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Photochemical transformations of O-containing radical-cations at low temperatures in CF_3CCl_3 matrix.

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Electron Paramagnetic Resonance spectroscopy is widely used to determine the behavior of paramagnetic species, such as ions, radical ions, complexes of transition metals, etc.

Radical cations (RC) are species that have unpaired electrons, similar to radicals, as well as a positive charge, similar to cations. The studies of the mechanisms guiding the reactions of electronically excited radicals and radical ions have attracted considerable interest. This is due to the significance of the processes various substances undergo under extreme conditions. The RC formed upon the irradiation of different solutions of oxiranes in the CF_3CCl_3 matrix at 77 K is described in this study. The purpose of this investigation was to find out how the nature of the substituents in the oxirane ring affected the structure of the resulting RC and its further transformations under the action of light.

Electron Paramagnetic Resonance and UV-vis absorption spectroscopy as well as quantum chemical calculations were used in this investigation. Different types of RC were formed upon the irradiation of solutions of oxiranes (epoxides) in freon-113a (CF_3CCl_3) at low temperatures (77 K) under similar conditions: for cyclopentene oxide and cyclohexene oxide, the RCs with elongated C-C bonds in their oxirane rings were produced. The RC of methyloxirane, 2,3-dimethyloxirane and tetramethyloxirane were stabilized in their ring-open forms (the distance between the carbon atoms in their oxirane rings exceeded the equilibrium length of the C-C bond).

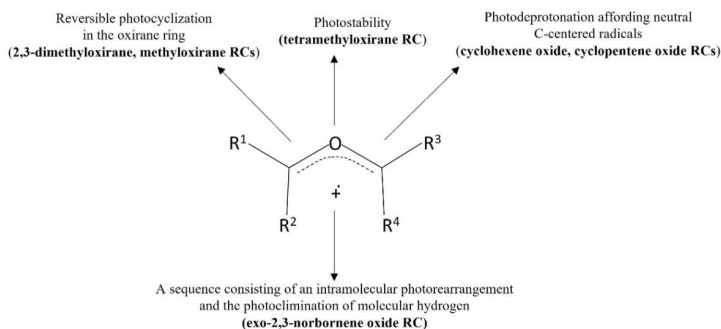
Beside these oxiranes, we studied exo-2,3-norbornene oxide and its corresponding RC since the structure of this precursor molecule included the structural motifs of cyclohexene oxide and cyclopentene oxide for which the photochemical transformations had already been established [1, 2].

The structure and nature of the underlying photochemical transformations of RC were established. It was found that the RC of methyloxirane [3] and 2,3-dimethyloxirane [4] underwent reversible photocyclization concerning the C—C bond in the oxirane cycle, while the tetramethyloxirane RC did not undergo any reactions under the action of light [3].

Upon the action of light, irreversible proton abstraction in the ring-open form of the cyclopentene oxide RC occurred, affecting the bridgehead carbon. This afforded unstable 6-oxabicyclo[3.1.0]hexan-1-yl radicals, which underwent rearrangement to form ring-open terminal C-centered alkyl radicals detected as final products [2]. The RC of cyclohexene oxide underwent similar phototransformations as RC of cyclopentene oxide [1].

It was found that, upon absorption of light, the C-C bond was formed again in the oxirane ring of the exo-2,3-norbornene oxide RC, with the spin and charge both localized in the cycloalkyl fragment. The resulting paramagnetic species is stable at 77 K. In a reaction similar to what was earlier reported for other RC [5], it underwent photoelimination of H_2 , affording the 3-oxatricyclo[3.2.1.0^{2,4}]oct-5-ene RC.

A sequence consisting of an intramolecular photorearrangement and the photoelimination of molecular hydrogen was found for the RC of exo-2,3-norbornene oxide [6]. Different mechanisms of phototransformations of RCs of some oxiranes are summarized in the scheme 1 [7].



Scheme 1. Different mechanisms of phototransformations of radical cations of oxiranes [7]

Thus, it can be concluded that the structure of the RC dramatically affects the further mechanism of transformations of these RCs under the action of light.

The quantum chemical calculations carried out for different types of RC of oxiranes showed that, upon radiolysis, either RC with elongated bonds between the carbon atoms in the oxirane ring or RC in their ring-open forms were formed.

Using UV-vis and Electron Paramagnetic Resonance spectroscopy allowed us to determine the sequence of photochemical transformations of the afforded RCs. Hence, the conclusion is that the further transformations of RC formed upon radiolysis in freon matrices cardinally depend on the nature of substituents at the oxirane ring.

The observed commonality in the nature of indirect ionization products for various oxirane-derived RCs cannot be extended to other parameters to predict the pathways of their phototransformations.

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