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RADICAL CATIONS OF VARIOUS ETHENE, ETHINE AND CYCLIC ETHERS

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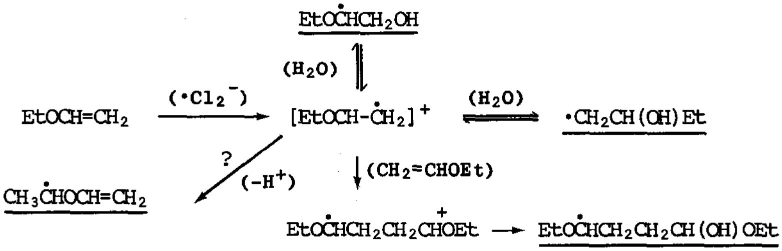
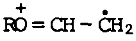
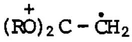
Abstract: We have prepared the cations $[(EtO)CH\dot{C}H_2]^+$, $[(MeO)_2\dot{C}CHMe]^+$ and $[(EtO)_2\dot{C}CHMe]^+$ by the action of ionizing radiation on dilute solutions of neutral precursors in freon at 77 K, and used e.s.r. spectroscopy to study their structures. We have also studied the cations of oxirane, oxitane and methoxyethine for comparative purposes.

We,[1,2] and others[3-5] have clearly established that the effect of ionizing radiation on dilute solutions of neutral compounds (X) in solvents such as $CFCl_3$ (freon) invariably yields the parent cation X^+ or some unimolecular breakdown product thereof, provided the ionization potential for X is less than ca. 11.9 eV. These systems are ideal for e.s.r. study. Three groups have independently studied the e.s.r. spectra of various ether cations,[6-10] which, like the related alkoxy radicals generally exhibit large coupling constants to protons β- to the cationic oxygen, as a result of strong σ-π conjugation. Our interest in vinyl ethers stemmed from the work of Gilbert et al.,[11] who have nicely unravelled some complex radical chemistry of vinyl ethers in terms of the parent radical cation (I) as a common intermediate, although these cations were not detected directly by e.s.r. spectroscopy. The postulated reactions are summarised in Scheme I, the radicals detected by e.s.r. spectroscopy being underlined. Schulte Frohlinde and his co-workers have directly detected the related cations (II) by e.s.r. spectroscopy[12] so these must be considerably more stable than I. E.s.r. parameters for some of these

Scheme I

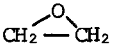
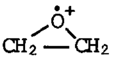
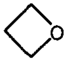
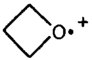


I 
$\overset{+}{R O}=CH-\dot{C}H_2$

II 
$(\overset{+}{RO})_2C-\dot{C}H_2$

radical cations are given in the Table. It is of interest to compare the results for these

TABLE: ESR Parameters for a Range of Ether Radical Cations

Source	Cation	^1H hyperfine coupling constants/G[a]
MeOMe[b]	$Me\dot{O}Me^+$	43(2Me)
$EtOCH=CH_2$	$Et\overset{+}{O}CH-\dot{C}H_2$	19.4(CH_2), ca. 3.5(OCH_2)
$(MeO)_2CHCH=CH_2$	$(MeO)_2\overset{+}{C}-\dot{C}HMe$	19(CH), 24(Me)
$(EtO)_2CHCH=CH_2$	$(EtO)_2\overset{+}{C}-\dot{C}HMe$	19(CH), 24(Me)
$MeOC\equiv CH$	$Me\overset{+}{O}C=\dot{C}H$	22(CH), 11(Me)
		16(4H)
		64(4H), 11(2H)
$(MeO)_2CHCH_2Cl$[c]	$(MeO)_2\overset{+}{C}-\dot{C}H_2$	20.55(CH_2), 3.1(OMe), 0.66(OMe)
$(MeO)_2CHCH(Me)OAc$[c]	$(MeO)_2\overset{+\cdot}{C}CHMe$	18.8(CH), 24.5(Me), 2.8(OMe), 0.7(OMe)
$(EtO)_2CHCH_2Cl$[c]	$(EtO)_2\overset{+}{C}-CH_2$	20.6(CH_2), 3.36(OCH_2), 0.6(OCH_2)

