

The nature and photochemistry of 2,2-dimethyloxirane radical cations in freonic matrices at 77 K

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DOI: 10.1016/j.mencom.2011.04.015

The X-ray irradiation of 2,2-dimethyloxirane in freonic matrices at 77 K results in the trapping of a cyclic radical cation form, presumably, complexed with a matrix molecule, which transforms into a C-centered distonic radical cation under the action of light.

Previous studies revealed that oxirane radical cations (RCs),^{1–4} including those of various methyloxiranes, were stabilized in ring-open forms in freonic matrices at 77 K. The stabilization of primary cyclic forms has been suggested at lower temperatures (4.2 K) for Freon 11, while warming the sample above 40 K supposedly leads to a bond cleavage in the oxirane ring.² However, the characteristics of paramagnetic centers observed at temperatures lower than 40 K (*i.e.*, magnetic resonance parameters, optical absorption spectra, *etc.*) were not reported in ref. 2. Note that published data⁴ indicate that the absorption spectra obtained for irradiated solutions of 2,2-dimethyloxirane in Freon 11 at 77 K differ from those of other oxiranes.

The aim of this study was to elucidate the nature of paramagnetic species stabilized upon the irradiation of 2,2-dimethyloxirane in Freon 11 and Freon 113a at 77 K[†] and to reveal the mechanism of their photochemically induced transformations.

The X-ray irradiation of frozen 0.5 mol% 2,2-dimethyloxirane/Freon 11 solutions at 77 K results in a well-resolved multiplet signal with at least 20 nearly equidistant lines in the EPR spectrum [Figure 1(a), the splitting amounts to 0.65–0.7 mT]. At the same time, a broad band with a maximum located at 435–440 nm arises in the optical absorption spectrum ($\epsilon_{436} \approx 7.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $f \approx 0.19$), which is characteristic of various ether RCs ($\lambda_{\text{max}} \approx 430\text{--}450 \text{ nm}$, $f \approx 0.1$).^{7–9} A similar absorption band with a maximum shifted to 425 nm ($\epsilon_{436} \approx 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $f \approx 0.25$) appears in the spectra of irradiated 2,2-dimethyloxirane/Freon 113a solutions at 77 K. However, only a poorly resolved signal could be detected in the corresponding EPR spectrum [Figure 1(b)], while warming the sample to 111 K led to a somewhat better resolution in the hyperfine structure and at 140 K the signal was finally proved to be of a multiplet nature (we observed practically equidistant lines with the splitting of $\sim 0.6 \text{ mT}$ [Figure 1(c)], substantially resembling those observed in a matrix of Freon 11). The transformations are reversed upon subsequent

[†] CFCl₃ (Freon 11, $\sim 99\%$, Aldrich) and CF₃CCl₃ (Freon 113a, obtained synthetically⁵ from Freon 113, 99%, Aldrich; the main product constituted more than 99% of the mixture) were used; in certain cases, Freons were purified additionally by a standard procedure. 2,2-Dimethyloxirane (97%, Aldrich) was used as received.

The dimethyloxirane/Freon solutions (0.3–0.5 mol%) were inserted into quartz or SK-4B glass tubes, evacuated to $\sim 0.1 \text{ Pa}$ and irradiated with X-rays at 77 K to doses of 2–4 kGy. A 5BHV6-W X-ray source (33 kV, 80 mA) was used.

