

Reversible photochemical transformations of *cis*- and *trans*-2,3-dimethyloxirane radical cations in freonic matrices at 77 K

Ivan D. Sorokin, Vladimir I. Feldman, Ol'ga L. Mel'nikova,
 Vladimir I. Pergushov, Daniil A. Tyurin and Mikhail Ya. Mel'nikov*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
 Fax: +7 495 939 1814; e-mail: melnikov46@mail.ru

DOI: 10.1016/j.mencom.2011.04.014

The reversible photoinduced transformations of 2,3-dimethyloxirane radical cations in freonic matrices at 77 K are related to the conversion between the *cis*- and *trans*-isomers of an open form and a cyclic form.

The structure and photochemistry of radical cations (RCs) originating from small heterocycles are of considerable interest since these species exhibit high lability and reveal a variety of reaction pathways. It has been established^{1–4} that the RCs of oxiranes are stabilized in the ring-open form resulting from C–C bond cleavage in freonic matrices at 77 K. According to reported data,⁴ the action of visible light (400–600 nm) on the irradiated solutions of methyl-oxirane and *cis*-2,3-dimethyloxirane in Freon 11 at 77 K leads to irreversible changes in the optical and EPR spectra, which were attributed to the *cis*–*trans* isomerization of the ring-open forms of the oxirane RC.

The aim of this work was to identify paramagnetic species stabilized upon the irradiation of *cis*- and *trans*-2,3-dimethyloxirane in Freons at 77 K and to study their photochemically and thermally induced transformations.[†]

The nature of the paramagnetic centers formed upon the low-temperature irradiation of *cis*- and *trans*-2,3-dimethyloxiranes in Freons, as well as the pattern of their photochemical and thermal transformations, were found identical (as revealed by both EPR and optical spectroscopy). For this reason, we will not specify *cis*- or *trans*-isomer in the further discussion of our results.

The X-ray irradiation of the frozen 0.3 mol% 2,3-dimethyloxirane/Freon 113a solutions at 77 K results in an EPR spectrum [Figure 1(a)], which can be fitted as a superposition of two signals characterized by nearly binomial patterns consisting of nine and eight equidistant lines, respectively.

The former signal appears to be a result of an unpaired electron interacting with eight equivalent protons, and it can be charac-

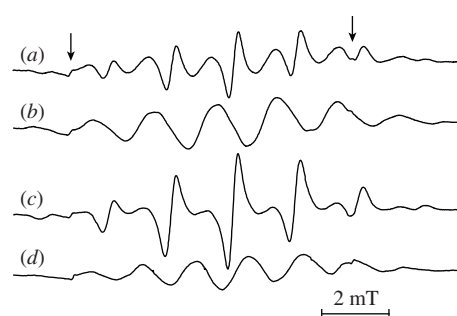


Figure 1 EPR spectra of the irradiated solutions of 2,3-dimethyloxirane in Freon 113a: (a) measured immediately after X-ray irradiation at 77 K, (b) after exposing the irradiated sample to light ($\lambda = 578$ nm) at 77 K, (c) after subsequent action of light with $\lambda = 436$ nm at 77 K, (d) after warming the sample to 111 K. Arrows show the components belonging to the spectrum of Mn^{2+} ions, used as an external standard.

terized by the hyperfine coupling (hfc) constant $a(8\text{H}) = 1.9$ mT, while the latter can be assigned to a species with seven equivalent protons and virtually identical hfc constant. The optical absorption spectrum recorded at 77 K shows the appearance of a radiation-induced absorption band in the region of $\lambda > 380$ nm. A standard photobleaching technique (photolysis with $\lambda > 690$ nm light) was used to eliminate the ionic products of matrix irradiation.¹³ The subsequent action of light at $\lambda = 578$ nm at 77 K led to a nearly complete transformation in the EPR spectra: the nine-line spectrum was converted to an eight-line spectrum, while the total amount of paramagnetic species remained virtually unchanged [Figure 1(b)].

At the same time, an absorption band at 575 nm in the optical spectra disappears, while the intensity of a band at 465 nm increases

A high-pressure mercury lamp (DRSh-250) supplied with glass filters and/or interference filters [$\lambda = 436$ nm, peak transmission (T_{max}) = 27%, $\Delta\nu_{1/2} = 2400$ cm^{-1} ; $\lambda = 578$ nm, $T_{\text{max}} = 30\%$, $\Delta\nu_{1/2} = 297$ cm^{-1}] was used as a light source. The absolute light intensities at the specified wavelengths were 1.28×10^{-8} and 2.2×10^{-9} Einstein $\text{cm}^{-3} \text{s}^{-1}$, respectively. Quantum yields in photochemical reactions were derived from the increase in the number of resulting paramagnetic species or the decrease in the number of initial RC versus the light dose absorbed by the sample.

