systems without locked geometries. For para-poly(phenyl) chains we find eq A.2 for the geometry of rings in Figure 14. The interaction between p orbitals in the ring is β, and the interaction between p orbitals on atoms connecting the rings is γ. The ratio of these quantities is $\nu = \gamma/\beta$.

$$\epsilon + \frac{1}{\epsilon} = \frac{(E/\beta)^4 - (E/\beta)^2(5 + \nu^2) + (4 + \nu^2)}{2\nu} \quad \text{(A.2)}$$

Because the HOMO–LUMO gap is a few electronvolts in these systems and ν is on the order of the cosine of the angle between the rings, the small backscattering approximation is most likely not generally appropriate. Taking $\nu = \cos 50°$, the equilibrium geometry of biphenyl, we find the E–ϵ relation shown in Figure 14. The maximum decay of the rate with distance occurs for the tunneling energy at the center of the gap ($E = 0$) where

$$\epsilon(E = 0) = \nu/2 \quad \text{(A.3)}$$

For a 50° angle, therefore, the rate is expected to change by no more than a factor of 10 per ring. Because of the relatively small band gap, ϵ (and hence the distance decay of the rate) may be considerably different for (photoinduced) forward transfer compared to reverse (thermally activated) electron transfer in these systems.

ESR Studies of the Thietane and Thiirane Radical Cations in Freon Matrices. Evidence for Ethylene Molecule Extrusion from the σ* Thiirane Dimer Radical Cation [C₂H₄S–SC₂H₄·⁺]

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Abstract: ESR spectroscopy has been used to study the structures and reactions of the radical cations produced from the three- and four-membered sulfur-containing ring compounds, thiirane and thietane, the radical cations being generated by γ irradiation of dilute solutions of the parent compounds in Freon matrices at 77 K. With use of $CFCl_3$ as the matrix, the monomer radical cations have been identified and characterized as having $^2B_1$ ring-closed structures with the unpaired electron localized on the sulfur atom. The hyperfine coupling to the four equivalent β-hydrogens in the thietane cation (31.1 G) is normal, but the corresponding value for the thiirane cation (16.1 G) is lower by almost a factor of 2, suggesting that hyperconjugation to methylene groups is much reduced in three-membered rings. In the more mobile $CFCl_2CF_2Cl$ and CF_3CCl_3 matrices, dimer radical cations of thiirane and thietane are produced by the combination of a monomer radical cation with a neutral molecule at low temperatures (<100 K). ESR studies show that these dimer species are centrosymmetric, the binding between the molecules resulting from the formation of a 3-electron $\sigma^2\sigma^{*1}$ S–S bond. Both of the dimer cations are unstable above 105 K in the $CFCl_2CF_2Cl$ matrix, the thietane dimer radical cation decomposing to give the 2-thietanyl radical as a result of hydrogen atom or proton transfer, whereas the thiirane dimer radical cation undergoes a novel reaction involving the extrusion of an ethylene molecule. Evidence for ethylene formation in the latter reaction comes indirectly from the ESR observation of secondary radicals with the structure RCH_2CH_2 on annealing γ-irradiated solutions of thiirane in $CFCl_2CF_2Cl$. Similar radicals are also generated in γ-irradiated thiirane solutions in CF_3CCl_3 at 145–150 K, the ESR spectrum being indistinguishable from that of identically treated ethylene solutions. The ethylene extrusion is depicted as a concerted reaction in which the driving force is supplied by the transfer of the unpaired electron from the σ^* (S–S) orbital of the dimer cation to a vacant p orbital on the terminal sulfur atom of the remaining $C_2H_4S_2^+$ moiety.

The radical cations of oxirane and aziridine clearly display the extraordinary reactivity that is commonly associated with strained three-membered rings. Thus, it has been shown by ESR studies[1–4] that the respective $^2B_1$ and $^2A'$ ground states of these species resulting from heteroatom lone-pair ionizations are unstable even at 77 K and undergo C···C ring opening to give either delocalized[1,2,4] or localized[3] carbon-centered radicals. A similar conclusion regarding the ease of ring opening in the oxirane cation was reached earlier by means of detailed gas-phase studies,[5–7] and additional evidence for this rearrangement comes from the interpretation of electronic absorption spectra associated with the delocalized forms of the ring-opened oxirane and tetramethyloxirane cations.[8,9] Moreover, high-level theoretical calculations predict that the delocalized ring-opened forms of the oxirane[10] and aziridine[11] radical cations are more stable than their ring-

closed forms by 19.6 and 26.5 kcal mol⁻¹, respectively, and that the barrier to the ring opening of the oxirane cation is likely to be less than 3.7 kcal mol⁻¹.[12]

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(2) Qin, X.-Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1985**, *107*, 3366.

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In contrast to the above results for heterocyclopropane radical cations, ESR studies show that the radical cations of the corresponding heterocyclobutanes, oxetane[1] and azetidine,[4] remain ring closed under the same experimental conditions, the SOMO in each case being derived from the ionization of the lone-pair orbital on the heteroatom, as expected.

The original objective of the present study was to see whether the above diversity with respect to internal rearrangement also applies to the radical cations of the three- and four-membered sulfur heterocycles, thiirane and thietane. In fact, the radical cation of thiirane, as well as that of thietane, is found to be ring closed. This turns out to be the first example of a ring-closed heterocyclopropane radical cation and our studies show that the β-hydrogen hyperfine coupling constant is only about half of that for the thietane cation. This interesting effect of ring size on hyperconjugation in these heterocycloalkanes has been the subject of a preliminary communication.[13]

Further interest in the thiirane system developed as a result of our observation that an unusual ion–molecule reaction of the thiirane cation previously reported in the gas phase[14] and proceeding through the dimer radical cation can be monitored by ESR in suitable Freon matrices, and this is the main subject of this report. A byproduct of this work is that it clearly disproves a recent assignment of a five-line ESR spectrum characterized by a 23-G hyperfine splitting to the ethylene radical cation,[15] an assignment that has also been questioned by others on the basis of different criteria.[16]

Experimental Section

Thietane (trimethylene sulfide, 97%) was supplied by Aldrich and used as received. Thiirane (ethylene sulfide) was obtained from two sources (Aldrich and Fluka), the stated purity being 99% in each case. These materials were treated similarly and gave identical results. Each compound was degassed at −196 ° with repeated freeze–pump–thaw cycles and then transferred in vacuo to a trap held at −78 °C, the noncondensible vapors being removed by pumping. This procedure was designed to remove any traces of ethylene in the thiirane starting materials, and no trace was detected on subsequent GC analysis (vide infra). Ethylene (C.P. grade, 99.5% min. purity) from Matheson Gas Products was used as received.

Thiirane samples were analyzed by gas chromatography on a Perkin-Elmer Model 800 instrument with a flame ionization detector. The column (Catalog No. 8408-PC from Alltech Associates Inc.) consisted of a 6 ft × 0.125 in. o.d. × 0.085 in. i.d. stainless steel coil packed with 10% Carbowax 20 M on 80/100 Chromosorb W-HP. With use of a carrier gas (nitrogen) flow rate of 18 mL min⁻¹ and a column temperature of 100 °C, ethylene and thiirane were cleanly separated with retention times of 15 and 27 s, respectively.

The Freon solvents used in this study were trichlorofluoromethane (Aldrich, Matheson, and PCR/SCM Specialty Chemicals), 1,1,1-trichlorotrifluoroethane (Aldrich), and 1,1,2-trichlorotrifluoroethane (Aldrich and PCR/SCM Specialty Chemicals). These materials were degassed at −196 °C and stored under vacuum in portable glass reservoirs fitted with greaseless valves (Kontes). Sample preparation techniques have been described.[17] Identical results were obtained for solutions made up from different batches of a particular Freon solvent, irrespective of the source of this material.

The radical species were generated by γ irradiation of ca. 1 mol % solutions of each of the sulfur heterocyclic compounds and ethylene in the various halocarbon solvents at 77 K, the usual dose being from 0.3 to 0.5 Mrad. ESR measurements were made with a Bruker ER 200 D SRC spectrometer equipped with variable-temperature accessories.[17]
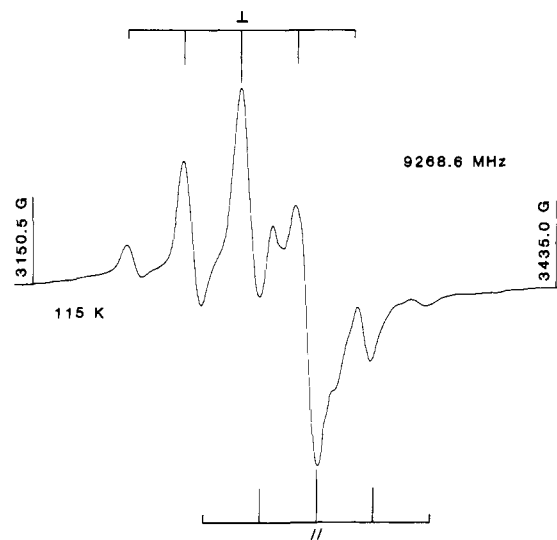

Figure 1. First-derivative ESR spectrum of the monomer radical cation of thietane in CFCl₃. The stick diagrams provide an analysis of the spectrum in terms of binomial quintet patterns consisting of parallel and perpendicular features.

Results

Thietane Solutions. The ESR spectrum of the radical generated from thietane in CFCl₃ is shown in Figure 1. Although more complicated at lower temperatures, the spectrum is well-defined at 95 K and shows little further change until the signal decays near the softening point of the matrix at 158 K. The assignment of this well-resolved spectrum (Figure 1) to the ring-closed thietane cation is unambiguous, given the anisotropic form of the **g** tensor and consideration of the isotropic hyperfine data. Thus, two binomial quintet patterns, one associated with $g_\perp$ and the other with $g_\parallel$, are revealed such that $g_\perp > g_\parallel$, as observed for the isostructural oxetane radical cation.[1] Also, the hyperfine coupling to the four equivalent β-hydrogens is nearly isotropic, and its magnitude ($a(4H) = 31.1$ G) exceeds the $a(6H)$ value of 20.4 G for the dimethyl sulfide radical cation[18] by a factor of 1.52, in keeping with the usual $\cos^2 \theta$ dependence of β-hydrogen couplings on dihedral angle in π radicals.[19] A similar ratio (1.52) between these couplings in the oxetane[1] and dimethyl ether[20] radical cations was noted earlier.[1,21] It is also interesting that the β-hydrogen couplings in the thietane and dimethyl sulfide cations are lower than those in their oxygen counterparts[1,20] by a factor of 0.47. A corresponding reduction in the γ-hydrogen couplings from 11 G in the oxetane cation[1] to 5.2 G in the thietane cation might similarly have been expected but no γ-couplings are resolved in the spectrum of the thietane cation (Figure 1). However, the large line widths (ca. 8 G) associated with this spectrum could be due to unresolved hyperfine interactions with the 2 γ-hydrogens.

