

Perkin Communications

An E.S.R. Study of Radical Cation Cyclization in the Radiolytic Oxidation of But-3-en-1-ol Solutions in Freon Matrices

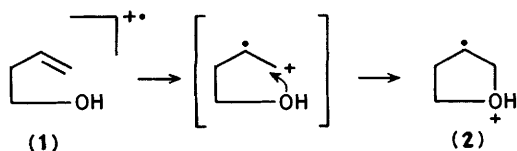
Sheng Dai, Jih Tzong Wang, and Ffrancon Williams*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, U.S.A.

The radiolytic oxidation of but-3-en-1-ol in halogenoethane matrices produces e.s.r. signals from both the protonated tetrahydrofuran-3-yl radical and the allyl radical; the former species is readily attributable to the nucleophilic *endo* cyclization of radical cations generated from unassociated solute molecules whilst the allyl radical is thought to originate from the fragmentation of the alkoxy radical produced from radical cations generated within solute clusters.

Recently, the radical cation *endo* cyclization of hexa-1,5-diene to cyclohexene was observed through e.s.r. studies in Freon matrices at low temperatures.¹ This addition reaction occurs by ring closure to the cyclohexane-1,4-diyl radical cation intermediate followed by an effective 1,3-hydrogen transfer, this latter step being assisted by thermal or photoinduced activation.¹ We now report that for the radical cation of a suitably substituted alk-1-ene, the nucleophilic attack of a pendant alcohol group on the positive hole located mainly at the terminal olefin also leads to ring closure in the *endo* mode although the product is now distonic² and not subject to further rearrangement. This is exemplified below by the 1,5-*endo* cyclization of the but-3-en-1-ol radical cation. This reaction apparently competes, however, with allyl radical formation, and this feature is attributed to the special conditions of alcohol solute clustering in Freon matrices.

The upper spectrum (a) in the Figure shows e.s.r. signals from the radicals produced by the radiolytic oxidation at 77 K of a solid solution of but-3-en-1-ol (99%, Wiley Organics) in CF_3CCl_3 . As indicated by the stick diagram, the main pattern is a well-resolved 1:4:6:4:1 quintet of doublets with hyperfine splittings of 34.8 G (4 H) and 22.6 G (1 H). These parameters are very similar to those of the tetrahydrofuran-3-yl radical (see Table) and the spectrum is therefore assigned to the protonated form of this radical (2) formed by *endo* cyclization of the but-3-en-1-ol radical cation (1). A set of weaker signals marked by arrows is also present in the spectrum of Figure (a), and these partially overlapped components can be assigned to the spectrum of the allyl radical (*vide infra*).



Similar oxidation studies were also carried out in the CFCl_3 , $\text{CF}_2\text{ClCFCl}_2$, and $\text{CFCl}_2\text{CFCl}_2$ matrices. While the CFCl_3 experiments gave poorly defined spectra even at 140–150 K from which only the outer lines of radical (2) were distinguishable, much clearer and somewhat unexpected results were obtained with the other two Freons. In particular, the spectrum of the oxidized $\text{CF}_2\text{ClCFCl}_2$ solid solution in the Figure (b) shows stronger signals from another radical

