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Study of Dialkyltellurium Radical Cations by Electron Spin Resonance Spectroscopy *

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The ESR spectra are reported for the radical cations $(CH_3)_2Te^+$ and $(C_2H_5)_2Te^+$ produced by exposure of very dilute solutions of $(CH_3)_2Te$ or $(C_2H_5)_2Te$ in $CFCl_3$ to ^{60}Co γ-rays at 77 K. The results show that the species are π radicals and that the unpaired electron is strongly confined to the tellurium $5p_z$ orbital. As expected for such π radicals, $g_x > g_y > g_z \approx 2.00$, *e.g.* for $(CH_3)_2Te^+$, $g_x = 2.26_0$, $g_y = 2.13_6$ and $g_z = 1.99_0$. Linear correlations between the spin–orbit coupling constants and the g_x, g_y values and between the methyl-group proton hyperfine coupling constants and ionisation potentials for $(CH_3)_2X^+$ (X = O, S, Se or Te) are presented. When more concentrated solutions of $(CH_3)_2Te$ in $CFCl_3$ were similarly irradiated some evidence in the ESR spectrum was found for the presence of the σ* three-electron bonded species $[CH_3)_2Te–Te(CH_3)_2]^+$.

Recently there has been a resurgence of interest in organotellurium compounds[1] because of their wide-ranging applications in the semiconductor industry,[2] in organic synthesis,[1] and as reagents in nuclear medicine.[3] We have recently carried out a thorough spectroscopic study of the compounds R_2Te [R = CH_3, C_2H_5 or $(CH_3)_3C$] utilising the techniques of infrared, Raman, ultraviolet–visible and multinuclear NMR spectroscopy together with mass spectrometry.[4,5] One of the principal aims of our work was to search for weak adducts formed between R_2Te and organocadmium acceptor molecules, such as $Cd(CH_3)_2$, since such adducts may be important intermediates in the formation of thin layers of the semiconductor materials CdTe and cadmium mercury telluride by metal organic vapour phase epitaxy (MOVPE).[6] In this context it is of interest to learn something of the structure and bonding of the R_2Te molecules, and, as a part of this work, we undertook a study of the ESR spectra of the R_2Te^+ (R = CH_3 or C_2H_5) radical cations.

These radical cations are of considerable interest in their own right. To our knowledge there are no previous reports of the ESR spectra of organotellurium cations. Indeed there has been relatively little work on any inorganic or organometallic cations containing heavy atoms. The series of cations $(CH_3)_2X^+$ (X = O, S or Se) have all been studied by ESR spectroscopy when trapped in solid $CFCl_3$ at 77 K.[7–9] Thus observation of the $(CH_3)_2Te^+$ cation assumes an importance in completing this series and in allowing us to study trends in the ESR spectra on descending the group. We also hoped that by recording these spectra we might learn something of the nature of the highest-occupied non-bonding molecular orbital(s) of the R_2Te^+ cations. As these cations are likely to have a similar structure to those of the neutral parent R_2Te molecules, identification of the highest-occupied molecular orbital in R_2Te allows substantiation of the donor orbital involved in adduct formation with organocadmium acceptor molecules.

For *small* cations, *e.g.* H_2O^+, CH_4^+, H_2CO^+, *etc.*, a convenient way to observe their ESR spectra is to trap the species in noble-gas matrices.[10–12] Such methods have been developed by Knight,[13] where the cations are produced by a variety of methods immediately prior to or during deposition. For larger cations, such as the ones we describe here, the method developed in part by one of us,[14] in which very dilute solutions (*e.g.* in $CFCl_3$ solvent) of substrates are frozen and then exposed to ionising radiation, is more successful. Recently, such methods have been used to study dialkylmercury derivatives.[15] It is the view of many chemists that ionising radiation represents a 'sledgehammer' which will break molecules indiscriminately into a wide variety of products. However, it is becoming increasingly apparent, that, for properly controlled systems, the products formed are often simpler and more readily predictable than those produced by high-energy ultraviolet light.[7] Alongside a study of R_2Te^+ cations one of our aims was to search for the σ* radicals $[R_2Te–TeR_2]^+$ formed by reaction (1) which contain unusual two-centre three-electron bonds.