In the more mobile CF₃CCl₃ and CFCl₂CF₂Cl matrices, the monomer radical cation of thietane is not detected after irradiation at 77 K. Instead, the ESR spectra at ca. 80 K in these matrices appear to consist almost exclusively of signals from the dimer radical cation, although the hyperfine structure is not resolved. Fortunately, the spectrum in CF₃CCl₃ becomes partly resolved at 120 K and is shown in Figure 2a. A reconstruction in terms of nine binomial line components provides a satisfactory analysis as indicated by the stick diagram, although there appear to be distortions in the relative intensities of the outer lines at high field.

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(20) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1981**, *103*, 6994.

(21) The corresponding ¹H hfs ratio for the radical cations of azetidine[4] and dimethylamine[22] is 1.61.[4]

(22) (a) Danen, W. C.; Rickard, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 3254. (b) Fessenden, R. W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857.

Table I. ESR Parameters for Radical Cations and Related Radicals from Thiirane, Thietane, and Dimethyl Sulfide

| radical cation or radical	matrix or solvent	T/K	hyperfine couplings/G	g_z	g_y	g_x	g_{av} or g_{iso}	ref
thiirane cation	$CFCl_3$	90	16.1 (4 H)	2.002	2.028[a]	2.028[a]	2.019	b
thietane cation	$CFCl_3$	90	31.1 (4 H)	2.003	2.027[a]	2.027[a]	2.019	b
	$CFCl_3$	ca. 120	31 (4 H)	2.002	2.023[a]	2.023[a]	2.016	27
Me_2S^+	CF_3CCl_3	81	20.4 (6 H)	2.0023	2.019[a]	2.019[a]	2.0134	b
	$CFCl_3$	124	20.4 (6 H)	2.0076	2.0145	2.0190	2.0137	18
	$CFCl_2CF_2Cl$	77	20.3 (6 H)	2.002	2.017	2.033	2.017	31
	$CFCl_3$	77	21.2 (6 H)[c]	2.001	2.016	2.033	2.017	31
	$CFCl_3$	77	3.3 (6 D)[d]	2.002[d]	2.015[d]	2.032[d]	2.0163[d]	27
thiirane dimer cation	$CFCl_3$	90	5.8 (8 H)				2.012	b
	CF_3CCl_3	120	5.7 (8 H)				2.012	b
thietane dimer cation	$CFCl_2CF_2Cl$	95	9.4 (8 H)				2.012	b
	CF_3CCl_3	110	8.7 (8 H)				2.012	b
$Me_2S\overset{+}{\cdot}SMe_2$	CF_3CCl_3	120	6.5 (12 H)				2.010	b
	H_2O	ca. 295	6.8 (12 H)				2.0103	37
	$c-C_3H_6$	158	6.3 (12 H)				2.0102	38a
thietanyl radical	$CFCl_2CF_2Cl$	120	16.4 (1 H), 29.5 (2 H)				2.0043	b
$MeSCH_2$	$CFCl_2CF_2Cl$	118	16.7 (2 H), 3.3 (3 H)				2.0048	b
	Me_2S	133	17.54 (1 H_α), 16.70 (1 H_α) 3.25 (3 H_γ)					e

[a] Only two g components observed so $g_\perp = g_x = g_y$. [b] This work. [c] Average of 20.5, 21.4, and 21.6 G. [d] Results for $(CD_3)_2S^+$. [e] Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.

Strong evidence for the dimer radical cation assignment comes from a comparison of the hyperfine coupling and average g factor with the known parameters of the dimethyl sulfide dimer radical cation (Table I). As in the case of the corresponding monomer cations (vide supra), the hyperfine coupling to the β hydrogens is a factor of ca. 1.5 greater for the thietane than for the dimethyl sulfide species. Taken with the fact that the average g factors of these two species are very similar, there can be little doubt that the spectrum in Figure 2a is correctly assigned to the thietane dimer radical cation.

The reactivity of the dimer radical cation above 100 K in the $CFCl_2CF_2Cl$ matrix (vide infra) precluded the use of higher temperatures to obtain well-resolved spectra for the species in this matrix. Nevertheless, comparison between spectra a and b in Figure 2 shows a good match except for the inferior resolution in $CFCl_2CF_2Cl$, the g factor for the broad envelope pattern in b agreeing well with the value calculated from the dimer cation spectrum a in CF_3CCl_3 (Table I). The low-temperature spectrum in $CFCl_2CF_2Cl$ is therefore similarly assigned to the dimer cation.

On raising the temperature above 105 K in the $CFCl_2CF_2Cl$ matrix, an irreversible spectral change occurs and strong signals from another radical grow in gradually. This process is complete at 110 K and the spectrum of the product radical is quite well resolved at 120 K, as shown in Figure 2c. The hyperfine pattern consists of a clear 1:2:1 triplet (2 H) of doublets (1 H) that can unambiguously be assigned to the neutral carbon-centered 2-thietanyl radical (Table I). This reaction is also observed in the CF_3CCl_3 matrix above 140 K although the growth of strong signals from the matrix radical CF_3CCl_2[23] obscures the process.

Thiirane–$CFCl_3$ Solutions. Figure 3 shows ESR spectra of the radical species generated in this system. The 90 K spectrum b can be analyzed into two sets of overlapping features, one at low field ($g_\perp = 2.028$) consisting of a well-resolved quintet pattern ($A(4H) = 16.1$ G) with anisotropic line shapes, and the other centered at higher field ($g = 2.002$) and comprising a nonet of narrowly spaced lines ($A(8H) = 5.8$ G). These two line groups evidently possess the expected hyperfine structure for the thiirane monomer and dimer radical cations, and the g factors given in Table I compare closely with those for the counterpart species from dimethyl sulfide and thietane. What is most interesting, however, is that if these assignments to the thiirane cations are

(23) Walther, B. W.; Williams, F. *J. Chem. Phys.* **1983**, *79*, 3167.
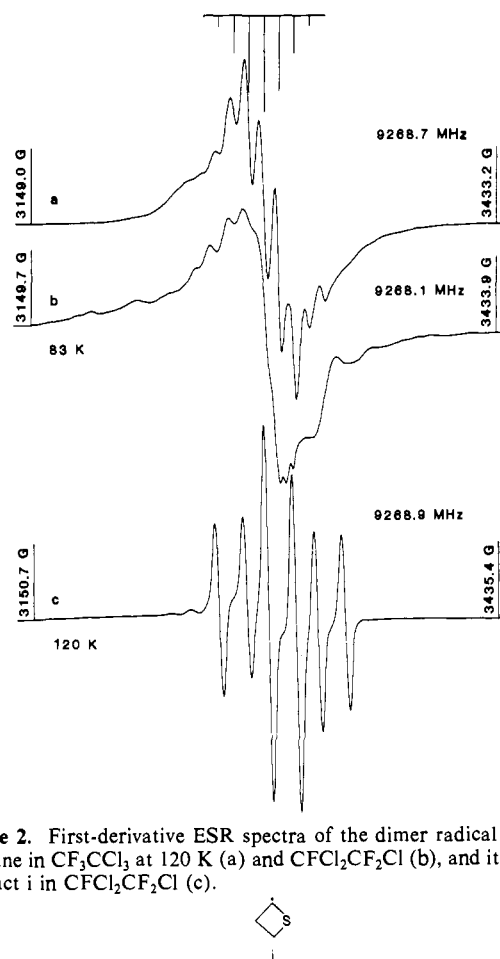
Figure 2. First-derivative ESR spectra of the dimer radical cation of thietane in CF_3CCl_3 at 120 K (a) and $CFCl_2CF_2Cl$ (b), and its reaction product i in $CFCl_2CF_2Cl$ (c).

correct, the hyperfine couplings to the β-hydrogens are a factor of 0.57 ± 0.05 smaller than those for the corresponding thietane derivatives (Table I). Strong support for this decreased hyperconjugation effect in the three-membered ring comes from MNDO calculations by Glidewell[24] that predict 1s spin densities of 0.016
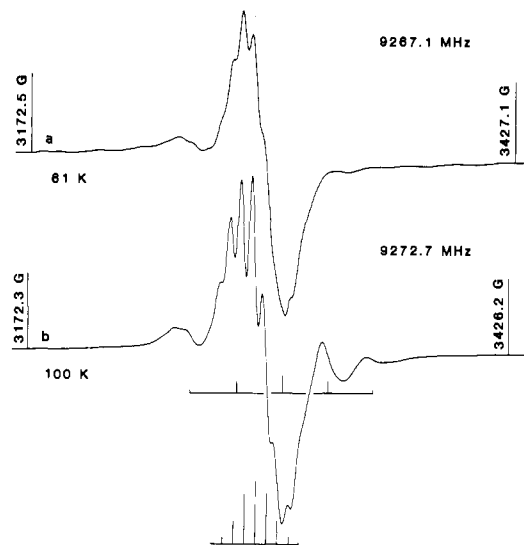
ESR Studies of the Thietane and Thiirane Radical Cations

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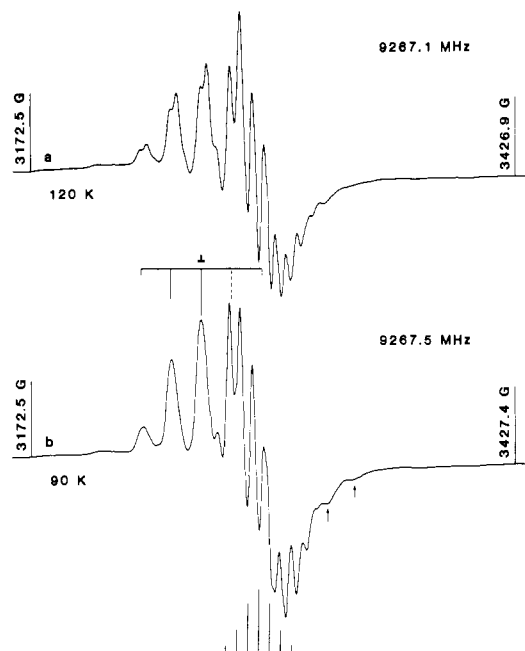
Figure 3. First-derivative ESR spectra of monomer and dimer radical cations of thiirane in $CFCl_3$. The upper stick diagram in spectrum b shows the perpendicular features of the thiirane monomer radical cation while the arrows on the right are thought to represent the two outermost high-field peaks of the corresponding parallel features. Spectrum a reveals extra fine structures for the monomer cation which can be attributed to a weak $CFCl_3$ solvent interaction. The lower stick diagram in spectrum b represents the hyperfine components of the thiirane dimer radical cation.

and 0.027 for the four β-hydrogens in the thiirane and thietane monomer radical cations, respectively, yielding a very similar ratio of 0.59.[25] Thus, these calculations are nicely consistent with our spectral assignments to the thiirane cations.