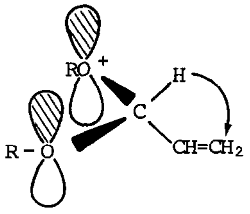
[a] $G = 10^{-4}$ T; [b] Ref. 7; [c] Ref. 12

cations with those for saturated ether cations on the one hand, and with substituted ethene cations[13] on the other. We also thought it of interest to compare these results with results for the cations of an ethine derivative ($HC\equiv COMe$) and of the 3- and 4-membered cyclic ethers, oxirane and oxetane.

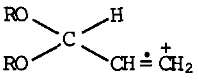
$EtOCH=CH_2$. - The e.s.r. spectrum for this cation comprises a triplet of broad lines with a(^1H) 19.4 G assigned to the terminal methylene protons. Extra triplet features separated by ca. 3.5 G assigned to the CH_2 protons of the ethyl group were apparent during the annealing process. These radicals decayed as the medium softened, without the formation of secondary species.

$(RO)_2CH-CH=CH_2$. - The cations derived from the methyl and ethyl derivatives had e.s.r. spectra (Fig. 1) which cannot be reconciled with expectation for either of the extreme structures III or IV. In particular, structure III should exhibit an extremely large hyperfine coupling to the

III



IV



bridging C-H proton because of π-σ-π conjugation.[8,10]

Shida and his co-workers have found that radical cations of type III with vinyl replaced by alkyl readily lose the alkyl radical, which is detected by e.s.r. spectroscopy[14] (equation 1).

$$[(RO)_2CHR]^+ \longrightarrow (RO)_2CH^+ + R\cdot \quad .... [1]$$

Our results, which are in good accord with expectation for the vinyl ether cations

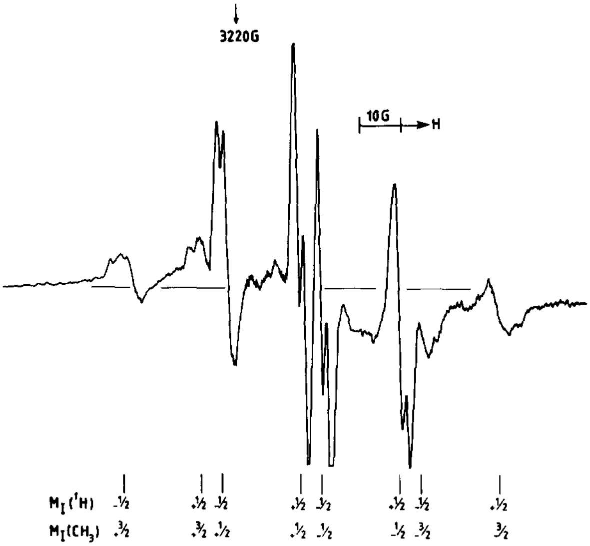


Figure 1

First derivative X-band e.s.r. spectrum for $(MeO)_2CH\text{-}CH{=}CH_2$ in $CFCl_3$, showing features assigned to $[(MeO)_2C\text{-}\dot{C}HMe]$ cations.

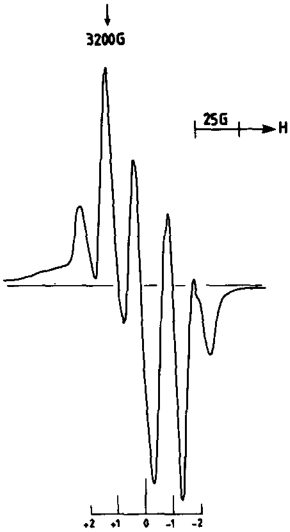


Figure 2

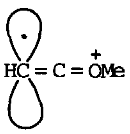
As for Fig. 1, for oxirane in $CFCl_3$ showing features assigned to oxirane cations.

