolane RC loss in the Freon-113 matrix under the action of light of various wavelengths are given in Table 2.

Photolysis with light at $\lambda = 436$ and 546 nm leads to the loss of 1,3-dioxolane RCs in the Freon-113a matrix at 77 K without formation of paramagnetic products, which points to the occurrence of photoinduced charge transfer to matrix molecules with the quantum yields listed in Table 2.

Exposure of 1,3-dioxane RCs in the Freon-11 matrix at 77 K to light with $\lambda = 546$ nm leads to their loss, while the overall concentration of paramagnetic centers remains unaltered; concurrently, new paramagnetic species are generated that give rise to an EPR spectrum close to the spectrum observed on exposure to light of 1,3-dioxolane RCs (Fig. 5*b*).

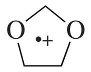
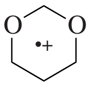
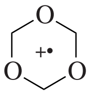
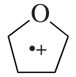
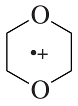
Exposure to light with a wavelength of 436 and 546 nm leads to the loss of 1,3-dioxane RCs in the Freon-113 matrix, while the overall PC concentration remains the same: during photolysis, an EPR spectrum appears and builds up, which can be assigned to $O{=}CHOCH_2C^{\bullet}H_2$ radicals. The best-fit HFC constants are $a^{\alpha}(2H) = 20$ G and $a^{\beta}(1H) = 30$ G.

When illuminated at 546 nm, the 1,3-dioxane RCs in the Freon-113a matrix (the ionization potential, 11.8 eV, is the same as that of Freon-11) are lost without formation of new paramagnetic species; i.e., charge transfer to the matrix takes place. An analogous situation is also observed for 1,3-dioxolane RCs in the Freon-113a matrix exposed to light with $\lambda = 546$ nm.

Thus, the RCs of cyclic acetals (1,3 dioxane, 1,3-dioxolane) enter into identical photochemical reactions almost in all cases.

The quantum yields of the loss of 1,3-dioxane RCs in various matrices during photolysis with light of various wavelengths are given in Table 2. The quantum yield of formation of species with spin density localized at the chlorine atom in the Freon-11 matrix is almost the same as the quantum yield for the analogous reaction of 1,3-dioxolane RCs, although this equality is achieved under the action of light in different spectral ranges ($\lambda = 546$ and 700 nm for 1,3-dioxane and 1,3-dioxolane, respectively). It should be noted that, for

Table 2. Quantum yields of reactions of cyclic acetal and ether RCs in different matrices at 77 K

Radical cation	Matrix	λ, nm	Reaction/reaction product	Quantum yield Φ	Reference
	SF_6	436	Distonic RC	0.02	[7]
	Freon-11	436	Charge transfer	0.1	[7], *
		546		0.07	
		578, 700		0	
	Freon-11	436	Paramagnetic complex	?0.02	[7], *
		578		0.1	
		700		0.4	
	Freon-113	436	Deprotonation	0.08	[7], *
		546		0.07	
	CF_3CCl_3	436	Charge transfer	0.1	[7], *
		546		0.06	
	Freon-11	546	Paramagnetic complex	0.44	*
	Freon-113	436	Deprotonation	0.02	
		546		0.02	
	Freon-113a	546	Charge transfer	0.02	
	Freon-11	546	$^{+}CH_2{=}COCH_2O^{\bullet}$	0.24	[18]
	Freon-113	546		0.26	
	Freon-113a	546		0.36	
	Freon-11	436	Charge transfer	0.3 ± 0.1	[20]
	Freon mixture**	436	Charge transfer	0.06 ± 0.03	
	Freon-11	365	Charge transfer	0.15 ± 0.05	*
	Freon-113	365	Deprotonation Charge transfer	?0.02 ?0.04	
	Freon-113a	365	Charge transfer	0.08 ± 0.04	

*This work.