Returning to Figure 3, it is clear that the low-field quintet structure in spectrum b represents the perpendicular features of the monomer cation. The corresponding parallel features are largely obscured by the strong signals from the dimer cation so *g* has been estimated from the two outermost features at high field. Above 100 K, the ESR spectra of the thiirane cations in $CFCl_3$ showed line shape changes. In particular, a fine structure developed in the perpendicular features of the monomer cation, as illustrated in spectrum a recorded at 120 K. This fine structure is typical of a weak $CFCl_3$ solvent interaction which has been thoroughly documented for a number of radical cations.[1,17,26-29] In our experience, however, it is unusual for such solvent hyperfine interactions to become more resolved at higher temperatures. Above 140 K, the signals from the monomer and dimer cations decayed irreversibly, the dimer cation disappearing more rapidly than the monomer cation between 140 and 150 K. New ESR signals did not grow in during this decay.

Thiirane–$CFCl_2CF_2Cl$ Solutions. The initial spectrum of 81 K (Figure 4a) is dominated by a broad resonance from the thiirane

(24) Glidewell, C. *J. Chem. Soc., Perkin Trans 2* **1984**, 407.

(25) AM1 calculations by Nelsen on the hypothetical ring-closed $^2B_1$ cation of oxirane and the oxetane cation predict β-hydrogen coupling constants of 35.9 and 61.5 G, respectively, the latter agreeing reasonably well with the value of 65.6 G obtained from experiment.[1] The ratio of these calculated couplings is 0.58, almost the same as the experimental and calculated ratios discussed here for the corresponding sulfur heterocyclic cations; Nelsen, S. F., private communication.

(26) (a) Becker, D.; Plante, K.; Sevilla, M. D. *J. Phys. Chem.* **1983**, *87*, 1648. (b) Sevilla, M. D.; Becker, D.; Sevilla, C. L.; Plante, K.; Swarts, S. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 71.

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Figure 4. First-derivative ESR spectra of the dimer radical cation of thiirane in $CFCl_2CF_2Cl$ at 81 and 100 K. The quintet stick diagram in spectrum b indicates the spectrum of the radical (assigned mainly to $CF_2ClCFClCH_2CH_2$) that grows in at 100 K.
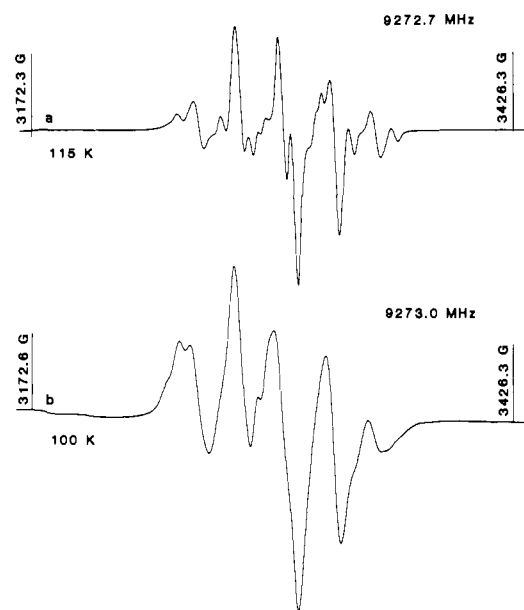
Figure 5. First-derivative ESR spectra assigned to the $CF_2ClCFClCH_2CH_2$ radical formed in $CFCl_2CF_2Cl$ formed by γ-irradiation of a 1 mol % solution of thiirane at 77 K and by subsequent annealing to 115 K. Spectrum b was recorded after the sample was cooled to 100 K.

dimer cation with no indication of features from the monomer cation, these results being similar to those obtained for thietane in this matrix. The thiirane dimer cation spectrum becomes better resolved at higher temperature but starts to lose intensity at about 100 K. Also, a new species grows in concurrently, its spectrum (Figure 4b) consisting of a quintet of broad lines with a ca. 23 G splitting and a *g* factor of 2.0033. These parameters are remarkably close to those recently reported for the ethylene radical cation at 105 K in this matrix.[15] The decay of the dimer cation is complete at about 110 K, leaving only the new species whose ESR spectrum is shown in Figure 5 both at 115 K and on subsequent cooling to 100 K.

Since the quintet pattern obtained after cooling from 115 to 100 K (Figure 5b) is virtually the same as the pattern that grows in originally at 100 K (Figure 4b), there can be little doubt that the spectrum at 115 K (Figure 5a) also refers to the same species. This spectrum shows unusually clear line resolution, and a tentative analysis suggests that the quintet pattern at low temperatures becomes partially resolved into an apparent doublet ($A(1H) =$

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Table II. ESR Parameters for RCH_2CH_2 Radicals

| radical assignment	matrix/solute or solvent	T/K	hyperfine couplings/G	g values	ref
$CF_3CCl_2CH_2CH_2$	CF_3CCl_3/C_2H_4S	150	23.6 (4 H)	2.0029	a
$CF_3CCl_2CH_2CH_2$	CF_3CCl_3/C_2H_4	150	23.7 (4 H)	2.0031	a
$C_2H_5CH^+CH_2\cdots CH_2CH_2$[b]	CF_3CCl_3/C_2H_4	142	23.5 (4 H)		16
$CF_2ClCFClCH_2CH_2$	$CFCl_2CF_2Cl/C_2H_4S$	100	23.4 (4 H)	2.0029	a
$CF_2ClCFClCH_2CH_2$	$CFCl_2CF_2Cl/C_2H_4$	105	23.5 (4 H)	2.0031	a
$C_2H_4^+$[b]	$CFCl_2CF_2Cl/C_2H_4$	105	23.3 (4 H)	2.0030	15
$CCl_3CH_2CH_2$	$c\text{-}C_3H_6$	145	22.3 (2 H_α), 22.3 (2 H_β)	2.00366	48
$CH_3SCH_2CH_2$	C_2H_4	203	21.60 (2 H_α), 14.89 (2 H_β)		c
$Me_3CSCH_2CH_2$	C_2H_4	200	21.65 (2 H_α), 16.87 (2 H_β)		c
$CF_3SCH_2CH_2$	C_2H_4	190	22.03 (2 H_α), 13.82 (2 H_β), 4.34 (3 F)		c

[a] This work. [b] See text for discussion of these alternative assignments. [c] Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.
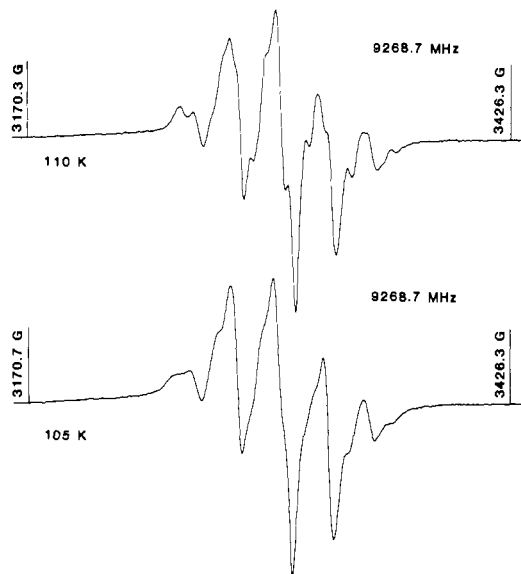
Figure 6. First-derivative ESR spectra assigned to the $CF_2ClCFClC$-H_2CH_2 radical formed in $CFCl_2CF_2Cl$ by γ-irradiation of a 1 mol % solution of ethylene at 77 K and by subsequent annealing to 110 K. Spectrum b was recorded after the sample was cooled to 105 K.

Figure 7. First-derivative ESR spectrum of the dimer radical cation of thiirane in CF_3CCl_3. The asterisks indicate unidentified components in the spectrum.

27.3 G) of approximately 1:3:3:1 quartets (A(3H) = 22.1 G), the three inner lines of the "quintet" each showing two components separated by the difference in the hyperfine couplings. In addition, the 115 K spectrum shows additional features flanking the main components by 11.2 G, these features being particularly noticeable on the outside of both the first two and the last two lines of the eight-line pattern. These extra features are attributed to residual hyperfine anisotropy, the magnitude being typical of coupling to α-hydrogens in alkyl radicals.

