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Photoisomerization of methylthiirane radical cations in freonic matrices at 77 K

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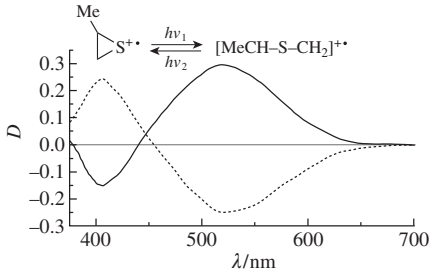
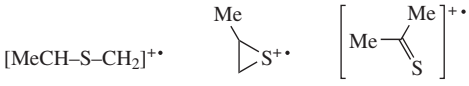
A reversible photochemical transition between an open pseudoallylic form and a cyclic form has been discovered for methylthiirane radical cations in the matrices of $CFCl_3$ and CF_3CCl_3 at 77 K.



High lability and a wealth of possible reaction channels are the key characteristics of radical cations (RCs) originating from small cycles, which ensures their frequent role as model compounds in the studies of various effects that direct these species along certain reaction pathways, both thermally induced and photochemical. The possibility of stabilizing these intermediates in their both open pseudoallylic form and cyclic form, affording photochromism in the test systems, is especially intriguing. Regarding methyl-substituted oxiranes, the stabilization of corresponding RCs in open pseudoallylic and/or cyclic forms has been found upon the treatment of solutions in freonic matrices with ionizing radiation at 77 K,[1–5] while, in the case of methyloxirane and 2,3-dimethyloxirane RCs, mutual transitions between them could be detected when investigating photochemical reactions.[3,5] For aziridine RCs in a temperature range of 77 to 150 K, it has been shown that it is possible to stabilize them in $CFCl_3$ and CF_3CCl_3 in the open pseudoallylic[6] and cyclic forms; in the CF_3CCl_3 matrix, the cyclic form irreversibly transforms into the open one upon the action of visible light.[7] Upon the action of ionizing radiation, thiiranes are prone to forming both monomeric (in $CFCl_3$) and dimeric (in $CF_2ClCFCl_2$ and CF_3CCl_3) RCs depending on the matrix and the substrate concentration.[8,9] Among the reactions of thiirane RCs in freonic matrices, only the thermally induced dissociation of dimeric thiirane RCs in the $CF_2ClCFCl_2$ matrix is known (it results in the elimination of ethylene[8,9]). Up to now, no research on phototransformations of thiirane RCs has been conducted.

The aim of this work was to study the stabilization of various forms of methylthiirane RCs in freonic matrices while researching their ability to reversibly transform into each other by photochemical means.†

The quantum chemical calculations‡ point to three minima existing on the PES, each corresponding to a different RC type originating from the methylthiirane molecule: pseudoallylic **1** formed upon the cleavage of the C–C bond, cyclic **2** and thioketone **3**; the forms correspond to those found previously.[16,17]



1 **2** **3**

Note that, in contrast to the methyloxirane RC,[5] no support for the existence of two different cyclic forms has been found in our calculations for the methylthiirane RC (the forms differ in their orbital symmetry along with the distribution of spin and charge density). The computed data show that form **3** is the

† $CFCl_3$ (~99%, Aldrich) and CF_3CCl_3 (>99% according to NMR data, obtained using a known technique[10] from ~99% $CF_2ClCFCl_2$, Aldrich) have been employed as matrices. Methylthiirane (~98%, Aldrich) was used without additional purification. The sample preparation procedures, the irradiation techniques (employing ionizing radiation in the dark), the detection methodology related to EPR spectra and optical absorption spectra and the procedure of the photochemical experiments were described earlier.[3]

‡ Calculations were performed by the unrestricted DFT method using the ORCA 3.0.3 program package.[11] B3LYP functional together with the full-electron def2-TZVP basis set[12] were used to calculate the geometry of potential energy surface minima, geometries at minima and transition states were additionally checked for the presence or absence of imaginary vibration frequencies. The spin-Hamiltonian parameters were calculated using the B3LYP functional together with the full-electron N07D basis set,[13] dipole contributions to the anisotropic hfc constants were calculated on the UKS/PBE0/def2-QZVPP level.[12] To estimate the solvent effect in the calculations, either the continuous COSMO model was employed[14] or the influence was accounted for explicitly: the cage of the solvent was modelled with the GROMACS program package[15] with the subsequent RC geometry optimization by means of B3LYP/def2-SVP[12] calculations. The effect of molecular dynamics upon magnetic parameters was evaluated by the direct averaging of calculated isotropic hyperfine coupling constants over a 5 ps BOMD trajectory (B3LYP/def2-SVP). Initial velocities were taken to correspond to 77 K; the step was chosen as 0.5 fs. After 5 ps of equilibration, a trajectory of the same length was collected; approximately 500 configurations were then uniformly extracted from this trajectory. The hfc constants averaged over these configurations were found lower than those in the equilibrium geometry by no more than 20%, with no noticeable influence on qualitative description of the EPR spectra. From here on out, only hfc constants calculated with stationary geometries in a vacuum are suggested.