$$R_2Te^+ + R_2Te \longrightarrow [R_2Te–TeR_2]^+ \qquad (1)$$

The R_2Te compounds discussed in this paper have previously been studied by both ultraviolet–visible absorption and photoelectron spectroscopy.[5,16] By the latter method an ionisation potential of 7.9 eV is obtained for $(CH_3)_2Te$. Thus $(CH_3)_2Te^+$ cations should readily be formed in $CFCl_3$ frozen solutions since the ionisation potential for $CFCl_3$ is *ca.* 11.8 eV.[17] Furthermore if any solvent interaction were to be seen in this system it is likely to be *via* ^{19}F rather than *via* ^{35}Cl or ^{37}Cl.[9]

Experimental

Method of Preparation.—Samples of $(CH_3)_2Te$ and $(C_2H_5)_2Te$ were kindly supplied by Professor D. J. Cole-Hamilton. These samples and $CFCl_3$ (Aldrich, *ca.* 99.5% pure) were subjected to trap-to-trap distillation on an all-glass vacuum line before use. Very dilute solutions of $(CH_3)_2Te$ and $(C_2H_5)_2Te$ in $CFCl_3$ (*ca.* 2 mmol dm^{-3}) were prepared in silica ESR tubes (diameter 5 mm). The tubes were sealed under vacuum and, after cooling to 77 K, were exposed to ^{60}Co γ-rays in a Vickrad source with doses in the 0.5–1.0 Mrad range.[14,18]

Spectra.—The ESR spectra were measured using a Varian E 109 spectrometer at 77 K. Samples were annealed by allowing them to warm in an empty Dewar with continuous monitoring of the spectra. They were recooled to 77 K when significant

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* *Non-SI units employed:* eV ≈ 1.60 × 10^{-19} J, rad = 10^{-2} J kg^{-1}, G = 10^{-4} T.

Table 1 Experimental ESR parameters for R_2Te^+ radicals

	Hyperfine coupling/G						
		^{125}Te*					
Radical	^1H	x	y	z	g_x	g_y	g_z
$(CH_3)_2Te^+$	10 (6 H)	$\pm 80 \pm 10$	$\pm 90 \pm 10$	$\pm 960 \pm 20$	2.26_0	2.13_6	1.99_0
$(C_2H_5)_2Te^+$	10 (2 H) 20 (2 H)	$\pm 100 \pm 20$	$\pm 120 \pm 20$	$\pm 950 \pm 20$	2.25_0	2.13_0	1.99_0

* The magnetic moment of ^{125}Te is negative.

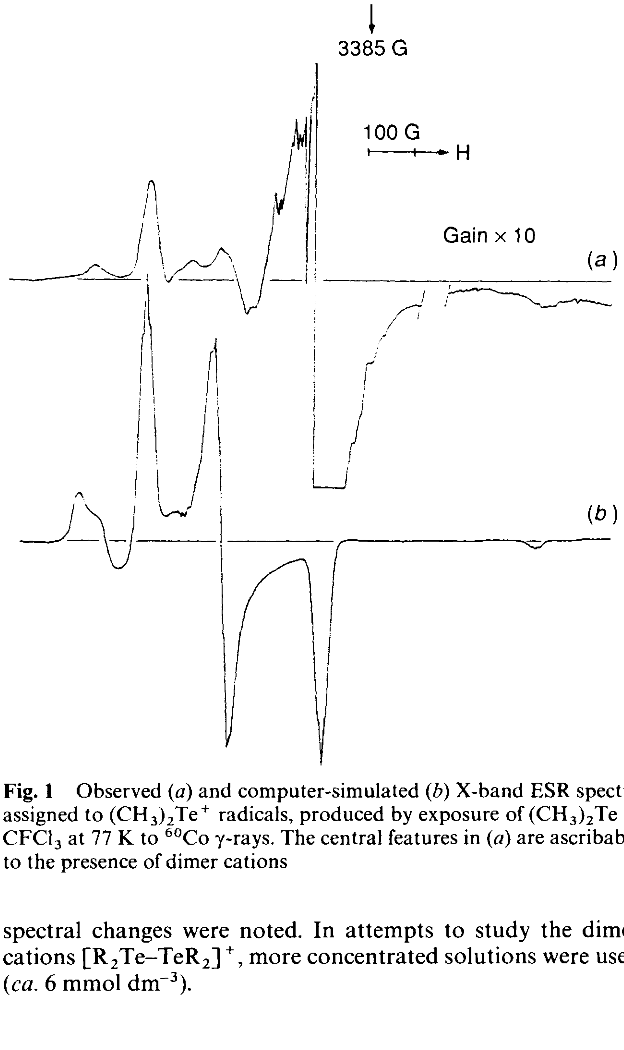

Fig. 1 Observed (*a*) and computer-simulated (*b*) X-band ESR spectra assigned to $(CH_3)_2Te^+$ radicals, produced by exposure of $(CH_3)_2Te$ in $CFCl_3$ at 77 K to ^{60}Co γ-rays. The central features in (*a*) are ascribable to the presence of dimer cations

