

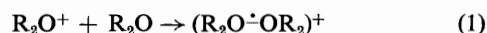
Ether Radical Cations: An Electron Spin Resonance Radiation Chemical Study

Martyn C. R. Symons* and Brendon W. Wren

Department of Chemistry, The University, Leicester LE1 7RH, U.K.

Evidence for electron delocalisation in the cations of dioxan and 1,3-dioxolan is presented.

Several years ago we attempted to use ionizing radiation to generate ether cations, R_2O^+ , from R_2OH^+ cations in sulphuric acid glasses.¹ These experiments were largely unsuccessful. Recent studies²⁻⁴ have shown that $FCCl_3$ and related solvents are ideal for forming radical cations from solutes at 77 K, so we returned to our search using these media. We had two specific questions in mind: (i) is the hyperfine coupling to β protons very large, as is expected by comparison with $MeO\cdot$ and (ii) will R_2O^+ radicals form σ^* dimers [equation (1)]



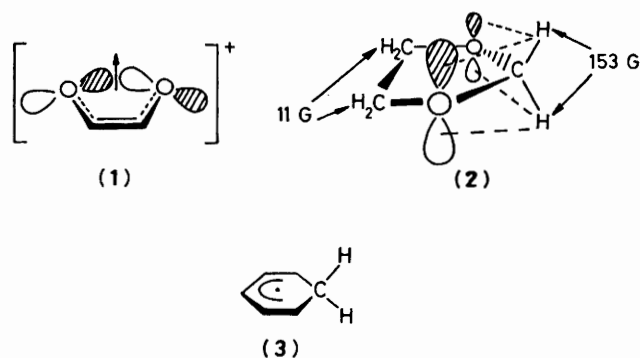
as is found, for example, for R_2S^+ radicals.^{5,6} During the course of our studies, Shida and co-workers have reported their exciting results for a range of R_2O^+ cations in these media.⁷ Wang and Williams have also studied Me_2O^+ .⁸ The results show, indeed, that $a(^1H)$ is very large (ca. 43 G† for Me_2O^+). Iwasaki and co-workers obtained 52 G for $MeO\cdot$.⁹ If this large coupling stems mainly from hyperconjugative delocalisation, then 43 G represents an effective increase, because delocalisation is now into two methyl groups. This result should be compared with that for $MeO\cdot$ radicals in the gas phase,¹⁰ for which $a(^1H)$ is calculated to be only 23.2 G. This remarkably low value is completely out of line with solid-state results, and the difference does not seem to be understood.

For more concentrated solutions and on warming above 77 K neutral ether radicals are formed [equation (2)]. For



long-chain ethers, intramolecular hydrogen atom transfer occurs. Thus we have detected Et_2O^+ but not $Pr^i_2O^+$ at 77 K. It seems certain that the formation of σ^* dimer cations is not favoured, even though there is good evidence for XO^+OX σ^* radicals in other systems.¹¹

In an attempt to remove the possibility of hydrogen atom transfer, we have studied the radical cations of dioxan. The species formed, independent of concentration, has a total β



proton coupling (60 G) which is only ca. a quarter of those observed for other ether cations.^{7,8} The reduction is far too large to be explained in terms of changes in ring conformation, and includes, in our view, the characteristic fall in $a(^1H)$ on going from monomer radicals to the corresponding σ^* dimers [cf. $a(^1H) Me_2S^+ = 20.4$; $a(^1H) Me_2S-SMe_2^+ = 6.3$; $a(^1H) Me_3P^+ = 12$; $a(^1H) Me_3P^+-PMe_3^+ \approx 3.2$ G]. We therefore propose the formation of a σ -bond between the two oxygen atoms, as in (1), with consequent confinement of the unpaired electron into the σ^* (O-O) orbital. We have attempted to prepare the corresponding cation of tetrahydropyran for comparison. However, we have not yet been able to interpret the very complex spectrum obtained, but suspect that, at least to some extent, hydrogen atom transfer from the *para* CH_2 group to oxygen has occurred at 77 K.