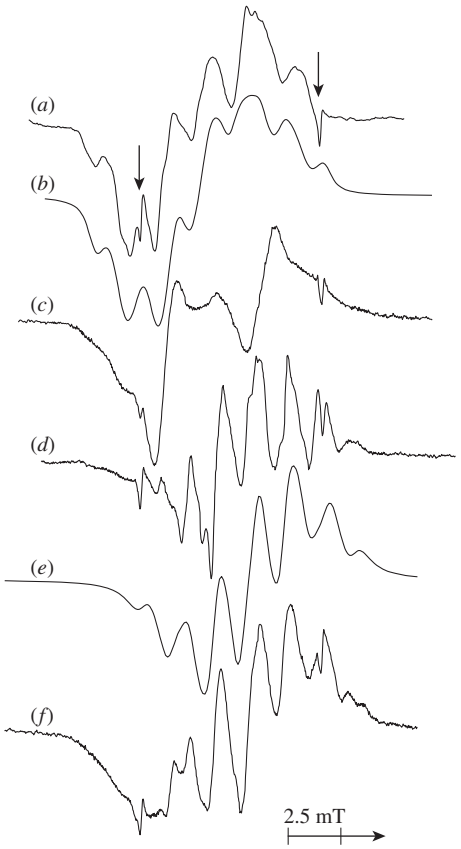


Figure 1 EPR spectra detected in irradiated methylthiirane solutions immediately after X-ray irradiation at 77 K and the subsequent action of light with λ = 546 nm on the irradiated sample at 77 K in the $CFCl_3$ matrix [(*a*) experimental, (*b*) simulation] and (*c*) the CF_3CCl_3 matrix, and the subsequent action of light with λ = 405 nm in the $CFCl_3$ matrix [(*d*) experimental, (*e*) simulation] and (*f*) light with λ = 436 nm in the CF_3CCl_3 matrix. Arrows point to the third and fourth components of the hyperfine structure of the additional Mn^{2+} ions in MgO powder. Fitting parameters are given in Table 1.

most stable one, with form **2** lying ~46 kJ mol^{-1} above the energy minimum (form **1** lies ~53 kJ mol^{-1} above the minimum). The geometric and spectral parameters of methylthiirane RC with consideration for solvation are in good agreement with those obtained without accounting for the solvent.

Upon the X-ray irradiation of frozen methylthiirane/$CFCl_3$ solutions (0.3–0.5 mol%) at 77 K, a complex multiplet EPR spectrum can be detected [Figure 1(*a*)]. Correspondingly, in the optical spectrum, absorbance arises in the region of 380–750 nm. As a result of photobleaching, which removes the species attributed to matrix-related intermediates,[18] and the subsequent action of light with λ = 546 nm, a multiplet signal with well-resolved hyperfine structure is revealed in the EPR spectra [Figure 1(*a*)], while an absorption band at 530 nm perishes in the optical absorption spectra with the corresponding increase in an absorption band at 385–390 nm. Owing to the subsequent action of light with λ = 405 nm upon the sample, a seven-line signal with splittings of 1.6–1.7 mT arises in the EPR spectra [Figure 1(*d*)], whereas this leads to an almost complete restoration of a band at 530 nm in the absorption spectra. The specified process can be repeated several times, leading to the restoration of the corresponding signals in the EPR and optical spectra and pointing to photoreversibility, similar to that observed for the methyloxirane RC.[5]

The application of the parameters calculated for **2** (Table 1) allows for the satisfactory fitting of the EPR spectrum [Figure 1(*a*)] that can be detected alongside the absorption band at 385–390 nm in the optical absorption spectra if anisotropy is assumed for the *g*-tensor while the hfc constants with all of the hydrogen atoms are approximated as isotropic [Figure 1(*b*)]. Relying upon the fitting results based on the quantum chemical calculations, we assume that the species characterized by an absorption band at 385–390 nm can be attributed to the cyclic form of the methylthiirane RC. The position of the maximum in the short-wave absorption band provides an additional argument for this attribution (for the cyclic methyloxirane RC form, the maximum lies at 435 nm[5]).

The EPR spectrum attributed to the paramagnetic species characterized by the absorption band at 530 nm in the optical spectra can be adequately fitted using the magnetic resonance parameters (Table 1) obtained in quantum chemical calculations for **1** with the subsequent optimization in the approximation of free rotation for the methyl group [Figure 1(*e*)]. Note that absorption in that spectral region is characteristic of pseudoallylic forms for various methyloxirane RCs (for the methyloxirane RC, the absorption maximum of an analogous form lies at 525 nm[5]). Therefore, the open pseudoallylic form **1** of methylthiirane RC is predominantly yielded in the test system upon the action of light with λ = 405 nm. The same form is found in the EPR spectra of the samples immediately upon radiolysis at 77 K (along with cyclic form **2**). Previous studies of the unsubstituted thiirane RC in freonic matrices at 77 K have only revealed them in their cyclic form.[9]

Table 1 UKS/B3LYP/NO7D calculation results along with fitting results for hfc constants with hydrogen atoms and *g*-tensor components for various forms of the methylthiirane RC (for forms **1** and **2**, H^1 is the methine atom; H^2, H^3 are the methylene atoms; and H^4, H^5, H^6 are the methyl atoms).