Ethylene–$CFCl_2CF_2Cl$ Solutions. In view of the above results indicating that the quintet spectrum that grows in during the progressive annealing of thiirane solutions at 100 K resembles the spectrum generated from ethylene solutions in the same matrix,[15] we sought further comparisons between the spectra from these two sources at different temperatures. Figure 6 shows the spectra obtained from ethylene solutions at 110 and 105 K. First, the spectrum at 105 K is remarkably similar to that obtained from thiirane at 100 K after annealing (Figure 5b), both spectra consisting of quintet envelope patterns with weak but superimposable inflections. The only significant difference resides in the outermost feature at low field where the spectrum from thiirane appears to possess some other strong component, which renders the spectrum asymmetric in appearance. Second, except for slightly inferior resolution, the ethylene-derived spectrum at 110 K is very similar to that observed from thiirane at 115 K (Figure 5a) in terms of line structure. Unfortunately, a direct comparison at 115 K was mooted by the fact that the spectrum derived from ethylene at this temperature, which contained additional lines, did not revert to the low-temperature quintet pattern on cooling. It appears, therefore, that other radical species begin to predominate in ethylene solutions at or above 115 K, thereby vitiating a really stringent comparison between well-resolved spectra at these
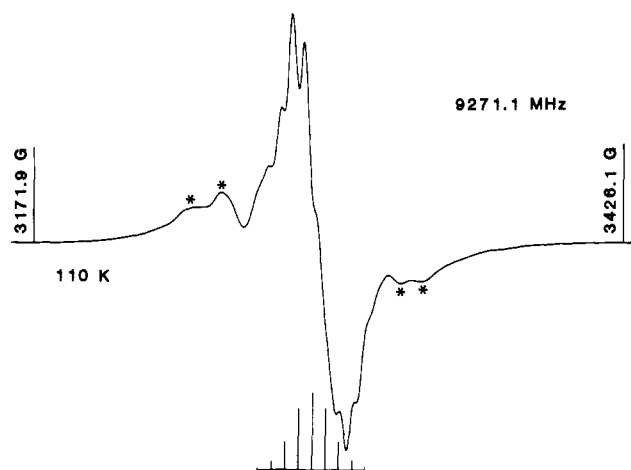
higher temperatures. Nevertheless, when allowance is made for the temperature dependence of the quintet pattern, the spectra shown in Figures 5 and 6 are sufficiently similar to establish a prima facie case that similar radicals are being generated above 100 K in the two systems.

Thiirane–CF_3CCl_3 Solutions. The thiirane dimer cation is also produced to the exclusion of the monomer cation in the CF_3CCl_3 matrix, and its spectrum (Figure 7) can be observed up to 140 K before decay sets in close to the softening point (145 K) of this matrix. Until this thiirane study, our experience had been that the phase transition in this γ-irradiated matrix is always accompanied by the growth of the CF_3CCl_2 radical,[23] irrespective of whether or not a solute is present. However, in the present case, the characteristic isotropic spectrum of CF_3CCl_2 is not observed and the sharp quintet spectrum a shown in Figure 8A is produced instead. While this work was in progress, a report[16] appeared describing a virtually identical spectrum obtained from γ-irradiated ethylene solutions in this matrix at 142 K, the onset of this spectrum again coinciding with the phase transition. This spectrum was assigned to propagating radicals initiated by the addition of 1-butene or 2-butene cations to ethylene monomer.[16] Since further work on the comparison of these high-temperature spectra in CF_3CCl_3 was desirable, we also studied ethylene solutions in this matrix, as described below.

Ethylene–CF_3CCl_3 Solutions. As shown in Figure 8A, ethylene-derived spectrum b at 150 K matches spectrum a obtained from the thiirane solution. Since the spectra are well-resolved and possess several features in addition to the sharp isotropic quintet (A(4H) = 23.7 G; g = 2.0032), the match is quite remarkable in that the entire pattern is reproduced with complete fidelity. A further test of this identity is provided by a comparison of the spectra obtained from these systems after the samples had been cooled from 150 to 100 K. The results are shown in Figure 8B, and again there is essentially a perfect match between the spectra which are now broadened by anisotropic interactions. We conclude that these results in CF_3CCl_3 demonstrate unambiguously that the same secondary radical is formed at 145 K from γ-ir-
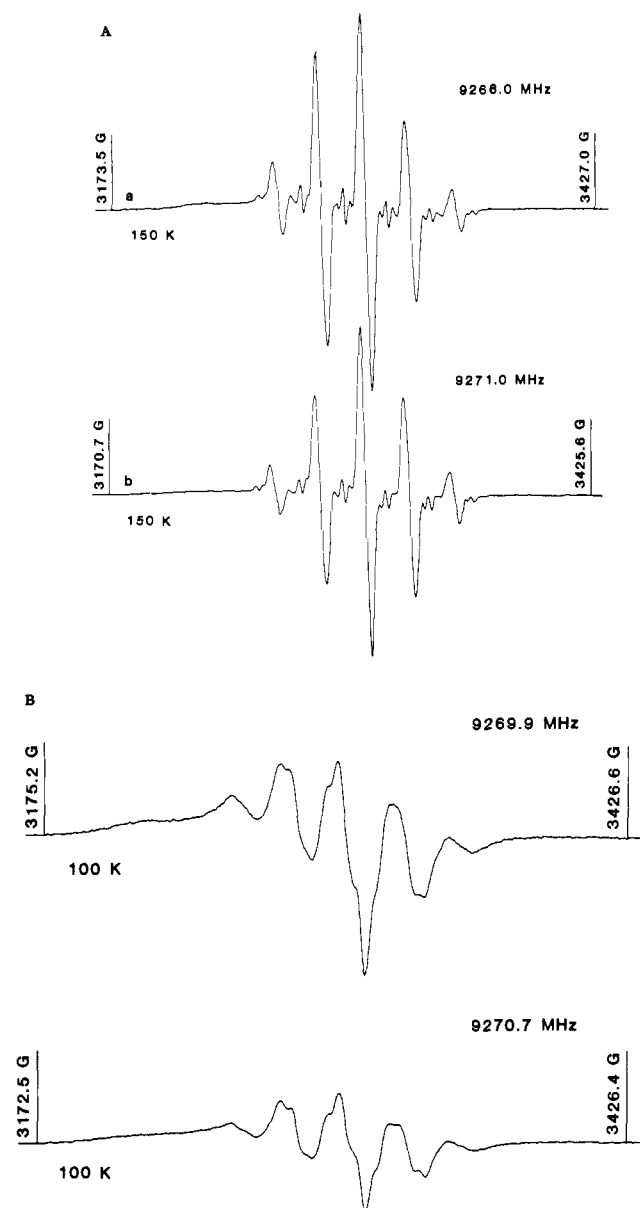
Figure 8. Comparisons of first-derivative ESR spectra assigned to the $CF_3CCl_2CH_2CH_2$ radical formed in CF_3CCl_3 under identical conditions after γ-irradiation of 1 mol % solutions of thiirane (a) and ethylene (b). In each case the sample was irradiated at 77 K and then annealed to 150 K. The 150 K spectra are shown in (A) and the corresponding spectra obtained after subsequent cooling to 100 K are compared in (B).

radiated solutions of both thiirane and ethylene. The ESR parameters extracted from the spectra are collected in Table II.

It is also interesting to note that while the broad quintet patterns obtained in CF_3CCl_3 (Figure 8B) closely resemble those obtained similarly from the two solutes in $CFCl_2CF_2Cl$ (Figures 5 and 6) at about the same temperature (100–110 K), these two sets of spectra do not match. Thus, exactly the same secondary radical does not appear to be formed in CF_3CCl_3 and $CFCl_2CF_2Cl$, although a very similar structure seems to be required to accommodate these findings.

Liquid Thiirane. Supplementary to the main investigation involving ESR detection of isolated cations in solid Freon matrices, a few product–analysis experiments were undertaken. These were carried out on γ-irradiated samples of neat liquid thiirane, the reasoning being that product yields originating from ion–molecule reactions should be maximized in the pure liquid phase. Also, the incompatability of Freons with the hydrogen flame ionization detector in the gas chromatograph (vide supra) meant that Freon solutions could not be analyzed directly for ethylene with this GC instrument.

Ethylene was always detected after the exposure of liquid thiirane samples at ambient temperature (30 °C) to γ-irradiation doses of a few Mrad, while unirradiated controls showed no response. Although a quantitative study was not attempted, the ethylene signal did not appear to increase linearly with dose in the 1–5-Mrad range, and the slope of the growth curve declined even further at higher doses. However, these effects may have resulted in part from the volatility of ethylene when the liquid thiirane sample was drawn into the syringe, the relatively high melting point (10 °C) of thiirane being a serious drawback in this respect. In any event, qualitative evidence has been obtained for the formation of ethylene in the radiolysis of liquid thiirane.

Traces of insoluble polymer were observed both in the melted Freon solutions and in the liquid thiirane samples after irradiation at −196 °C and room temperature, respectively. The soluble polymer fractions were also precipitated with methanol. After recovery of all the polymer produced from an irradiated sample of liquid thiirane, the isolated material represented a conversion of ca. 1.7% by weight for a dose of 4.9 Mrad. This corresponds to a 100-eV yield or G value of 32.8 thiirane molecules converted to polymer. The composition of this polymer was determined by elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN) and found to contain 33.86% C, 5.75% H, and 59.07% S. For comparison, the analysis of a sample of polythiirane, which had spontaneously polymerized in the laboratory, gave 31.29% C, 5.34% H, and 63.26% S whereas the calculated values are 39.95% C, 6.71% H, and 53.34% S for a polymer containing only the repeating unit $-[-CH_2-CH_2-S-]$.