UV and EPR spectroscopy techniques were employed; the photochemical experiments and quantum chemical computations were performed as described earlier for the isomers of dimethyloxirane.⁶

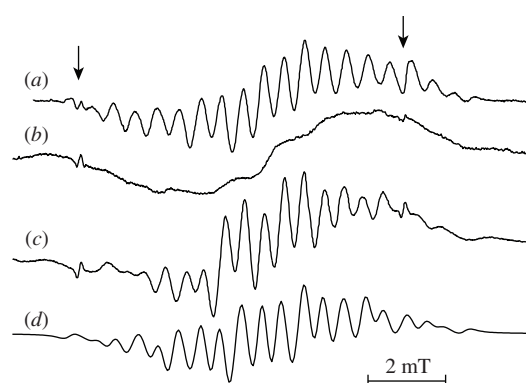
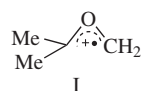
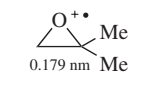
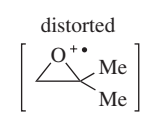


Figure 1 EPR spectra of the irradiated solutions of 2,2-dimethyloxirane: (a) in Freon 11 at 77 K (model background signal pertaining to the matrix subtracted), (b) in Freon 113a at 77 K (experimental background signal pertaining to the matrix subtracted), (c) in Freon 113a at 140 K, (d) the results of modeling for the spectrum in Freon 11 at 77 K [$a(4\text{H}) = 1.63 \text{ mT}$, $a(3\text{H}) = 1.13 \text{ mT}$, $a(^{19}\text{F}) = 0.67 \text{ mT}$]. Arrows show the components belonging to the spectrum of Mn²⁺ ions used as an external standard.

cooling to 77 K. These observations lead us to believe that the species stabilized in the two Freons have the same nature.

As computations show conclusively (Table 1), this kind of EPR spectra cannot be accounted for by ring-open form I of this RC. The C–O bond cleavage would have led to an RO-type radical; such species are characterized by very large hfc constants with β -protons (5.2–5.5 mT for neutral radicals^{10,11} and $> 8 \text{ mT}$ for

Table 1 Calculated hfc (mT) for various forms of 2,2-dimethyloxirane RCs.

Structure ^a	$a(3\text{H-Me})$	$a(1\text{H-CH}_2)$
	$\sim 0.7; \sim 1.3$	$\sim 2.2; \sim 2.3$
	$\sim 1.6; \sim 1.2$	$\sim 1.6; < 0.1$
	$\sim 1.6; \sim 1.4$	$\sim 1.5; \sim 0.7$

^aI – the ring-open form of RC (C–C bond cleavage); II – cyclic RC structure with the elongated C–C bond; III – distorted cyclic RC structure (see the text).

distonic RC,¹² which, obviously, do not agree with the experimental spectrum). Meanwhile, cyclic form II with a substantial elongation of the C–C bond (from 0.146 nm in the uncharged original molecule to 0.179 nm in form II), which was found in calculations, can be characterized using the following set of expected hyperfine constants (hfc): $a(3\text{H-Me}) \approx 1.6$ mT, $a(3\text{H-Me}) \approx 1.2$ mT, $a(1\text{H-CH}_2) \approx 1.6$ mT and $a(1\text{H-CH}_2) < 0.1$ mT (with the assumption of averaging calculated hfc constants for each methyl group as the arithmetic mean for the three values). This set can be used to fit the experimental spectrum, but only if we assume an additional splitting [~ 0.6 mT, Figure 1(d)] to it. Specifically, this splitting can originate from the distortion of the original cyclic RC structure (owing to matrix effects). As preliminary computations showed (see Table 1), a slight deviation from the optimal calculated geometry of the cycle (namely, that arising from the distortion of dihedral angles) could result in an increase of up to 0.7 mT for the second methylene proton hfc constant (while the other hfc constants change insignificantly). Note that this deformation affects the calculated energy only slightly. Detailed analysis would require more demanding and extensive calculations on this issue, which are in progress. Alternatively, the matrix effect may be associated with the formation of a π -complex yielded by the cyclic RC and a Freon 11 molecule. In this case, the additional splitting can be ascribed to hyperfine interaction with the fluorine nucleus. It is known¹³ that small hfc constants (0.5–1.0 mT), assigned to interactions with ¹⁹F nuclei in Freon molecules, are observed in the EPR spectra of various RCs. At present, we are unable to make an unequivocal choice between these two options. Nevertheless, it is necessary to emphasize that, in any case, we are dealing with a cyclic form of the RC with an elongated C–C bond. The feasibility of a similar oxiranyl RC structure was discussed earlier.¹⁴