RC		$a_{iso}(H^1)$/mT	$a_{iso}(H^2)$/mT	$a_{iso}(H^3)$/mT	$a_{iso}(H^4)$/mT	$a_{iso}(H^5)$/mT	$a_{iso}(H^6)$/mT
1	Quantum chemical	–1.30	–1.76	–1.82	2.90	0.03	2.94
					a(3H) = 1.96		
		g_{xx} = 1.999, g_{yy} = 2.002, g_{zz} = 2.002; g_{iso} = 2.001					
	Fitting for the EPR spectrum of **1** (optimized)	1.49	1.37	1.37	1.98	1.98	1.98
		g_{iso} = 2.001					
2	Quantum chemical	1.31	2.03	1.79	–0.05	–0.05	0.46
					a(3H) = 0.19		
		g_{xx} = 2.002, g_{yy} = 2.026, g_{zz} = 2.037					
	Fitting for the EPR spectrum of **2** (non-optimized[a])	1.31	2.03	1.79	0.19	0.19	0.19
		g_{xx} = 2.000, g_{yy} = 2.028, g_{zz} = 2.039					
3	Quantum chemical	0.03	0.04	0.06	0.07	0.04	0.02
		g_{xx} = 2.003, g_{yy} = 2.016, g_{zz} = 2.022					

[a] In this particular case, optimization does not lead to a better qualitative agreement between the fitted and experimental spectra.

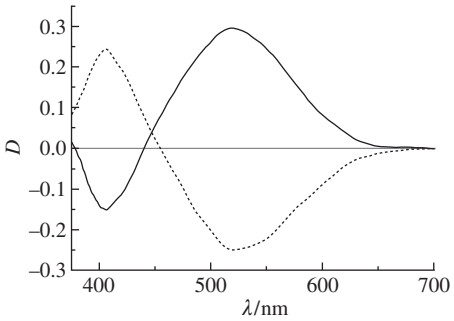


Figure 2 Difference absorption spectra detected upon the action of light with λ = 546 nm on the irradiated methylthiirane/CF_3CCl_3 sample at 77 K (solid line) and the subsequent action of light with λ = 405 nm (dotted line).

Despite the computations pointing to form **3** being the most stable among the possible methylthiirane forms, its magnetic resonance parameters do not allow for placing it anywhere in the EPR spectra experimentally observed in freonic matrices. Consequently, the detected reaction can be attributed to the reversible photocyclization of the pseudoallylic form of the methylthiirane RC.

The experiments with frozen irradiated methylthiirane/CF_3CCl_3 solutions (0.3–0.5 mol%) at 77 K indicated that the reversible photoprocesses in this freonic matrix were analogous to the above ones (we also could repeat them several times). Note that the detected EPR [Figure 1(*f*)] and optical absorption (Figure 2, absorption band at 520 nm) spectra for **1** (the open form of the methylthiirane RC) are almost identical to those detected in the $CFCl_3$ matrix. However, the absorption maximum of species **2** (Figure 2, absorption band at 410 nm) is noticeably shifted to the long-wave region in comparison with its spectrum in $CFCl_3$, while the set of hfc constants obtained for **2** in computations (Table 1), successfully employed to fit the EPR spectrum of the cyclic methylthiirane RC in $CFCl_3$, does not provide sufficient accuracy in the interpretation of the EPR spectrum detected in the CF_3CCl_3 matrix under analogous conditions [Figure 1(*c*)]. Since quantitative reversible phototransformations occur in the methylthiirane RC in both of the freonic matrices, with spectroscopic characteristics of form **1** being close in $CFCl_3$ and CF_3CCl_3, we suggest that the absorption band at 410 nm and the EPR spectrum in Figure 1(*c*) belong to **2**, the cyclic form of the methylthiirane RC. Unfortunately, the wide variety of the quantum chemical techniques employed in this work did not allow us to adequately interpret the EPR spectrum of form **2** in CF_3CCl_3. The underlying reasons behind this disparity may be assigned to specific interactions between the methylthiirane RC and the CF_3CCl_3 matrix, with the red shift of the absorption maximum of **2** (as compared to its position in $CFCl_3$) pointing towards this explanation.

Based on the comparison of the EPR and optical absorption spectra in the CF_3CCl_3 matrix, where methylthiirane RCs could be yielded in higher concentrations, we have estimated the molar absorption coefficients of forms **1** and **2** in their absorption bands: $\varepsilon_{546} \approx 8.8 \times 10^2$ dm^3 mol^{-1} cm^{-1} and $\varepsilon_{436} \approx 9.4 \times 10^2$ dm^3 mol^{-1} cm^{-1}, respectively. These values allowed us to estimate the quantum yields of the photochemical transformations of methylthiirane RCs in the CF_3CCl_3 matrix at 77 K: $\varphi_{546} \approx 0.7$ upon the action of light with λ = 546 nm on form **1** and $\varphi_{436} \approx 0.1$ upon the action of light with λ = 436 nm on form **2**. Reversible transformations of methyloxirane RCs are also characterized by similarly high quantum yields.[5]

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