Discussion

Thietane and Thiirane Monomer Radical Cations. The ESR parameters for these radical cations are given in Table I, the β-hydrogen hyperfine coupling of 31.1 G for the thietane cation being in accord with the expected 50% increase over the value for the dimethyl sulfide cation.[18] On the other hand, the much smaller β-hydrogen coupling of 16.1 G for the thiirane cation seems at first sight to be anomalous. However, the respective calculations of Glidewell[24] and Nelsen[25] on ring-closed sulfur and oxygen heterocyclic cations provide firm theoretical support for a greatly reduced β-hydrogen coupling in three-membered as compared to four-membered rings.[13] In fact, the observed ratio of 0.52 for the thiirane–thietane pair agrees reasonably well with the calculated value of 0.59.[24] We conclude that both thiirane and thietane yield ring-closed sulfur-centered cations, the SOMOs of which are illustrated in structures **1** and **2**.
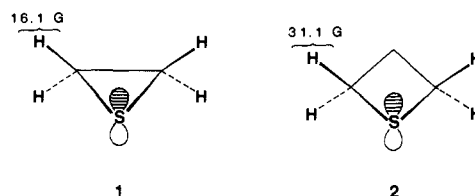
It should be noted that a smaller-than-expected β-hydrogen coupling was originally advanced as an argument for the ring opening of the oxirane cation.[1] In this case, however, the coupling of 16.4 G for the oxirane cation must be referenced to the much larger value (65.6 G) for the oxetane cation[1] yielding a ratio of only 0.25, well below the ratio of 0.58 predicted by theoretical calculations on the ring-closed cations.[25] Since there is little question that the oxetane cation is ring closed, the original argument for the ring-opening of the oxirane cation is still valid,[30] although the expected β-hydrogen coupling for a $^2B_1$ ring-closed oxirane cation must now be revised downwards to about 36 G.[25]

Returning to the sulfur-centered cations, the serious discrepancy between our work and that of Ramakrishna Rao et al.[27] concerning the thiirane monomer cation has been eliminated.[13] Almost

(30) Additional evidence for the C···C ring opening of the oxirane cation comes from an ESR study of the doubly labeled ^{13}C species.[2] The form of the ^{13}C hyperfine anisotropy is characteristic of an allylic planar structure with large spin densities in the carbon p orbitals directed perpendicular to the molecular plane.

identical ESR spectra were reported for the thiirane and thietane monomer cations in $CFCl_3$ at ca. 120 K,[27] but now it appears that the sample of thiirane used by these authors[27] must have contained thietane so that the spectrum of the latter cation dominated under the conditions used.[13]

The apparent g tensors for these two cations are almost identical (Table I), each showing appreciable anisotropy ($\Delta g = 0.025$) as well as being axially symmetric. These findings are quite similar to those for the *ring-closed* oxetane cation.[1] Since $g_\parallel$ is much less than $g_\perp$, the unique direction is readily assigned to the symmetry (z) axis of the sulfur 3p orbital (SOMO) that is perpendicular to the CSC plane of the molecule, as shown in structures **1** and **2**. In order to be consistent with the coordinate system employed in the recent paper by Bonazzola et al.,[31] and the one used later in this paper for the description of the dimer cations, the y axis is taken along the bisector of the CSC angle in the molecular plane. According to the detailed analyses of the g tensors for Me_2O^+ [20,32] and Me_2S^+,[31] $g_x > g_y > g_z$, and therefore in the present case the two largest components are probably averaged to give $g_\perp$ by a rotation of the molecular plane around the z axis.

A specific comparison between the g tensors for the oxetane and thietane cations is suggested by the work of Bonazzola et al.[31] These authors extracted the complete tensor for Me_2S^+ from ESR spectra at low temperatures and showed that each of its principal components g_S could be related to the corresponding component g_O of the Me_2O^+ tensor[20] through the simple expression

$$g_S - g_e = (\lambda_S/\lambda_O)(g_O - g_e)$$

where λ_S (382 cm^{-1}) and λ_O (151 cm^{-1}) are the spin–orbit coupling constants for sulfur and oxygen atoms, respectively,[33] and g_e (2.0023) is the g factor for the free electron. Applying this formula[34] to the calculation of the g components for the thietane cation from the previous data for the oxetane cation, one obtains $g_\parallel = 2.0081$ and $g_\perp = 2.0306$ in reasonably good agreement with the observed values of 2.003 and 2.027. Thus, it is clear from g-tensor data, as well as from the earlier comparison of β-hydrogen hyperfine couplings, that the cations of thietane and oxetane are related to each other in precisely the same manner as are the cations of dimethyl sulfide and dimethyl ether. The conclusion that both oxetane and thietane cations have ring-closed structures with the unpaired electron on the heteroatom is thereby strongly reinforced.

The consideration of the g tensor assumes even more importance for establishing the structure of the thiirane cation, since the ring-closed oxirane cation is not available for experimental comparison in this case and the β-hydrogen hyperfine couplings for thiirane and thietane, which differ by almost a factor of 2, are reconciled only with the aid of theoretical calculations[24] (vide supra) and interpretations of data from photoelectron spectroscopy.[13] The g-tensor arguments in favor of a ring-closed thiirane structure are twofold. First, the finding of almost identical g-value components for the thietane and thiirane cations (Table I) is highly suggestive of closely comparable structures, and second, a planar C···C ring-opened thiirane cation should have a much lower and less anisotropic g factor by analogy to the experimental results for the ring-opened oxirane cation where the spin is primarily localized on the two carbons.[30] The conclusion that the thiirane cation is also ring-closed can therefore be reached independently of the hyperfine data.

Thietane and Thiirane Dimer Radical Cations. Considerable interest has been shown in the dimer radical cations of simple dialkyl sulfides since their initial observation by pulse radiolysis[35,36]

and ESR[37,38a] techniques in solution. However, until the advent of the Freon generation method[39] and its application to this problem,[18] the corresponding monomer cations were unknown save for that of di-*tert*-butyl sulfide where steric factors probably prevent dimer cation formation.[38] While the solid-state Freon method has nicely filled this gap in our knowledge,[18,27,31] all of the prior reports on organic sulfides using this technique describe only the generation of monomer cations in $CFCl_3$. By using CF_3CCl_3 and $CFCl_2CF_2Cl$ matrices in addition to $CFCl_3$, we have now succeeded in generating both monomer and dimer cations in the solid state so that a comparison of these species under similar conditions is now possible for the first time.

Although the work on dimethyl sulfide will be reported elsewhere in connection with a detailed study of ion–molecule reactions in $CFCl_2CF_2Cl$ and CF_3CCl_3, the ESR parameters obtained for the monomer and dimer cations of Me_2S are included in Table I. For the dimer cation, there is excellent agreement between the solid-state parameters and those derived from solution studies.[37,38a] It is also of interest that the β-hydrogen hyperfine couplings of 9.3[37] and 8.6[38a] G for the previously reported dimer radical cation of tetrahydrothiophene in solution correspond closely to the average value of 9.05 G obtained for the closely related dimer radical cation of thietane in the present work. Such comparisons indicate that the structure of these dimer cations must be very similar in the solid and liquid states.

The most detailed source of information about the structure of such dimer cations comes from the single-crystal ESR study of Nishikida and Williams on the congeneric $(Me_2Se)_2^+$ species.[40] In particular, they showed that the principal axes for the g and ^{77}Se hyperfine tensor components are mutually related in a way that defines the $\sigma^2\sigma^{1*}$ structure. Thus, the direction associated with the lowest g-tensor component also corresponds, as expected, to that for the largest element of the ^{77}Se hyperfine tensor, so this direction must be along the σ-bond axis. This model for the dimer cation structure,[40] which has been widely accepted,[36b,38a] is depicted for thiirane in **3**, and by analogy to the structure of the monomer cations, we expect the order $g_x > g_y > g_z$ to also apply in this case.
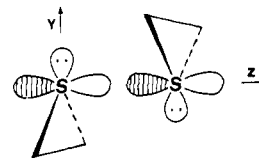
3

Another important experimental guide to the structure of the dimer cations comes from a comparison of the β-hydrogen hyperfine couplings for the monomer and dimer species. As noted earlier in connection with studies on Me_2S and Me_2Se,[18] the ratio of these couplings for each monomer–dimer pair is about 3 rather than 2. In fact, this ratio is 3.1–3.2 for both Me_2S and Me_2Se. On the other hand, a much lower ratio of ca. 1.1 applies to a similar comparison of ^{1}H couplings in Me_3Si to those in $Me_6Si_2^+$, and also between those in Me_3Ge and $Me_6Ge_2^+$.[18] This striking

(31) Bonazzola, L.; Michaut, J. P.; Roncin, J. *J. Chem. Phys.* **1985**, *83*, 2727.

(32) In ref 20, the y and z axes are interchanged from the coordinate system used here. In ref 27, the x and y axes are similarly interchanged so that the order of the g-tensor components in their Table I should be $g_y > g_x > g_z$ rather than $g_x > g_y > g_z$.

(33) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row: New York, NY, 1967; p 138.

(34) The formula assumes that spin density distributions in the ground and excited states, as well as the energy differences between these states, are similar for oxygen- and sulfur-centered radicals.

(35) Meissner, G.; Henglein, A.; Beck, G. *Z. Naturforsch. A* **1967**, *22b*, 13.

(36) (a) Bonifacic, M.; Mockel, H.; Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 675. (b) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.

(37) Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1748.

(38) (a) Gara, W. B.; Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1444. (b) We thank a referee for calling our attention to a slightly earlier report (Petersen, R. L.; Nelson, D. J.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 225) in which a broad ESR line showing defined features at g 2.034 and 2.000 was observed after γ irradiation of pure di-*tert*-butyl sulfide at 77 K. This signal was tentatively assigned to the monomer cation. We should add, however, that the monomer cation assignment given in ref 38a is particularly definitive, based as it is on a coupling of 32.5 G to one ^{33}S nucleus and a g factor of 2.013 for an isotropic spectrum.

(39) (a) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. (b) Symons, M. C. R. *Chem. Soc. Rev.* **1984**, *12*, 393.

(40) Nishikida, K.; Williams, F. *Chem. Phys. Lett.* **1975**, *34*, 302

difference has been attributed to the character of the MO formed between the heavy atoms in the dimer species, the large ratios being linked to a σ^* SOMO while the ratios near unity are associated with a σ SOMO.[18] Subsequent calculations by Glidewell[41] at the MNDO level strongly support this correlation. For example, he reports ^{1}H spin densities of 0.0212 and 0.0051 for Me_2S^+ and $(Me_2S)_2^+$, respectively, corresponding to a ratio of 4.1. Also, he found that little change occurred in the bond angles of the Me_3Si and Me_2S^+ radicals on going to their dimeric forms, suggesting that geometry changes at the heavy atom do not contribute to this effect. Thus, both experiment and theory agree that the nature of the SOMO in the dimer is the decisive factor in determining the ratio of ^{1}H couplings between conjugate monomer and dimer radicals.

Accepting this correlation, the monomer–dimer ^{1}H coupling ratios of 3.4 and 2.8 for the thietane and thiirane cations, respectively, are fully consistent with the expected σ^* structure for these dimer species. This characterization is further substantiated by the fact that the average g value for both dimer cations (2.012) is reasonably close to the isotropic value of 2.010 for the prototype $(Me_2S)_2^+$ species. Indeed, it appears from the solution studies that an isotropic g factor in this rather narrow range is diagnostic for this class of radicals. Finally, in view of the importance of the thiirane dimer cation to the subsequent discussion, it is worth stressing that its ESR parameters show no anomalies. Given the monomer–dimer relationship, this in turn indicates that the ESR spectrum of the thiirane monomer cation has been properly identified in the present work.

