10. On the Structure of Oxirane Molecular Cation

Preliminary Communication

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Dedicated to Prof. *Christoph Tamm* on the occasion of his 60th birthday

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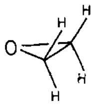
Summary

A recent controversy on the interpretation of the ESR spectrum of ionized oxirane is clarified on the basis of the electronic absorption spectra of ionized tetramethyloxirane and 9,10-octalineoxide. The results favour a ring-opened structure for oxirane molecular cation, resulting from C–C bond cleavage and being iso-π-electronic to allyl radical.

Two research groups [1] [2] have recently reported the ESR spectrum of oxirane **1** ionized in a *Freon* matrix using the techniques pioneered by *Shida & Kato* [3]. Both agree in the basic experimental finding of a quintet of protons with a hyperfine coupling of 16 G. However, they differ decisively in the interpretation of these findings: while *Symons & Wren* [1] conclude that ionized **1** retains a ring-closed structure (*i.e.* $\mathbf{1}^{+}$), *Williams et. al.* [2] favour the ring-opened structure $\mathbf{2}^{+}$.



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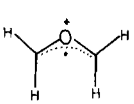

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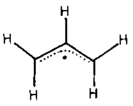

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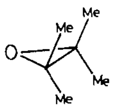

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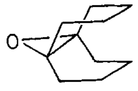

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To clarify this important matter we set out to compare the electronic absorption (EA) spectra of two similarly alkyl-substituted ionized oxiranes, one of which ($\mathbf{4}^{+}$) could open to give an allyl-like structure analogous to $\mathbf{2}^{+}$ while this possibility remains unaccessible to the other ($\mathbf{5}^{+}$) due to steric constraints.

Fig. 1 shows the EA spectra of ionized **4** and **5**¹) in two different media (one of them being identical to that used in the cited ESR studies). It is obvious that the two spectra differ substantially although they were obtained under identical experimental conditions²). Apart from the strong matrix cation absorptions peaking at 305 nm for

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¹) The oxiranes were prepared by oxidation of the corresponding olefins with *m*-chloroperbenzoic acid and purified by spinning-band distillation (**4**) or preparative GC (**5**).

²) 0.02-M solutions of the neutral precursors in the *Freons* indicated in *Fig. 1*, 4 h X-ray irradiation [5] in a 0.5-mm cuvette at 77 K.

F11 and 390 nm for *F113*, ionized **5** shows no discernible absorption in the near-UV/VIS range while ionized **4** gives a relatively broad band centered at 560 nm. Assuming effective C_{2v}-symmetry for both ions this is precisely what one would expect on the basis of qualitative theoretical considerations outlined below.