spectral changes were noted. In attempts to study the dimer cations $[R_2Te–TeR_2]^+$, more concentrated solutions were used (*ca.* 6 mmol dm^{-3}).

Results and Discussion

Data.—The experimental results are summarised in Table 1. There are several problems in detailed spectral interpretation, the major one being the presence of central ($g = 2$) features which are in part due to dimer cations and in part to impurity species and radicals in the silica tube.

Spectra.—By analogy with results for similar π radicals,[14,18,19] we expect to find that $g_x > g_y > g_z \approx 2.00$, with septet splitting for $(CH_3)_2Te^+$ from six equivalent protons. Since ^{125}Te has $I = \frac{1}{2}$ and is *ca.* 7% abundant, there should be satellite septets flanking each major feature. For an electron in a p_z orbital we expect $A_x \approx A_y \ll A_z$ with A_z positive.[19] (N.B. the magnetic moment of ^{125}Te is actually negative, but for ease of presentation of arguments leading to spin-density estimates the negative sign has been omitted: thus for absolute data all signs need to be reversed.) It should be noted that ^{123}Te is in such low abundance (0.9%) that ^{123}Te radicals make a negligible contribution to the spectra considered herein.

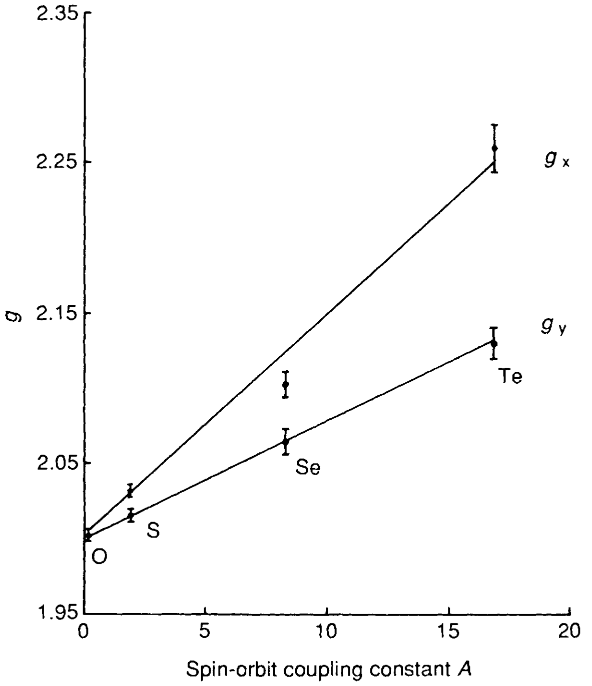

Fig. 2 Plots of g_x and g_y values against spin–orbit coupling constants for the series of ions $(CH_3)_2X^+$ (X = O, S, Se or Te)

The form of the g and $A(^{125}Te)$ components is such that all $+\frac{1}{2}$ features should be intense, since the x, y and z components are all close together. However, all $-\frac{1}{2}$ features should be correspondingly weak, especially the $-\frac{1}{2}(A_z)$ feature which is well removed from all others. This is shown in Fig. 1(*b*), which is a computer simulation based on our best fit for the low-field features.

The g *values*.—The large shift in g_x and g_y from 2.00 is the result of coupling between the singly occupied molecular orbital (SOMO) ($^1b_1$) and the $\sigma_z(a_1)$ and $\sigma_y(b_2)$ orbitals, and is rendered large by the high value of the spin–orbit coupling constants for Te. Experimental g_x and g_y values are plotted as a function of the spin–orbit constants for X (X = O, S, Se and Te) for a series of Me_2X^+ cations in Fig. 2. There is a good correlation for both g_x and g_y in this series, which suggests that the structures of all the radicals are very similar.