Decomposition of the Thietane Dimer Cation. The observation that the decay of the thietane dimer cation at 100–110 K in the $CFCl_2CF_2Cl$ matrix is accompanied by the appearance of the 2-thietanyl radical (Figure 2) seems to point to the occurrence of the decomposition reaction 1. A similar process appears to take

$$(CH_2)_3S \overset{+\cdot}{-} S(CH_2)_3 \longrightarrow (CH_2)_3SH^+ + \overset{\cdot}{\square}S \qquad (1)$$
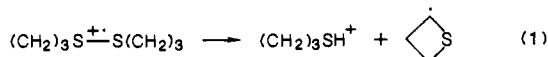
place in the CF_3CCl_3 matrix above 140 K. Also, ESR evidence for the analogous decomposition of $(Me_2S)_2^+$ by reaction 2 has been obtained in the $CFCl_2CF_2Cl$ matrix at ca. 110 K.[42] It is
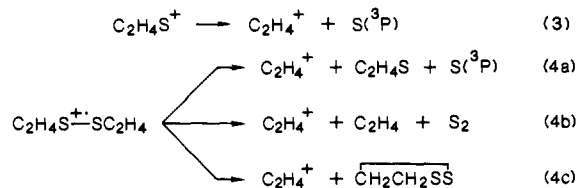
$$Me_2S \overset{+\cdot}{-} SMe_2 \longrightarrow Me_2SH^+ + CH_2SMe \qquad (2)$$
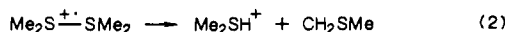
also of interest to recall that the CH_2SeMe radical was identified together with the $(Me_2Se)_2^+$ species in the ESR spectrum of a γ-irradiated single crystal of dimethyl selenide.[40]

The mechanism of reactions 1 and 2 can be formulated in terms of either hydrogen atom or proton transfer pursuant to, or concerted with, the dissociation of the dimer cation. In the former case the reaction can be viewed as a free-radical process in which the hydrogen atom is donated from a separating neutral molecule to the ionized sulfur atom in the monomer cation. Alternatively, the mechanism can involve a proton transfer from a separating cation to a neutral sulfide molecule. A deprotonation reaction between the Me_2S monomer cation and a base (hydroxide ion, water, ammonia, or EDTA) has been postulated to explain the pH-dependent formation of CH_2SMe in the aqueous oxidation of dimethyl sulfide by redox reagents[38a] and hydroxyl radicals.[37] However, we cannot distinguish between deprotonation and H atom transfer mechanisms in the present case, and further discussion of this general topic is deferred to another paper dealing with a wide variety of similar ion–molecule reactions.[42]

Ethylene Molecule Extrusion from the Thiirane Dimer Radical Cation. Our ESR results demonstrate that the same radical is formed when γ-irradiated CF_3CCl_3 solutions of thiirane and ethylene are annealed to 150 K. A similar correspondence is observed at ca. 110 K between the ESR spectra of γ-irradiated $CFCl_2CF_2Cl$ solutions of these solutes. Two different interpretations of this finding will be considered. First, it might be thought

that the radical in each case is in fact $C_2H_4^+$, as proposed by Shiotani et al.[15] on the basis of their observation of a five-line ESR pattern from ethylene solutions in $CFCl_2CF_2Cl$. However, Fujisawa et al.[16] have questioned this assignment, arguing from their ESR results that the 1-butene cation is initially formed by an ion–molecule reaction at 77 K and that the five-line pattern observed at 105 K is due to propagating radicals produced by the consecutive addition of ethylene to the 1-butene cation.

Our results go a considerable step further in disproving the $C_2H_4^+$ assignment.[15] In order for $C_2H_4^+$ to be the radical responsible for the five-line spectrum, it would have to be produced from thiirane as well as from ethylene. The only reasonable path in this case is from the monomer cation by reaction 3, or from the dimer cation by reactions 4a, 4b, or 4c.

$$C_2H_4S^+ \longrightarrow C_2H_4^+ + S(^3P) \qquad (3)$$

$$C_2H_4S \overset{+\cdot}{-} SC_2H_4 \begin{cases} \longrightarrow C_2H_4^+ + C_2H_4S + S(^3P) & (4a) \\ \longrightarrow C_2H_4^+ + C_2H_4 + S_2 & (4b) \\ \longrightarrow C_2H_4^+ + \overline{CH_2CH_2SS} & (4c) \end{cases}$$

A thermochemical cycle shows that (3) is endothermic by an estimated 3.01 eV, this being made up of the calculated energy (1.54 eV) for the dissociation of neutral C_2H_4S to C_2H_4 and $S(^3P)$[43] and of the difference in ionization potentials (1.47 eV) between those of C_2H_4 (10.52 eV) and C_2H_4S (9.05 eV).[44] Similarly, reaction 4a is more endothermic than (3) by the enthalpy difference that accompanies dimer cation formation. Moreover, consideration of the low S–S bond energy (1.45 eV)[45] suggests that reactions 4b and 4c would also be highly endothermic.

In addition to these thermochemical arguments, a $C_2H_4^+$ assignment also seems to be inconsistent with the fact that the sharp five-line spectrum grows in at the same temperature (ca. 145 K) in CF_3CCl_3 irrespective of whether it is ethylene or thiirane that is initially present in the solution. Such a coincidence is difficult to reconcile with $C_2H_4^+$ formation by a direct path from ethylene and an indirect one from thiirane. However, this coincidence is just what would be expected for a *secondary* radical that originates from a common precursor or set of reactants in the two systems.

The logical antecedent to the formation of the secondary radical with the five-line ESR pattern in the two solutions is ethylene itself, provided that a mechanism exists for the generation of neutral ethylene from the thiirane monomer or dimer cations. Just such a reaction has been observed in an ICR mass spectrometer,[14] as indicated by the ion–molecule process 5a. This reaction could

$$C_2H_4S^+ + C_2H_4S \rightarrow C_2H_4S_2^+ + C_2H_4 \qquad (5a)$$

equally well be represented in the condensed phase by the formation and subsequent decomposition of the dimer radical cation, as in (5b). It is significant that the secondary radical is only produced during and after the decay of the thiirane dimer cation

$$C_2H_4S^+ + C_2H_4S \longrightarrow C_2H_4S \overset{+\cdot}{-} SC_2H_4 \longrightarrow$$

$$\overline{\square}S^+ \!\!-\! \dot{S} + C_2H_4 \qquad (5b)$$
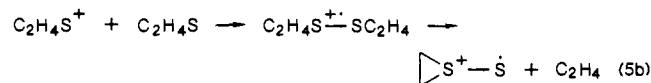
in both the $CFCl_2CF_2Cl$ and CF_3CCl_3 matrices, so reaction 5 can be the source of ethylene for the formation of this secondary radical.

We therefore propose that ethylene functions as a spin trap to produce an RCH_2CH_2 radical. However, the concentration of C_2H_4 must be relatively low in the thiirane system even though its generation probably involves a short chain reaction (vide infra).

(41) Glidewell, C. *J. Chem. Res. (S)* **1983**, 22.
(42) Qin, X.-Z.; Williams, F. *Radiat. Phys. Chem.* **1988** (Milton Burton Commemorative Issue), in press.

(43) (a) Strausz, O. P.; Gunning, H. E.; Denes, A. S.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1972**, *94*, 8317. (b) Strausz, O. P.; Gosavi, R. K.; Denes, A. S.; Csizmadia, I. G. *Theor. Chim. Acta* **1972**, *26*, 367.
(44) McAlduff, E. J.; Houk, K. N. *Can. J. Chem.* **1977**, *55*, 318.
(45) (a) Walling, C. *Free Radicals in Solution*; J. Wiley & Sons: New York, NY, 1957; p 335. (b) Fairbrother, F.; Gee, G.; Merrall, G. T. *J. Polym. Sci.* **1955**, *16*, 459.

Accordingly, a high efficiency of radical addition to ethylene is required in competition with radical–radical reactions. Just this situation can arise under solid-state conditions if the C_2H_4 molecule can diffuse to react with immobile matrix radicals. In fact, a similar reaction resulting in the formation of RO_2 radicals from the presence of adventitious traces of oxygen has occasionally been observed in γ-irradiated neat $CFCl_2CF_2Cl$ matrices over the same temperature range (80–130 K), the **g** tensor for RO_2 in this system being very similar to the values reported for CF_3O_2 and CCl_3O_2.[46]

Before focussing on reaction 5b, the structure of the secondary radical will be considered briefly. Although we agree with Fujisawa et al.[16] that this radical has the generic structure RCH_2CH_2, we suggest that the group R is derived from the matrix rather than from the solute. In this connection, it is striking that the α- and β-hydrogen hyperfine splittings are virtually identical in the well-resolved spectrum of the secondary radical produced in CF_3CCl_3 at 150 K. This situation is rarely encountered for radicals of this type.[47] Indeed, it was this accidental equivalence that led inadvertently to the $C_2H_4^+$ assignment.[15] However, as shown in Table II, the radical $CCl_3CH_2CH_2$[48] possesses equal ^1H coupling constants and a g factor which are not dissimilar to the parameters of the secondary radical produced in CF_3CCl_3. Even more revealing, the CF_3CCl_2 radical is not observed with the secondary radical at 145 K in the thiirane and ethylene solutions, although it is the normal product of matrix annealing at this temperature for other γ-irradiated CF_3CCl_3 solutions.[23] These observations strongly suggest that the secondary radical is produced in CF_3CCl_3 by the simple addition of CF_3CCl_2 to ethylene, giving CF_3C-$Cl_2CH_2CH_2$. Similarly, we can expect closely related secondary radicals to be formed in $CFCl_2CF_2Cl$ by the addition of matrix radicals such as $CF_2ClCFCl$ to ethylene,[49] thus accounting for the results.