$[(RO)_2C\text{-}\dot{C}H(Me)]^+$, suggest that, in this case, a 1-3 hydrogen shift has occurred, as indicated by the arrow in III.

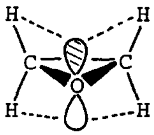
Structural Aspects. - The results confirm that the simple limiting valence-bond structures depicted in I and II are good approximations for the SOMO's for these species. This is not surprising since this was known to be true for the isostructural radicals such as $H_2\dot{C}CO_2H$ and $H_2\dot{C}CO_2^-$. If 22 G is taken as a reasonable value for unit spin-density on the $-\dot{C}H_2$ unit, delocalisation is ca. 11% for I and ca. 11.7% for II. Conversely, using a value of ca. 43 G for the methyl protons for a formal unit spin-density on oxygen[7] we estimate ca. 8% spin-density on oxygen for I and ca. 7% for II using liquid-phase data. It is well established that the extent of σ-π conjugation increases with increasing positive charge. However, for the ethyl radical and for $(RO)_2\overset{+}{C}\text{-}\dot{C}HMe$ cations the ratio of the β-proton to the α-proton coupling is 1.21, showing that there is a negligible positive charge effect for these cations. So there has been no extra donation of electrons from the $\dot{C}$-Me groups for these cations, in marked contrast, for example, with results for methyl groups in olefin cations.[13] This again accords with the limiting structures (I) and (II).

It is noteworthy that the initially formed radical cation $(MeO)_2\overset{+}{C}\text{-}\dot{C}HMe$ exhibited coupling to one set of methoxy methyl protons of ca. 1.5 G, which is half the liquid-phase value. However, the lines broadened irreversibly on annealing, suggesting an increase in coupling to the methyl protons presumably due to changes in conformation of these groups.

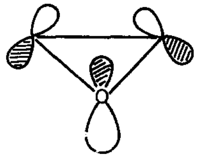
The $[HC{\equiv}C\text{-}OMe]^+$ Radical Cation. - As expected, results for this cation again favour the limiting structure (V), but, judging from the relatively large methyl proton hyperfine coupling delocali-



V



VI



VII

sation of the unpaired electron onto the oxygen atom is greater than for radicals (I) and (II). Using the arguments outlined above, the oxygen spin-density is *ca.* 0.25. Evidently, as with aromatic methine protons, the Q-value for the methine proton in these cations is greater than 22 G. These results require a Q-value of *ca.* 29 G.

The Oxirane and Oxitane Cations. - The results for the oxirane cation show that all four protons are equivalent, with a coupling constant of 16 G (Fig. 2). We are surprised at the low magnitude of this coupling. For $(MeOMe)^+$ the average proton coupling is *ca.* 43 G, and since the four C-H bonds are constrained to favour overlap with the oxygen $2\underline{p}(\pi)$ orbital (VI) we had expected proton splittings of at least 60 G for these cations. Indeed the four similarly placed protons for oxitane have coupling constants of 64 G. The only chemically reasonable rearrangement that we can formulate gives the vinyl alcohol cation $[H_2\dot{C}\text{-}CH(OH)]^+$, for which a triplet similar to that for radical (I) is expected. In our view, the SOMO is not the normal π $(\underline{b}_1)$ orbital depicted in (VI), but is the "non-bonding" σ $(\underline{a}_1)$ orbital depicted in (VII). This should give much smaller proton coupling because there is no direct overlap as in (VI). There has been controversy regarding the SOMO for the oxirane cation, some favouring $\underline{b}_1$[15] and others $\underline{a}_1$.[16] It is possible that strong interaction in the $(CH_2\text{-}CH_2)$ unit inhibits hyperconjugation in the $\underline{b}_1$ orbital, but our results for the sulphirane cation suggest a $\underline{b}_1$ SOMO with large proton coupling, so we strongly favour the $\underline{a}_1$ description.

Finally, we note with interest that there is no tendency for the two isomeric $C_3H_6O^+$ cations $[H_2\dot{C}CH(OMe)^+$ and the oxetane cation] to interconvert under our conditions.

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