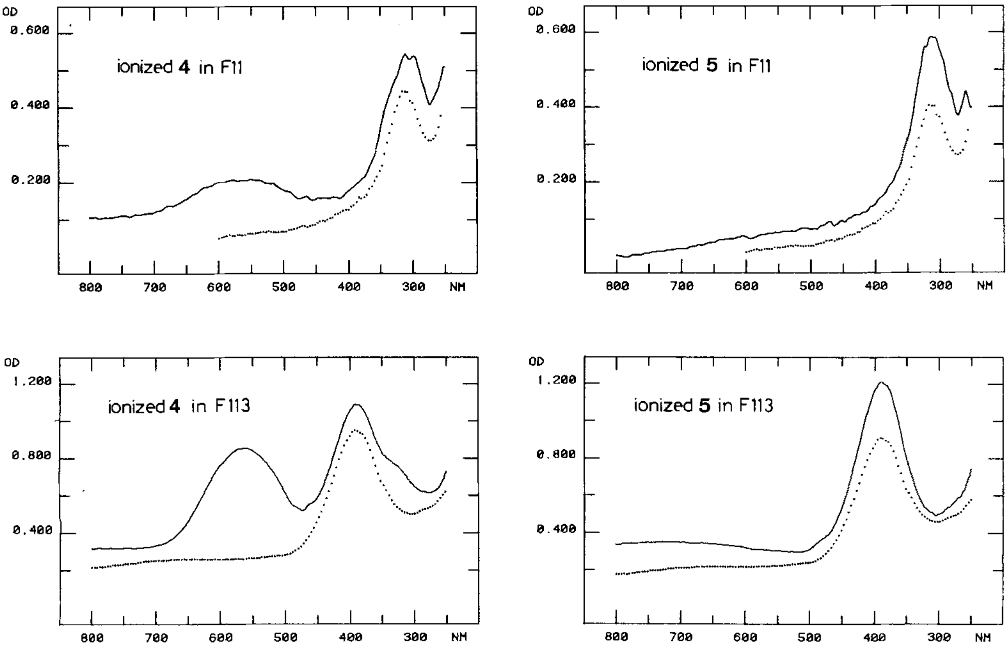

Fig. 1. *Electronic absorption spectra of 4 and 5 after X-ray irradiation in* F11 ($CFCl_3$) *or* F113 ($CFCl_2$–CF_2Cl). The spectra measured prior to irradiation were digitally subtracted. The dotted lines show the spectra of the respective ionized matrix materials (same irradiation time).

System $\mathbf{2}^+$ is iso-π-electronic with allyl radical **3** which has three π-orbitals two of which are symmetrically disposed about the NBMO level. Consequently a degenerate pair of lowest excited doublet configurations of b_1-symmetry (x and y in *Fig. 2*) arise which combine to give two first-order states $^2B_1$ (x + y) and $^2B_1$ (x – y) with CI coefficients of equal magnitude. The electronic transition to the lower energy state has a zero transition moment in a nearest-neighbour π-approximation; indeed, only a very weak absorption is observed for **3** at 408.5 nm [5]. Substitution of the central CH-unit by O^+ lifts the degeneracy of these first two excited configurations such that the HOMO-LUMO excited one (x) becomes lower-lying in energy and dominating the lowest excited state. Equally, the respective transition moments will no longer cancel for $^2B_1$ (x – y). This yields some intensity to the first electronic transition which is concomitantly shifted to longer wavelengths, in accord with open-shell PPP-CI-calculations (**3**:

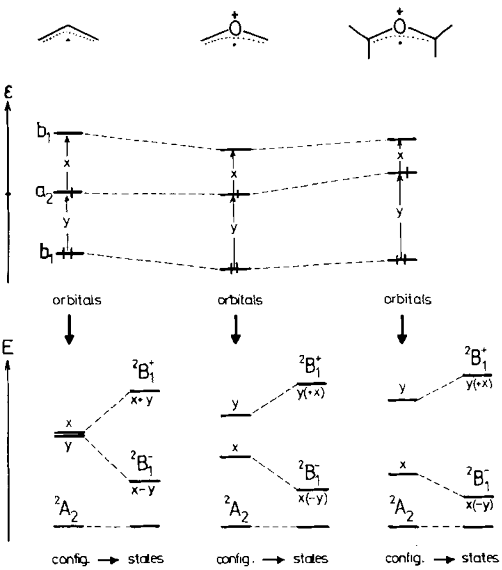

Fig. 2. *π-Orbitals* (upper part), *configurations and states* (lower part) *for* **3**, **2^+**, *and ring-opened* **4^+** *as obtained from HMO-type qualitative considerations* (see text)

424 nm, f = 0.00; **2^+**: 445 nm, f = 0.04[3]). The second, strongly allowed transition (at 213.5 nm in **3** [5]) is blue-shifted by 6 nm according to the same calculations.