The occurrence of an ethylene elimination reaction as in (5) is also supported by the GC detection of ethylene as a product from the radiolysis of liquid thiirane. In this case other reactions may also contribute since in the mass-spectrometric studies of the ion chemistry of thiirane,[14] evidence was obtained from double resonance experiments for the additional ion–molecule reactions 6 and 7. This series of consecutive ion–molecule reactions[14]

$$C_2H_4S_2^+ + C_2H_4S \rightarrow C_2H_4S_3^+ + C_2H_4 \tag{6}$$

$$C_2H_4S_3^+ + C_2H_4S \rightarrow C_2H_4S_4^+ + C_2H_4 \tag{7}$$
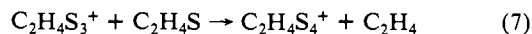
(46) The RO_2 radicals produced in $CFCl_2CF_2Cl$ were identified from 80–90 K ESR spectra showing the characteristic line shape for an axially symmetric g tensor ($g_\parallel$ = 2.038, $g_\perp$ = 2.003). This spectrum changed reversibly to give an intense narrow line (g_{iso} = 2.015) at 120 K (unpublished work by Q.-X. Guo, X.-Z. Qin, J. T. Wang, and F. Williams). These parameters are similar to those reported for the powder spectra of CF_3O_2 ($g_\parallel$ = 2.0374, $g_\perp$ = 2.0029, g_{iso} = 2.0144) and CCl_3O_2 ($g_\parallel$ = 2.0374, $g_\perp$ = 2.002–2.003, g_{iso} = 2.013–2.015): (a) Bennett, J. E.; Mile, B.; Thomas, A. *Proc. 11th Int. Symp. Combustion* **1967**, *63*, 262. (b) Hesse, C.; Le Ray, N.; Roncin, J. *J. Mol. Phys.* **1971**, *22*, 137.

(47) (a) Fischer, H. In *Landolt-Bornstein*; New Series, Group II, *Magnetic Properties of Free Radicals*; Springer-Verlag: Berlin-Heidelberg, 1977; Vol. 9, Part b, pp 10–36. (b) Inspection of the tables in ref 47a reveals no support for the postulate by Fujisawa et al.[16] that a primary *n*-alkyl radical produced by the free radical polymerization of ethylene is likely to be responsible for the observed five-line ESR spectrum with equal or nearly equal α- and β-hydrogen hyperfine coupling constants. Neither the high-temperature nor the low-temperature spectra of *n*-butyl through *n*-decyl radicals reveal any such equivalence, the temperature dependence being due to hindered rotation at the radical center. Also, these tables show that for $RSCH_2CH_2$ radicals, the β-hydrogen couplings are consistently much smaller than those for the α-hydrogens (Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846). This rules out the remote possibility of an accidental spectral coincidence between radicals of this type formed directly from thiirane and the ones produced by addition to ethylene.

(48) Edge, D. J. E.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 6485.

(49) By analogy to the formation of the CF_3CCl_2 radical in the CF_3CCl_3 matrix,[23] both the $CF_2ClCFCl$ and $CFCl_2CF_2$ radicals would be expected to result from $CFCl_2CF_2Cl$ by chloride ion loss on dissociative electron attachment (Hasegawa, A.; Shiotani, M.; Williams, F. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 157). The $CF_2ClCFCl$ radical may predominate, however, because of the statistical effect and also because electron attachment may take place more readily at a dichloro-substituted than at a monochloro-substituted carbon. Evidence for this radical has been obtained: Qin, X.-Z.; Guo, Q.-X.; Wang, J. T.; Williams, F. *J. Chem. Soc., Chem. Commun.*, in press.
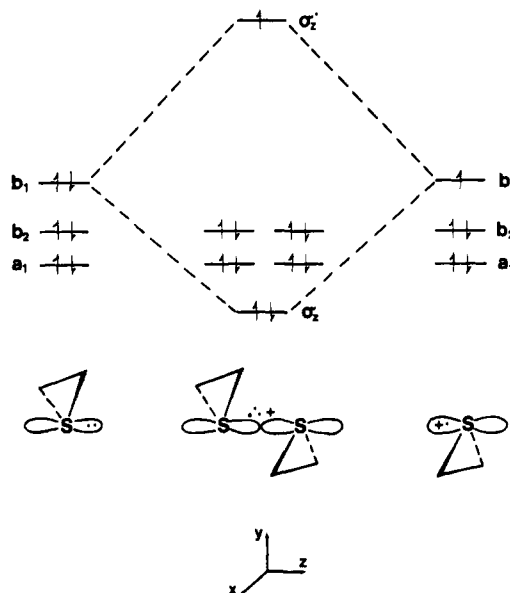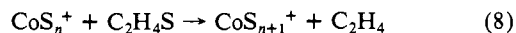

Figure 9. A qualitative MO energy-level diagram indicating how the electron configuration in the dimer cation is achieved by the combination of the thiirane monomer cation with a thiirane molecule. The MO representations used here and in Figures 10 and 11 for thiirane are referenced to the usual coordinate system for molecules in the C_{2v} point group (see ref 53).

represented by (5a), (6), and (7) constitutes a short chain in which the propagation step involves sulfur transfer to the growing ion accompanied by ethylene elimination. By analogy to the findings for radiation-induced cationic polymerization,[50] one would expect a chain reaction of this sort to occur with higher probability in the liquid thiirane than in a dilute solution of the thiirane in a solid matrix. However, there is a precipitous drop in the gas-phase rate constant from a collision value of ca. 10^{11} M^{-1} s^{-1} to about 2×10^9 M^{-1} s^{-1} in going from reaction 6 to reaction 7,[14] so a long kinetic chain may not be sustainable even with theoretically attainable free-ion lifetimes of ca. 10^{-3} s in the liquid phase under steady-state γ-irradiation.[50] At any rate, a detailed quantitative study of ethylene production would be needed to characterize the potential of this chain reaction in the liquid phase. Incidentally, elemental analysis of the polymer isolated from γ-irradiated liquid thiirane suggests that it consists mainly of the ring-opened addition polymer with the repeat structure $-[-CH_2CH_2S-]-$. Thus it appears that a simultaneous addition polymerization takes place, probably also by a cationic mechanism since this is well documented for the analogous radiation-induced ring-opening polymerization of various oxiranes.[51]

There are two features of the sulfur-transfer propagation reaction which require comment before we discuss the electronic changes that are involved in the reaction. First, the reaction appears to be independent of the nature of the initiator, as expected for a true propagation reacton. Perhaps the best indication of this comes from Freiser's mass-spectrometric work showing that cobalt and other transition-metal ions can also be suitable initiators, as evidenced by the detection of cobalt polysulfide ions in reaction 8.[52] Second, one can formulate the propagation reaction as proceeding through a generalized intermediate $X^+S_n{^-}-SC_2H_4$ that

$$CoS_n^+ + C_2H_4S \rightarrow CoS_{n+1}^+ + C_2H_4 \tag{8}$$

is essentially isostructural with the thiirane dimer radical cation, both possessing a 3-electron σ bond formed by the combination of a sulfide radical center with the electron pair in the sulfur

(50) Williams, F. In *Fundamental Processes in Radiation Chemistry*; Ausloos, P., Ed.; Interscience-Wiley: New York, NY, 1968; pp 515–598.

(51) Aikins, J. A.; Williams, F. In *Ring-Opening Polymerization*; ACS Symposium Series 286; McGrath, J. E., Ed.; American Chemical Society: Washington, DC, 1985; Chapter 24, pp 335–359.
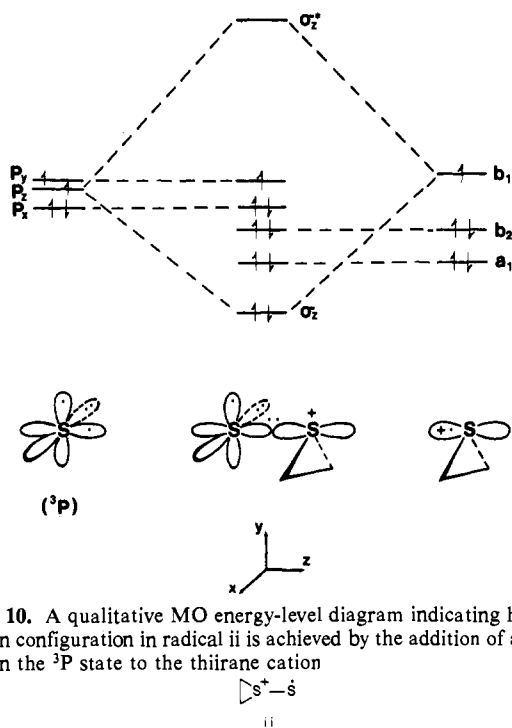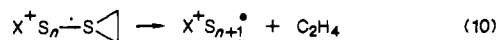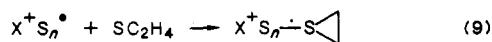
(52) Freiser, B., private communication.

Figure 10. A qualitative MO energy-level diagram indicating how the electron configuration in radical ii is achieved by the addition of a sulfur atom in the ^3P state to the thiirane cation

Figure 11. A qualitative MO correlation diagram for the dissociation of the thiirane dimer radical cation to radical ii and an molecule.

ii

$3p_z(b_1)$ orbital of thiirane.[53] Thus the sulfur-transfer propagation reaction can be regarded as a two-step process, (9) and (10), in

$$X^+S_n{}^{\bullet} + SC_2H_4 \longrightarrow X^+S_n{-}S\triangleleft \qquad (9)$$

$$X^+S_n{-}S\triangleleft \longrightarrow X^+S_{n+1}{}^{\bullet} + C_2H_4 \qquad (10)$$

which the first step represents the formation of this σ^* intermediate and the second is analogous to the decomposition of the dimer cation in (5b). Therefore, for the sake of simplicity, the dimer radical cation can be considered as the prototype intermediate in the propagation reaction.

In order to describe reaction 5b by means of an MO correlation diagram, it is necessary to specify the electron configuration for both the dimer cation and the disulfide product. In view of our earlier discussion, the structure of the dimer cation depicted in Figure 9 requires no further comment.[54] Turning to the structure of the disulfide product $C_2H_4S^+{-}S^{\cdot}$, this is best approached by considering the interaction of a ground-state ^3P sulfur atom with the monomer radical cation, as depicted in Figure 10. Essentially the only interaction is the coupling of two unpaired electrons along the z axis to form the S–S bond, leaving one unpaired electron in a p orbital perpendicular to this bond on the pendant sulfur atom. The local radical center in this disulfide species is therefore the same as that of the monomer cation or a monosulfide radical (RS·), the spin-bearing orbital being a sulfur 3p orbital in each case. A similar diagram may therefore be used to describe the structure of any polysulfide radical species of the type produced in reaction 10.