**Freon-11 (50%) + Freon-114B2 (50%).

1,3-dioxolane RCs exposed to light with $\lambda = 436$ nm, the quantum yields of formation of the distonic RC in the SF_6 matrix and the paramagnetic complex in the Freon-11 matrix are comparable, whereas the latter noticeably increase upon illumination with light in the range of the long-wavelength absorption band of the 1,3-dioxolane RC. Reactions in the other Freon matrices yield different products and are noticeably less efficient.

Illumination at $\lambda = 436$ or 365 nm leads to the loss of the 1,4-dioxane RCs in the Freon-11 and Freon-113a matrices (Fig. 3b) without formation of paramagnetic products, which points to the occurrence of photoinduced charge transfer to matrix molecules. The quantum yields of these reactions are listed in Table 2. In the Freon-113 matrix, the major paramagnetic product of the photochemical reaction of the RCs are 1,4-dioxan-2-yl radicals, characterized by the HFC constants $a^{\alpha}(1H) = 17.2$ G and $\Sigma a^{\beta}(2H) = 45.5$ G [21]. Our findings concerning the path and efficiency of photochemical reactions involving RCs of cyclic acetals in matrices of different nature allow us to return to consideration of the mechanism of these processes, as well as to elucidation of possible reasons for so-called "matrix" effects.

It was noted in [7] that close magnetic resonance parameters of RCs in matrices of sulfur hexafluoride and inert gases can be evidence of the absence of strong specific interactions between RCs and the molecules of these matrices. In this context, the formation of the distonic RC upon illumination of the 1,3-dioxolane RC in this matrix [7] can be considered as evidence of the mechanism of the process under conditions when the interaction of the initial RC with the matrix is minimized.

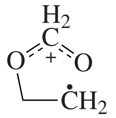
At the same time, for the Freon-11 matrix after irradiation of solutions of different organic compounds (aldehydes, lactones, methyl formate, alkyl halides, etc.), the EPR spectra often show HFC to the chlorine atom [22, 23], which can be explained by the formation of RC complexes with matrix molecules. In [22], it was shown for different types of RCs that, in the ionization potential (IP) range from 9 to 11 eV, there is a correlation between $a_{\|}(^{35}Cl)$ values and the IP of the substrate. RC complexes that form at 77 K directly under the action of ionizing radiation on the systems studied have been addressed in [22, 23]. In solutions of 2,4-dioxapentane and 1,3-dioxane in Freon-11, similar particles did not form after irradiation of the samples at 77 K; rather, they appeared upon subsequent illumination with light [7, 24]. It was assumed that phototransformation of acetal RCs leads to the formation of paramagnetic complexes of formaldehyde RCs and Freon molecules. The use of the value $a_{\|}(^{35}Cl) \approx 65$ G [7], obtained from the dependence in [22], allowed us to estimate the IP (~10.6–10.7 eV) of the precursor of the RC that forms the paramagnetic complex (with allowance for the error of such an approximation, the IP can be in the range 10.2–11.0 eV). These estimates do not contradict the hypothesis of formation of paramagnetic complexes of the formaldehyde RC (10.9 eV) with Freon molecules in the systems under consideration.

However, in our opinion, there are some factors that cast doubts on such an assignment of the EPR spectra observed after exposure to light. One of these factors is that irradiated dilute solutions of formaldehyde in the Freon-11 matrix contain, against the background of high concentrations of other PCs, an insignificant amount of species with magnetic resonance parameters ($A_x = A_y = 139$ G, $A_z = 141$ G, $g_x = g_y = 2.0045$, $g_z = 2.0025$) close to the parameters obtained for the formaldehyde RCs in the neon matrix at 4 K [26] ($A_x = 129.8$ G, $A_y = 134.5$ G, $A_z = 134.9$ G, $g_x = 2.0069$, $g_y = 2.0015$, $g_z = 2.0025$). Thus, there are grounds to believe that the formaldehyde RCs can be stabilized in the Freon-11 matrix without forming a complex with matrix molecules and, at the same time, give rise to an EPR spectrum other than the spectrum observed after exposure to light of acetal RCs in [7, 24].