All effects of this O^+-perturbation described above will be further enhanced by Me-substitution *(Fig. 2)*: the HOMO which has the highest coefficients at the C-atoms will be affected most strongly by inductive and hyperconjugative destabilization. Therefore the HOMO-LUMO gap will narrow and the first electronic transition will shift to even longer wavelengths (to 530 nm according to PPP-CI). Also the oscillator strenght for this transition will increase because the x- will be balanced less by the y-transition moment (resulting in f = 0.08 from PPP-CI). Thus, we expect a reasonably strong visible absorption for ring-opened tetramethyloxirane ion.

The lowest occupied b_1-π-orbital of **2^+** will mix strongly with Me-centered pseudo-π-orbitals, and the intense y-dominated UV transition will thus be split into several smaller bands, none of which occurs above 260 nm with f = 0.01 according to PPP-CI.

On the other hand stands the orbital scheme of oxirane **1** [7] employed in the assignment of its PE spectrum [8] and substantiated by correlating the PE spectra of various substituted derivatives [9] *(Fig. 3)*. Its extension to **4** on the basis of the PE-spectrum [10] indicates that no significant absorptions are to be expected for **4^+** in the near-UV/VIS region[4]) for the following reasons:

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[3]) Note that the photodissociation spectrum of $C_2H_4O^+$ generated from **1** has a peak at 480 nm in accord with the theoretical expectations for a ring-opened structure **2^+** [6].

[4]) For the kind of information that can be gained from a comparison between the PE spectrum of a molecule M and the EA spectrum of its ion M^+ as well as for the importance of *Non-Koopmans'* states see [11].

i) Promotion of an electron from the a_1- to the b_1-orbital (*i.e.* the HOMO) occurs in the IR region.

ii) Electron promotion from the b_2- to the b_1-orbital is electric dipole forbidden.

iii) Electron promotion from the a_2- to the b_1-orbital is associated with a small oscillator strength due to poor spatial overlap of the two wavefunctions.

iv) The two lowest unoccupied orbitals of **1** are of b_2-symmetry [6]. Assuming that this also holds for **4** we can conclude that no transitions involving electron promotion from the b_1-HOMO to these levels (so called *Non-Koopmans'*-transitions[4]) should occur in the near-UV/VIS region.

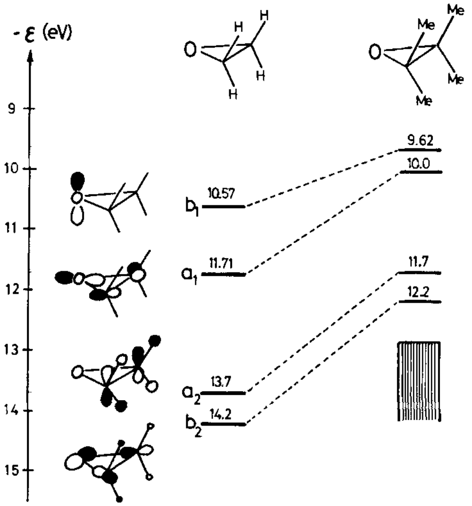

Fig. 3. *Orbital diagram of* **1** *and* **4** *resulting from the assignment of the PE spectra* (**1**: [8], **4**: [10]) *on the basis of* Koopmans' *theorem aided by* ab-initio *calculations* [7–9]. Numbers above bars refer to PE peak positions (vertical ionization energies).

On the basis of the pronounced spectral differences between ionized **4** and **5** and the theoretical arguments above we conclude that **4** undergoes ring-opening upon impact of ionizing radiation in the commonly used *Freon* matrices, in particular in *F11* which was used in the ESR studies cited above. It seems reasonable that the same happens also to parent oxirane in accord with theoretical predictions [12] [13], evidence obtained from gas-phase experiments [6] [13], and the previous conclusions of *Williams et al.* [2] from ESR work.

Preliminary results for **1** (which showed no discernible optical absorption under the present experimental conditions) as well as for **4** and **5** subjected to X-ray irradiation in solid Ar [4] support the present results and shall be reported together with the alternative preparation mode of oxirane ions *via Weller*-type electron transfer quenching in a full paper [14].

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