We are now in a position to consider the MO correlation diagram shown in Figure 11. The extrusion of the ethylene molecule

from a thiirane moiety in the dimer radical cation according to reaction 5b is seen to be a concerted process in which the two electrons of the a_1 thiirane orbital go into the newly formed ethylene π orbital and the b_2 electron pair is retained in the p_x orbital of the pendant sulfur atom. Thus the filled MOs which make up the two C–S bonds in one of the thiirane moieties[54] correlate naturally with ground-state orbitals in the reaction products. On the other hand, the $\sigma_z{}^*$ SOMO in the dimer cation does not correlate directly with the p_y SOMO of π symmetry in the disulfide radical product. Nevertheless, the $\sigma_z{}^* \rightarrow p_y$ change is strongly stabilizing and the symmetry restriction at the pendant sulfur atom should be relaxed as the reaction proceeds and an empty p_y orbital is made available. In fact, the driving force for the reaction must originate from this internal unpaired-electron transfer from antibonding to nonbonding sulfur p orbitals because otherwise the reaction is formally analogous to the highly endothermic conversion of thiirane to C_2H_4 and $S(^1D)$.

It can be inferred from the above description that the dimer radical cation represents a high-energy intermediate on the potential-energy surface for sulfur-transfer reaction 5a between the monomer cation and a neutral thiirane molecule. It follows that the structure of the transition state[55] must closely resemble this σ^* intermediate, again in keeping with the idea that little molecular change is needed to reach the barrier at which the unpaired-electron transfer can proceed. Clearly, the ability to form a high-energy σ^* intermediate facilitates the sulfur-transfer reaction.[56]

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(53) The b_1, b_2, and a_1 representations for the molecular orbitals of thiirane[44] are referenced to the usual coordinate system for molecules of C_{2v} symmetry with the C_2 axis along the z direction and the CSC ring in the yz plane. Thus, the p_x, p_y, and p_z sulfur atomic orbitals designated in Figures 10 and 11 are of b_2, a_1, and b_1 symmetry, respectively, when transformed to the above coordinate system.

(54) For the case of the generalized σ^* intermediate in reactions 9 and 10, the same correlation applies where the filled a_1 and b_2 orbitals correspond to the C–S bonds of the reacting thiirane molecule. These Walsh orbitals for thiirane have been discussed: (a) Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C.-C. *J. Am. Chem. Soc.* 1973, *95*, 7644. (b) Rohmer, M.-M.; Roos, B. *J. Am. Chem. Soc.* 1975, *97*, 2025.
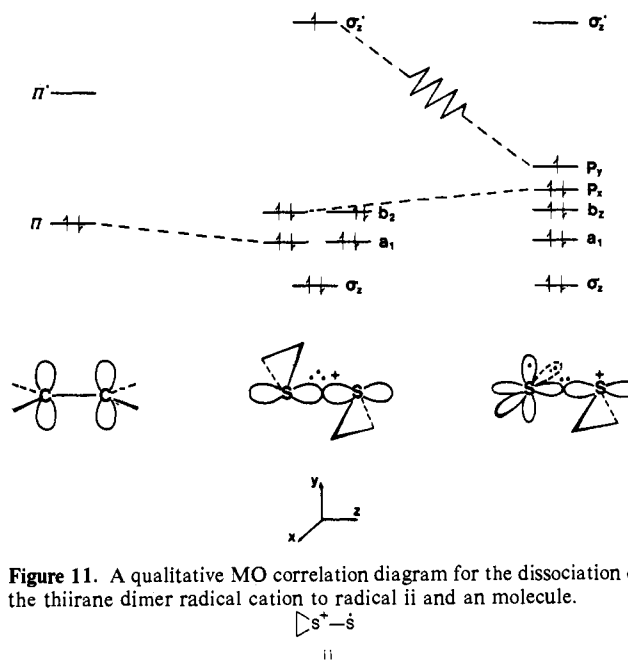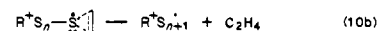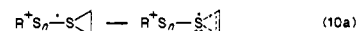
(55) Hammond, G. S. *J. Am. Chem. Soc.* 1955, *77*, 334.

(56) The sulfur-transfer propagation reaction represented by reactions 9 and 10 shows an interesting analogy to the general mechanism of the $S_{RN}1$ reaction[57] if we consider reaction 10 to proceed in two steps, as follows:

$$R^+S_n{-}S\triangleleft \longrightarrow R^+S_n{-}S\cdot\triangleleft \qquad (10a)$$

$$R^+S_n{-}S\cdot\triangleleft \longrightarrow R^+S_{n+1}{}^{\bullet} + C_2H_4 \qquad (10b)$$

Thus the overall mechanism consists of radical addition to a stable diamagnetic species (eq 9), an internal electron transfer (eq 10a) as discussed in the main text, and a dissociation step (eq 10b). The counterpart reactions in the generalized $S_{RN}1$ mechanism are[57c]

$$R + Y^- \rightarrow RY^-$$

$$RY^- + RX \rightarrow RY + RX^-$$

$$RX^- \rightarrow R + X^-$$
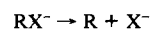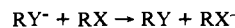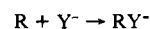
It could be argued, however, that the species represented as the product of reaction 10a is more properly regarded as the transition state for reaction 10.

Concluding Remarks. The ESR study described here provides evidence for ethylene extrusion reaction 5b and its analogues previously observed in the gas phase.[14] In addition, the structure of the dimer radical cation has been characterized. This σ^* species plays an important role as a high-energy intermediate along the reaction path leading to ethylene extrusion. The use of an MO correlation diagram further clarifies the fine details of this reaction, the driving force being attributed to a transfer of the unpaired electron from the σ^* orbital to the vacating p orbital on sulfur as the ethylene molecule is eliminated in a concerted manner.

(57) (a) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663; **1968**, *90*, 347. (b) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5662. (c) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

A Simple Model for the Kinetics of Dissociative Electron Transfer in Polar Solvents. Application to the Homogeneous and Heterogeneous Reduction of Alkyl Halides

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Abstract: A simple model describing the kinetics of electron transfer–bond breaking concerted reactions is developed. On the basis of a Morse curve description of the potential energy surfaces for bond breaking, it leads, for homogeneous and heterogeneous processes, to a quadratic activation-driving force free energy relationship with a standard activation free energy being the sum of two contributions characterizing bond breaking and solvent reorganization, respectively. The latter factor can be estimated on the basis of the Marcus dielectric continuum model. The bond-breaking contribution appears as equal to one-fourth of the bond dissociation energy. Application to the electrochemical and homogeneous reduction of alkyl halides shows a satisfactory agreement between the experimental data and the predictions of the theory. The bond-breaking contribution is typically 80% of the total, the remaining 20% concerning solvent reorganization.

Theoretical models of the kinetics of electron transfer in the liquid phase and attempts to test their predictions experimentally have so far dealt with reactions in which both members of the redox couple are chemically stable, not involving the breaking or formation of bonds, within the time scale of the experiment. In this context, the theory developed by Marcus and others[1] leads to a quadratic driving force–free energy relationship

$$\Delta G_1^* = \Delta G_0^* \left(1 + \frac{\Delta G^\circ}{4\Delta G_0^*} \right)^2 \qquad (1)$$

for both homogeneous and heterogeneous (electrochemical) electron transfers (ΔG_1^*, free energy of activation for the forward reaction; ΔG°, standard free energy of the reaction, $-\Delta G^\circ$ being a measure of the driving force of the reaction). The standard free energy of activation, ΔG_0^*, i.e., the free energy of activation at zero driving force, appears as the sum of two factors featuring the reorganization of the nucleii configuration accompanying electron transfer. One, the external reorganization factor, concerns the fluctuational reorganization of the solvent molecules. It can be expressed as a function of the reactant radii and of the optical and static dielectric constants of the solvent in the framework of a hard-sphere Born model of solvation. The other, the internal reorganization factor, features the changes in bond lengths and

angles accompanying electron transfer. It can be expressed as a function of the net variation in bond lengths and angles and of the corresponding force constants in the reactants and products. The theoretical predictions appear to be in fair agreement with the experimental observations both as regards the quadratic form of the activation driving force free energy relationship (1)[2] and the magnitude of the activation free energies in terms of internal[1d] and external[3] reorganization factors.

Recent investigations of the electrochemical reduction of aliphatic halides and of their homogeneous reduction by redox reagents[4] has provided a typical example of dissociative electron transfer, i.e., a reaction in which the transfer of the electron and the breaking of a bond are concerted processes.[5] The kinetics

(1) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (c) Waisman, E.; Worry, G.; Marcus, R. A. *J. Electroanal. Chem.* **1977**, *82*, 9. (d) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. (e) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(2) Savéant, J. M.; Tessier, D. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 57 and references cited therein.
(3) (a) Peover, M. E.; Powell, J. S. *J. Electroanal. Chem.* **1969**, *20*, 427. (b) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317. (c) Fawcett, W. R.; Jaworski, J. S. *J. Phys. Chem.* **1983**, *87*, 2972. (d) Jaenicke, W. *J. Chem. Phys.*, *Faraday Trans. 1* **1987**, *83*, 161. (e) As revealed by a systematic study of homogeneous and heterogeneous electron transfer in a large series of aromatic compounds in an aprotic dipolar solvent, dimethylformamide,[3b] the solvent reorganization factor appears smaller than predicted by the theory. This point is discussed in more details further on.
(4) (a) I.e., that are able to transfer an electron without the transient formation of an adduct with the substrate.[4b,c] (b) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *87*, 39. (c) Lexa, D.; Savéant, J. M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.*, in press.
(5) (a) Andrieux, C. P.; Merz, A.; Saveant, J. M.; Tomahogk, R. *J. Am. Chem. Soc.* **1984**, *106*, 1957. (b) Andrieux, C. P.; Merz, A.; Savéant, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 6097. (c) Andrieux, C. P.; Gallardo, I.; Saveant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638. (d) Andrieux, C. P.; Savéant, J. M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3815.