Another factor is the necessity of meeting the Stevenson–Audier rule. This rule states that, upon decay of an RC, the charge is localized in the part with lower ionization energy. Hence, upon thermally activated decay of 1,3-dioxolane and 1,3-dioxane RCs, the charge cannot be localized on the formaldehyde molecule since it has the highest ionization potential among the possible decay products.

In addition, we can refer to the results of [18] where it was found that the universal mechanism of photochemical reactions of 1,3,5-trioxane RCs in various Freon matrices involves their dissociation with opening of the ring and formation of the distonic RC in which spin is mainly localized at an oxygen atom. Quantum-chemical calculations (without consideration of interactions of the RC with the medium) showed that the nascent distonic RC is unstable and can decompose with elimination of a formaldehyde molecule and its coordination prevents further decay of the distonic RC $CH_2{=}O^+CH_2O^\bullet$. Thus, the data on 1,3,5-trioxane obtained in [18] show that the formation of formaldehyde as a possible product of transformation of the cyclic acetal RC in the Freon-11 matrix does not lead to the appearance of HFC to the chlorine atom in EPR spectra, which is typical of paramagnetic complexes.

We believe that a possible reason for the difference in the behavior of RCs of cyclic acetals (1,3-dioxolane, 1,3-dioxane, 1,3,5-trioxane) upon exposure to light is a different structure of intermediates of their photochemical reactions. This structure can be mainly predetermined by differences in the distribution of spin and charge density in the ground state of the RCs under consideration. In particular, the calculations in [27] predicted that the largest positive charge in the 1,3-dioxolane RC is localized on the methylene group of the –OCH_2O– moiety and that maximal spin populations are on the two oxygen atoms. At the same time, for the 1,3-dioxane RC, the localization of the maximal positive charge is retained, while the spin populations of the two oxygen atoms are disparate (0.67 and 0.03). For the 1,3,5-trioxane RCs, the spin populations of the oxygen atoms are also rather different (0.56, 0.05, 0.05) [27]. For the 1,3,5-trioxane RCs, we can state with confidence that the distonic RC $^+CH_2{=}OCH_2O^\bullet$ is formed and stabilized in different Freon matrices, whereas, in the case of 1,3-dioxolane and 1,3-dioxane RCs, we should assume the formation of distonic RCs of another structure to explain the effects observed in the Freon-11 matrix, namely,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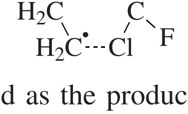
which are identical to the experimentally observed RCs in the SF_6 matrix [7]. We believe that it is precisely the products of transformation of such distonic RCs, which form upon elimination of a formaldehyde molecule, that can form paramagnetic complexes (**I**) with Freon-11 molecules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which are observed as the products of photochemical reactions of cyclic acetal RCs in this matrix.

The possibility of formation of intermediates with a similar structure in the Freon-11 matrix is supported by comparison of the experimental EPR spectrum (signals