There should also be a link between the g shifts and the ionisation potentials obtained from photoelectron spectra.[16,20] The shifts are expected to correlate approximately with the inverse of the differences in ionisation potentials between the coupled orbitals. Thus the shift in g_x of 0.26 correlates with 1/2.46 eV = $E(a_1 - b_1)$ and the shift of 0.13 in g_y with 1/3.43 eV = $E(b_2 - b_1)$. If the photoelectron spectroscopic results and the g_x values are accepted, g_y is expected to be greater (≈0.19) than is found (≈0.13). This difference probably reflects

Table 2 Proton hyperfine splittings for $(CH_3)_2X^+$ radicals and ionisation potentials (i.p.) for $(CH_3)_2X$ molecules (X = O, S, Se or Te)

X	$A(^1H)/G$	i.p./eV
O	42.3	9.94
S	21	8.7
Se	15	8.2
Te	10	7.9

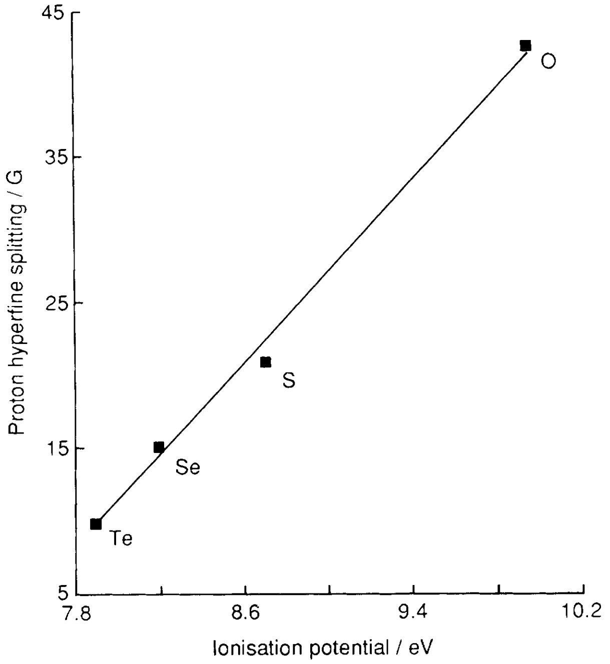

Fig. 3 Trends in the proton hyperfine coupling constant $A(^1H)$ for $(CH_3)_2X^+$ (X = O, S, Se or Te)

the fact that photoelectron spectroscopy (PS) gives the vertical ionisation potential whilst the *g* values relate to the fully relaxed cations.

Proton hyperfine coupling. Trends in $A(^1H)$ on going from Me_2O^+ to Me_2Te^+ are shown in Table 2 and Fig. 3 as a function of the first ionisation potentials of the parent molecules. There is a remarkably good linear correlation which lends strong support to the concept proposed many years ago[21] that hyperconjugation (σ–π delocalisation) involving electron donation from C–H σ bonds into the half-filled p orbital of π-type radicals is in part responsible for ^1H hyperfine coupling to β-protons (*i.e.* those on the C atom bound to the heteroatom). The steady fall in $A(^1H)$ on going from O to Te seems to be primarily controlled by the decrease in ionisation potential.

It is curious that the proton hyperfine splitting for the diethyl derivative is also *ca.* 10 G, and the number of lines is *ca.* 7. If there were free rotation of the CH_3CH_2 units about the C–Te bonds then a splitting of 10 G would be reasonable, but there should only be five lines. One possibility is that there is a small coupling to ^{19}F (from the $CFCl_3$ solvent) as is observed for Me_2Se^+ cations.[9] However, there is no sign of this for Me_2Te^+ so it is unlikely to occur for Et_2Te^+. The explanation that we favour is that there is a preferred conformation (**III** in Fig. 4) such that one β-proton for each $-CH_2-$ group is fixed close to the average 45° position, the other being close to the maximum-overlap site. In this case, couplings of *ca.* 10 and 20 G for the two pairs of protons give seven lines as required. This analysis gives a far better fit for the intensities of the septet features than does any model involving coupling to ^{19}F.