The 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 calculations.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 PRIRODA software package was employed for computations.¹²

[†] CFCl_3 (Freon 11, ~99%, Aldrich), CF_3CCl_3 (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 using a standard procedure. Commercial *cis*- and *trans*-2,3-dimethyloxiranes (97%, Aldrich) were used as received.

The dimethyloxirane/Freon solutions (0.3–0.5 mol%) were inserted into quartz or SK-4B glass tubes, evacuated to ~0.1 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.

The EPR spectra of paramagnetic species were recorded on a Varian E-3 spectrometer. The absolute error in the concentration of paramagnetic species determined by EPR was within $\pm 20\%$. The EPR spectra were simulated with the use of the PEST WinSim and Simfonia⁶ standard software packages. 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 in the electron transitions were derived from the equation⁷ $f \approx 4.32 \times 10^{-9} \varepsilon_{\text{max}} \Delta\nu_{1/2}$, where ε_{max} refers to the molar absorption coefficient at the absorption band maximum ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), and $\Delta\nu_{1/2}$ is the half-width of the absorption band (cm^{-1}).

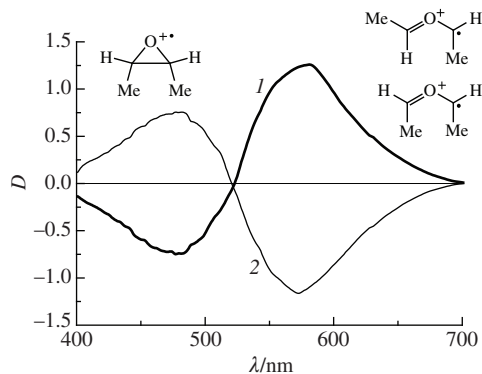
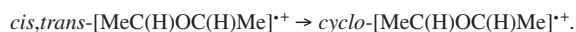


Figure 2 Difference optical absorption spectra measured after exposing the irradiated solutions of 2,3-dimethyloxirane in Freon 113a to light with different wavelengths at 77 K: (1) $\lambda = 578$ nm and (2) $\lambda = 436$ nm.

(Figure 2). 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 [Figure 1(c)] and optical absorption spectra (Figure 2). 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 made it possible to estimate the absorption coefficients for the species involved in the transformations: $\varepsilon_{578} \approx 5.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ($f \approx 0.56$) and $\varepsilon_{436} \approx 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ($f \approx 0.30$), respectively. On the basis of experimental and published⁴ data, we believe that the nine-line EPR spectrum [$a(8\text{H}) = 1.9$ mT] and the 575 nm absorption band are associated with the open configuration of the 2,3-dimethyloxirane RC, which is isoelectronic to the allyl radical (characterized by a delocalized π -electron structure). This species ($\text{MeCHO}^+\text{CHMe}$) resulting from the C–C bond cleavage may exist in both *cis*- and *trans*-forms. On the other hand, the eight-line EPR spectrum [$a(7\text{H}) = 1.9$ mT] can be attributed to the cyclic form of the 2,3-dimethyloxirane RC.

This interpretation is supported by the results of quantum chemical calculations, which show that such hfc constants are characteristic of the cyclic *trans*-isomer of the RC possessing an elongated C–C bond (~ 0.178 nm). The feasibility of a similar cyclic RC formation (including the notion of an elongated C–C bond) had been discussed earlier.¹⁴ Furthermore, the experimental absorption spectrum of the species revealed in our studies resembles that of the trimethylene oxide RC (detected in freonic matrices at 77 K). The latter RC exhibits an absorption maximum at 450 nm¹⁵ (although the absorption coefficient is substantially lower, $\varepsilon = 3.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, possibly, due to the transition being symmetry forbidden in this case).

Proposed scheme:



The quantum yields of the photochemical transformations of the RC at 77 K are $\varphi_1 \approx 0.39$ in the case of long-wave light ($\lambda = 578$ nm) and $\varphi_2 \approx 0.07$ in the case of short-wave light ($\lambda = 436$ nm).

According to our quantum chemical computations and data reported previously,⁴ the *cis*- and *trans*-isomers of the 2,3-dimethyloxirane RC should give similar optical spectra and magnetic resonance parameters. This is in apparent conflict with the experimental data. For this reason, we cannot ascribe the observed photochemical reactions of the 2,3-dimethyloxirane RC to the *cis*–*trans* transitions between the isomers of the RC open form.