In the case of the poorly defined EPR spectrum detected in irradiated solutions of 2,2-dimethyloxirane in Freon 113a at 77 K, the RC-matrix molecule π -complex hypothesis can be applied as well. However, in this instance, a significant broadening of the spectral lines [Figure 1(b)] should be taken into account. Presumably, this phenomenon can be associated with variations in the RC dynamics for different freonic matrices.

Note that the optical absorption of the primary species observed in this work is somewhat blue-shifted, as compared to that of the cyclic form of the 2,3-dimethyloxirane RC in the same matrix⁶ ($\lambda_{\text{max}} = 425\text{--}440$ and 465 nm, respectively). This difference may reflect the effect of complex formation on the RC optical absorption properties in the case of 2,2-dimethyloxirane.

The action of light with $\lambda = 436$ nm at 77 K results in the transformation of initial species in both Freons to new radicals, which can be characterized by a triplet of septets in the EPR spectrum: $a(6\text{H}) \approx 0.6$ mT and $a(2\text{H}) \approx 1.9$ mT [Figure 2(a)]. The best-fit simulation for this experimental EPR spectrum [Figure 2(b)] suggests the following set of hfc constants: $a(6\text{H}) = 0.58$ mT, $a(1\text{H}) = 1.85$ mT and $a(1\text{H}) = 1.96$ mT. The decay of induced absorption at $\lambda > 380$ nm (namely, a band with $\lambda_{\text{max}} = 425\text{--}440$ nm) correlates with the transformation of the initial EPR spectrum described above. The experimental data conclusively show that the photolysis product is a C-centered radical with both of its methyl groups intact (that is, no intramolecular hydrogen atom transfer occurs). We conclude that this species is a distonic RC, yielded from a complex composed of a matrix molecule and the cyclic 2,2-dimethyloxirane RC with the elongated C–C bond (or from a distorted cyclic RC with the elongated C–C bond). Unfortunately, the EPR spectrum corresponding to the photolysis product cannot be fitted adequately with the use of hfc constants obtained for ring-open form I (see Table 1) in our quantum chemical calculations (the computations provide us with significantly higher values for hfc constants with protons in one of the methyl groups).

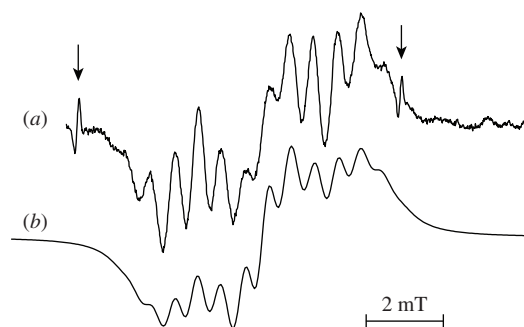


Figure 2 EPR spectra of the irradiated solutions of 2,2-dimethyloxirane in Freons after exposing them to light ($\lambda = 436$ nm) at 77 K: (a) with the experimental background signal pertaining to the matrix subtracted, (b) the results of modeling for the EPR spectrum of the photolysis product. Arrows show the components belonging to the spectrum of Mn^{2+} ions used as an external standard.

This may be ascribed either to overestimation of the spin density delocalisation 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 cyclic form in the same spectral region (in the latter case, the yield was found to be valued around 0.07 in Freon 113a or 0.03 in a matrix of Freon 11).⁶

We would like to acknowledge the RAS Interdepartmental Supercomputer Center for granting the computational resources. This study was supported by the Russian Foundation for Basic Research (project no. 10-03-00195).

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Received: 9th December 2010; Com. 10/3639