Ethyl substituents in radical cations often display restricted rotation with no clear preference for specific orientations.[17] In the present series, for Et_2O^+ the conformation must be close to **I** with two pairs of equivalent strongly coupled protons (one pair from each ethyl group) giving a value for $A(^1H)$ of 68.7 G.[7] In contrast, only three lines (from two equivalent protons) have been resolved for Et_2S^+,[8] the coupling being close to the average value. Thus the other two protons must be close to the nodal plane as in **II**. These protons and the CH_3 groups seem to have changed places in Et_2Te^+, **III**. We offer no explanation for these curious switches in preferred orientations. The trends seem to confirm that there is no strong hyperconjugation preference for C–H over C–C σ bonds in such systems.[14]

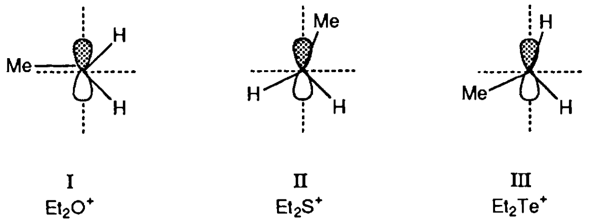

Fig. 4 Preferred orientations of the Et_2X^+ radical cations viewed along the axis of one of the C–X bonds (X = O, S or Te). For clarity only one ethyl group is shown in each case

The ^{125}Te hyperfine data. Although a range of ^{125}Te features are clearly defined for both Me_2Te^+ and Et_2Te^+ by the proton splittings [see Fig. 1(*a*)], it is not easy to be certain of the analysis because various predicted features proved to be undetectable. Nevertheless the results shown in Table 3 give rise to reasonable simulations of the observed features and show why the others were not detected. In order to obtain some idea as to the significance of the hyperfine data it is necessary to allow for orbital magnetic contributions to the coupling. This has been done after converting the data into MHz and using equations (2)–(4)[19] which are thought to be sufficiently accurate in view of the uncertainties involved.

$$A_z = A_{iso} + 2B(1 + \tfrac{5}{4}\Delta g_z) \tag{2}$$

$$A_y = A_{iso} + B(1 - \tfrac{5}{2}\Delta g_y) \tag{3}$$

$$A_x = A_{iso} + B(1 - \tfrac{5}{2}\Delta g_x) \tag{4}$$

The results for the 2*B* term are reasonable if A_x and A_y are taken to be either positive or negative (see Table 3). The values for A_{iso} are all reasonable for an R_2Te^+ radical, and show that the π structure must be correct. Hence it is not possible to determine the signs of the *x* and *y* components.

Using equations (2) + (3) or (2) + (4) should give the same value for A_{iso} and 2*B*. In fact there are small differences, but the overall results confirm that the spin density in the p_z orbital is close to unity as required. An average value has been used for the results in Table 3.

In calculating apparent orbital populations we have used two alternative sets of atomic parameters.[19,22] Neither set is ideal for heavy atoms but both indicate the expected high degree of localisation of the SOMO.

Dimer Cations $[R_2Te–TeR_2]^+$.—Although R_2O^+ radical cations show no tendency to form $[R_2O–OR_2]^+$ dimer cations,[7] these form readily for R_2S^+ (ref. 8) and R_2Se^+ (ref. 9) either on annealing or when relatively concentrated solutions are used.

Our results show clearly that, on annealing, features grow in the central region (expected for these σ* three-electron bonded species) as those for the parent cations decay. Also, for more concentrated systems the relative yields of R_2Te^+ radicals are reduced and those assigned to the dimer cations are increased. Unfortunately we have been unable to unravel these central features. This failure arises, in part, because of overlapping impurity lines and, in part, because of very poor resolution. We

Table 3 Isotropic (A) and anisotropic ($2B$) hyperfine coupling constants for ^{125}Te after allowing for orbital magnetic contributions. There are two sets of results because the signs of the x and y components are unknown (the sign of A_z must be negative in view of its large magnitude). Also shown are estimated 5s and 5p orbital contributions using (*i*) the A^0 and $2B^0$ values given in ref. 1 and (*ii*) the corresponding values given in ref. 9

			a_s^2 (%)		a_p^2 (%)	
	A_{iso}/MHz	$2B$/MHz	(*i*)	(*ii*)	(*i*)	(*ii*)
x,y, negative	1310	1361	4.8	2.4	81	103
x,y, positive	1016	1655	3.7	1.8	65	79

expect to have considerable overlap between x, y and z components, and, for $[Me_2Te{-}TeMe_2]^+$,[12] overlapping proton hyperfine components. The net result is unfortunately too poor for good spectral interpretation, but it seems certain that dimerisation does occur.

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