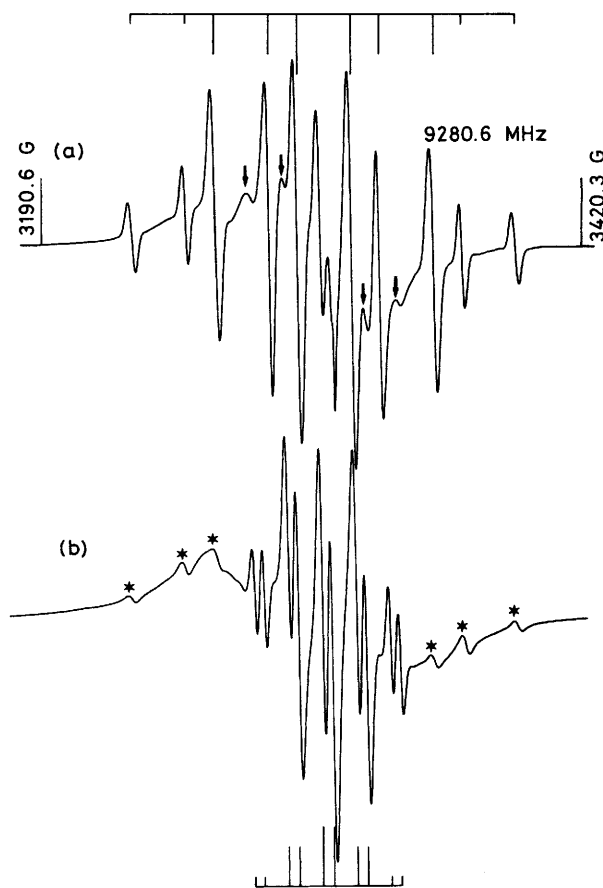


Figure. First-derivative e.s.r. spectra of radicals produced by γ -irradiation at 77 K of dilute (1 mol %) solid solutions of but-3-en-1-ol (a) in CF_3CCl_3 , recorded at 144 K, and (b) in $\text{CF}_2\text{ClCFCl}_2$, recorded at 115 K. The dominant hyperfine pattern in (a) represented by the upper stick diagram reconstruction is that of the protonated tetrahydrofuran-3-yl radical, while the weaker signals represented by arrows are spectral components of the allyl radical. Conversely, the intense pattern in (b) is from the allyl radical (lower stick diagram) while the weaker signals marked by asterisks are from the protonated tetrahydrofuran-3-yl radical. Similar results were obtained with solutions prepared from but-3-en-1-ol samples (99%) obtained from Wiley Organics and the Aldrich Chemical Company.

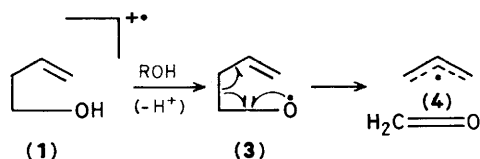
Table. E.s.r. parameters for radicals produced by radiolytic oxidation of but-3-en-1-ol and 3-methyl-but-3-en-1-ol in Freon matrices

Radical cation or radical	Substrate	Solvent	T/K	Hyperfine couplings/G ^a	<i>g</i> _{iso}	Ref.
(2)	But-3-en-1-ol	CF ₃ CCl ₃	140	22.6 (1 H _α), 34.8 (4 H _β)	2.0030	This work
Tetrahydrofuran-3-yl	Tetrahydrofuran	CF ₂ ClCFCl ₂	110	21.5 (1 H _α), 35.4 (4 H _β)	2.0025	3
(4)	But-3-en-1-ol	CF ₂ ClCFCl ₂	115	14.4 (4 H) ^c , 4.1 (1 H)	2.0030	This work
(4)	Propene	CF ₂ ClCFCl ₂	115	14.4 (4 H) ^c , 4.1 (1 H)	2.0029	<i>b</i>
3-Methyl-(2)	3-Methylbut-3-en-1-ol	CF ₃ CCl ₃	140	24.8 (3 H _{Me}), 31.5 (4 H _β)	2.0031	This work
2-Methyl-(4)	3-Methylbut-3-en-1-ol	CF ₂ ClCFCl ₂	120	14.1 (4 H) ^c , 3.2 (3 H _{Me})	2.0030	This work

^a 1 G = 10⁻⁴ T. ^b X.-Z. Qin and F. Williams, unpublished work. ^c The *exo* and *endo* hydrogen couplings were indistinguishable.

characterized by a narrower quintet [$A(4\text{ H}) = 14.4\text{ G}$] of doublets [$A(1\text{ H}) = 4.1\text{ G}$].* This pattern can be unambiguously assigned to the allyl radical (Table) since an identical spectrum was generated radiolytically from a propene solution in the same matrix, the allyl radical in this case being the expected product of proton transfer from the propene radical cation to the neutral molecule, a well-known ion-molecule reaction.³ The results obtained using CFCl₂CFCl₂ solutions of but-3-en-1-ol were intermediate between those described for CF₃CCl₃ and CF₂ClCFCl₂, the spectra showing signals of comparable intensity from (2) and the allyl radical.