Warming the sample containing the cyclic 2,3-dimethyloxirane RC (stabilized at 77 K) up to 111 K leads to the conversion of the

eight-line EPR spectrum [$a(7\text{H}) = 1.9$ mT] into the nine-line spectrum [$a(8\text{H}) = 1.7$ mT] [Figure 1(d)], while the optical spectrum remains unchanged. These transformations are reversible upon subsequent cooling (77 K), which can be explained by intramolecular motion dynamics in one of the RC *trans*-isomers (the one with the elongated C–C bond). These dynamics result in an increase in the hfc constant at one of the methine groups. Note that, in the case of the sample containing the open 2,3-dimethyloxirane RC, warming (from 77 to 111 K) results in transformation of the initial nine-line EPR spectrum [$a(8\text{H}) = 1.9$ mT, Figure 1(c)] to another nine-line spectrum [$a(8\text{H}) = 1.7$ mT, Figure 1(d)]. This conversion is accompanied by a change in the optical absorption spectrum (the band at 575 nm disappears while the intensity of the band at 465 nm increases). Cooling the sample down to 77 K results in the above transition (nine-line to eight-line signal) in the EPR spectra. Therefore, a slight increase in the temperature allows the cyclization of the 2,3-dimethyloxirane RC open form to occur in the matrix of Freon 113a. This result seems unexpected. Indeed, we may note that photocyclization is known for allyl radicals.^{16,17} Meanwhile, the thermal nature of the process for the isoelectronic RC revealed in the present study can only be explained by specific solvation of the RC cyclic form (in contrast to the open form), which is probably determined by variations in charge localization for the two types of structures.

A similar situation occurs for the intermediates produced in irradiated 2,3-dimethyloxirane in a Freon 11 matrix (some deviations can be ascribed to variations in the dynamics of paramagnetic particles in those matrices). Thus, we can conclude that the photochemical transformations of 2,3-dimethyloxirane radical cations (reported in ref. 4) can be attributed to the conversion between the *cis*-, *trans*-isomers of the open form and the cyclic form rather than to the *cis*–*trans* photoisomerization proposed earlier.

This study was supported by the Russian Foundation for Basic Research (project no. 10-03-00195).

References

- L. D. Snow and Ff. Williams, *Chem. Phys. Lett.*, 1988, **143**, 521.
- X.-Zh. Qin, L. D. Snow and Ff. Williams, *J. Phys. Chem.*, 1985, **89**, 3602.
- J. Rideout, M. C. R. Symons and B. Wt. Wren, *J. Chem. Soc., Faraday Trans.*, 1986, **82**, 167.
- K. Ushida, T. Shida and K. Shimokoshi, *J. Phys. Chem.*, 1989, **93**, 5388.
- W. T. Miller, E. W. Fager and P. H. Griswald, *J. Am. Chem. Soc.*, 1950, **72**, 705.
- D. R. Duling, *J. Magn. Reson.*, 1994, **104B**, 105.
- Einführung in die Photochemie*, ed. G. O. Bekker, Deutscher Verlag der Wissenschaften, Berlin, 1976.
- C. Adamo and V. Barone, *Chem. Phys. Lett.*, 1998, **298**, 113.
- C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
- D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
- D. N. Laikov, *Chem. Phys. Lett.*, 2005, **416**, 115.
- D. N. Laikov and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 804 (*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 820).
- M. Ya. Mel'nikov, D. V. Baskakov and V. I. Feldman, *Khim. Vys. Energ.*, 2002, **36**, 346 [*High Energy Chem. (Engl. Transl.)*, 2002, **36**, 309].
- T. Clark, *J. Chem. Soc., Chem. Commun.*, 1984, 666.
- (a) M. Ya. Mel'nikov, V. N. Belevskii, A. D. Kalugina, O. L. Mel'nikova, V. I. Pergushov and D. A. Tyurin, *Mendeleev Commun.*, 2008, **18**, 305; (b) M. Ya. Mel'nikov, A. D. Kalugina, O. L. Mel'nikova, V. I. Pergushov and D. A. Tyurin, *Khim. Vys. Energ.*, 2009, **43**, 355 [*High Energy Chem. (Engl. Transl.)*, 2009, **43**, 303].
- K. Holtzhauser, C. Cometta-Morini and J. E. M. Oth, *J. Phys. Org. Chem.*, 1990, **3**, 219.
- V. A. Radzig, L. Yu. Ustynyuk, N. Yu. Osokina, V. I. Pergushov and M. Ya. Mel'nikov, *J. Phys. Chem.*, 1998, **102/27**, 5220.

Received: 27th September 2010; Com. 10/3600