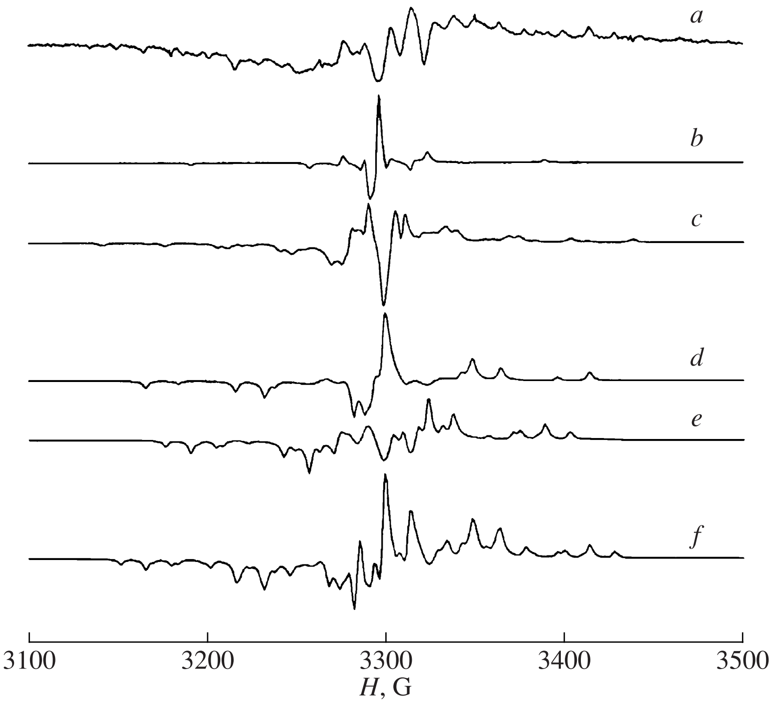
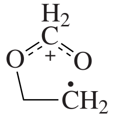


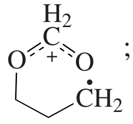
Fig. 6. EPR spectra observed upon illumination at $\lambda = 546$ nm at 77 K of (*a*) 1,3-dioxolane in the mechanically pulverized Freon-11 matrix (the signal were repeatedly accumulated) and (*b–f*) model EPR spectra for complex **I** with parameters $g_{\|} = 2.018$, $g_{\perp} = 2.015$, and $a(^{35}Cl)/a(^{37}Cl) \approx 1.2$ and HFC constants (*b*) $a_{\|}(^{35}Cl) = 64$ G and $a_{\perp}(^{35}Cl) = 13$ G; (*c*) $a_{\|}(^{35}2Cl) = 64$ G and $a_{\perp}(^{35}2Cl) = 13$ G; (*d*) $a_{\|}(^{35}Cl) = 64$ G, $a_{\perp}(^{35}Cl) = 13$ G, $a_{\|}(F) = 50$ G, and $a_{\perp}(F) = 22$ G; (*e*) $a_{\|}(^{35}Cl) = 64$ G, $a_{\perp}(^{35}Cl) = 13$ G, and $a_{iso}(2H) = 14$ G; (*f*) $a_{\|}(^{35}Cl) = 64$ G, $a_{\perp}(^{35}Cl) = 13$ G, $a_{\|}(F) = 50$ G, $a_{\perp}(F) = 22$ G, and $a_{iso}(2H) = 14$ G.

were repeatedly accumulated) (Fig. 6a) of the paramagnetic complex obtained upon illumination of 1,3-dioxolane RCs in the mechanically pulverized Freon-11 matrix with calculated EPR spectra (Figs. 6b–6f). Our data demonstrate that for an adequate description of the EPR spectra, we should assume the presence of considerable spin density not only on the complex moiety representing the matrix molecule, but also on the distonic RC. The fact that exposure to light of cyclic acetal RCs does not lead to the formation of paramagnetic complexes in the Freon-12 matrix, which has a similar structure, is evidently due to its high ionization potential (12.2 eV), which prevents the formation of π complexes between distonic RCs and matrix molecules.

Thus, confirming, on the whole, the scheme of transformations of RCs of cyclic acetals in [7], we should introduce refinements concerning the nature of species stabilized in the Freon-11 matrix. The differences observed in the behavior of cyclic acetal RCs can be associated with the fact that the photochemical reaction yields distonic RCs of different structure:

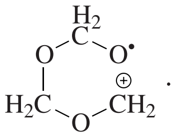
in 1,3-dioxolane and 1,3-dioxane,





;

in 1,3,5-trioxane,



The former eliminate the formaldehyde molecule and can form complex **I** with matrix molecules, whereas the latter undergoes monomolecular decay. For conclusiveness, quantum-chemical calculations (which we intend to perform in the future) and experimental studies of the nature of paramagnetic complexes in linear acetals (methylal) are required.

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