It seemed of interest to study the five-membered ring system, 1,3-dioxolan (3). The e.s.r. spectrum for the radical cation in this case indicates a large increase in the total β -proton hyperfine interaction (Figure 1). Clearly the large triplet splitting (153 G) originates from the protons of the CH_2 group between the two oxygen atoms, the quintet splitting (11 G) then being due to the $-CH_2-CH_2-$ protons which are equivalent at 77 K.

The electron cannot be transferring rapidly between the two oxygen atoms since the spectrum does not correspond to a reconstruction based on the data for the tetrahydrofuran cation.⁷ We invoke the Whiffen effect,¹² first observed for

† 1 G = 10^{-4} T.

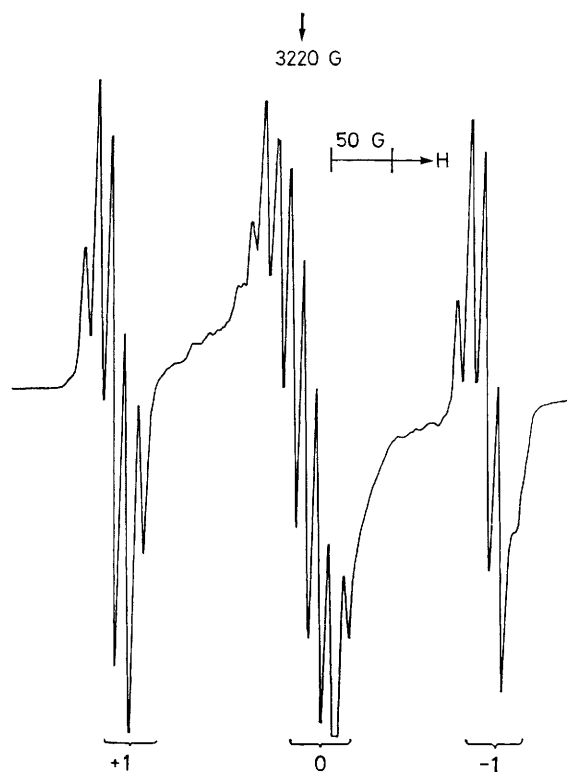


Figure 1. First derivative X-band e.s.r. spectrum for 1,3-dioxolan in Freon after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to the corresponding radical cation.

cyclohexadienyl radicals (**3**) to explain the uniquely large coupling detected for the $-\text{OCH}_2\text{O}-$ protons. The data are particularly interesting since, in contrast with the π -system of cyclohexadienyl radicals, the only way in which the electron can delocalise is *via* hyperconjugation with the methylene group.

Received, 27th April 1982; Com. 469

References

- 1 S. W. Bratt and M. C. R. Symons, unpublished results.
- 2 T. Kato and T. Shida, *J. Am. Chem. Soc.*, 1979, **101**, 6869.
- 3 M. C. R. Symons and I. G. Smith, *J. Chem. Res. (S)*, 1979, 382.
- 4 M. Iwasaki, K. Toriyama, and K. Nunome, *J. Am. Chem. Soc.*, 1981, **103**, 3591; *J. Phys. Chem.*, 1981, **85**, 2149.
- 5 B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1748.
- 6 R. L. Petersen, D. J. Nelson, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1978, 225.
- 7 H. Kubodera, T. Shida, and K. Shimokoshi, *J. Phys. Chem.*, 1981, **85**, 2564.
- 8 J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, 1981, **103**, 6994.
- 9 M. Iwasaki and K. Toriyama, *J. Am. Chem. Soc.*, 1978, **100**, 1964.
- 10 H. E. Radford and D. K. Russell, *J. Chem. Phys.*, 1977, **66**, 2222; 1980, **72**, 2750.
- 11 M. C. R. Symons and S. P. Mishra, *J. Chem. Res. (S)*, 1981, 214.
- 12 D. H. Whiffen, *Mol. Phys.*, 1963, **6**, 223.