These results in the halogenoethane matrices demonstrate that a process leading to allyl radical formation apparently competes with the *endo* cyclization of the but-3-en-1-ol radical cation. The likeliest explanation for this competition is that the results are linked to the degree of solute clustering in the matrix, an alternative reaction path becoming available when the radiolytic oxidation occurs in an alcohol cluster. Proton transfer from the alcohol radical cation⁴ in such a cluster would then yield the alkoxy radical (3) which presumably can undergo β-carbon scission to give the allyl radical (4) and formaldehyde.⁵



Similar studies on 3-methylbut-3-en-1-ol solutions (98%, Wiley Organics) gave the two corresponding radicals (see Table) although the relative signal intensity of the cyclized radical was smaller in this case, irrespective of which matrix was used. Nonetheless, the highest ratio of cyclized to allylic radical was again found in the CF₃CCl₃ matrix, suggesting that the association of these alcohol solutes is least in this matrix.

There is no reason why the mechanism of cyclization found here by matrix e.s.r. studies of radiolytic oxidation should not be generally applicable to other oxidation processes, including those carried out in solution. Indeed, a very similar mechanism has recently been suggested⁶ on the basis of product analyses to explain why the regioselectivity previously observed for the cyclization of pent-4-en-1-ol induced by certain oxidants⁷ differs from that obtained for the cyclization of the corresponding alkoxy radical.⁸

An interesting feature of the transition-state structure shown

for the rearrangement of (1) to (2) is that the *endo* mode of cyclization requires the least-substituted carbon of the olefin radical cation to develop considerable carbocation, as opposed to radical, character. Of course, the preference for *endo* cyclization is not surprising in the present case given that the alternative *exo*- or 1,4-cyclization would generate a strained oxetane ring much higher in energy than the tetrahydrofuran ring. Nevertheless, the simple fact that *endo* cyclization can occur here offers an interesting contrast to the virtual absence of 1,5-*endo* cyclization for olefin addition by neutral radicals.⁹ Also, it should be noted that in the detailed studies of Davies and co-workers¹⁰ on the cyclization of the protonated pent-4-en-1-oxyl radical, where the reaction is represented as an addition of a protonated alkoxy radical to the neutral olefin, *endo* cyclization (1,6-addition) is again found to be absent in accord with the usual rules for ring closure of neutral radicals.⁹

Acknowledgements

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG05-88ER13852).

References

- Q.-X. Guo, X.-Z. Qin, J. T. Wang, and F. Williams, *J. Am. Chem. Soc.*, 1988, **110**, 1974.
- B. F. Yates, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, 1984, **106**, 5805; S. Hammerum, *Mass Spectr. Rev.*, 1988, **7**, 123.
- F. Williams and X.-Z. Qin, *Radiat. Phys. Chem.*, 1988, **32**, 299.
- J. A. Wargon and F. Williams, *J. Am. Chem. Soc.*, 1972, **94**, 7917.
- Cf. J. K. Kochi, 'Free Radicals', ed. J. K. Kochi, Wiley, New York, 1973, vol. II, ch. 23, pp. 683-686.
- C. Arnoldi, A. Citterio, and F. Minisci, *J. Chem. Soc., Perkin Trans. 2*, 1983, 531; F. Minisci, A. Citterio, and C. Giordano, *Acc. Chem. Res.*, 1983, **16**, 27.
- A. Clerici, F. Minisci, K. Ogawa, and J.-M. Surzur, *Tetrahedron Lett.*, 1978, 1149.
- B. Taillez, M. P. Bertrand, and J.-M. Surzur, *J. Chem. Soc., Perkin Trans. 2*, 1983, 547; M. P. Bertrand and J.-M. Surzur, *Bull. Soc. Chim. Fr.*, 1973, 2393.
- A. L. J. Beckwith and K. U. Ingold, 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press New York, 1980, vol. 4, Essay 4, pp. 182-220; J.-M. Surzur, 'Reactive Intermediates,' ed. R. A. Abramovitch, Plenum Press, New York, 1982, vol. II, p. 121.
- A. J. Bloodworth, A. G. Davies, and R. S. Hay-Motherwell, *J. Chem. Soc., Perkin Trans. 2*, 1988, 575.

* 1 G = 10⁻⁴ T.