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The Fate of Thermally Produced Cyclohexyloxyl Radicals As Determined by Mass Spectrometry

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Abstract: Tandem mass spectrometry combined with in-source radical trapping was used to follow in detail the fate of gas-phase cyclohexyloxyl-*1*-d_1 radicals (**1b**) produced by the thermal decomposition of dicyclohexyl-α,α'-d_2 peroxide. Under the conditions of these experiments **1b** undergoes β-scission to produce ω-formyl hexyl radicals. The ω-formyl radicals are involved in reversible isomerization reactions except that isomerization to produce acyl radicals through a seven-membered transition state results in irreversible loss of carbon monoxide and production of primary pentyl radicals. Primary-to-primary and primary-to-secondary isomerizations were the lowest energy processes available to the pentyl radicals. Fragmentation of secondary pentyl radicals occurred at lower energy than fragmentation of the primary radicals.

Radicals are frequently involved in industrially important gas-phase chemical processes. Therefore, methods for studying gas-phase radical reactions are of considerable value. Conventional methods of chemical analysis are usually too insensitive to study radicals directly. Radical trapping followed by product collection and off-line analysis can sometimes be successfully applied, but interpretation of the results is often a complex process. Highly sensitive methods for studying radicals directly, such as mass spectrometry, require highly specialized equipment and conditions to distinguish the radicals from the chemical background.[1] Electron paramagnetic resonance spectroscopy, microwave spectroscopy, flash photolysis, laser spectroscopy, and even ultraviolet and infrared spectroscopy have been used to study radicals, but these methods are usually not suitable for studying polyatomic transient gas-phase radicals in complex mixtures.[2]

In this study we demonstrate the utility of dynamic radical trapping/tandem mass spectrometry[3-5] for studying in detail the fate of gas-phase cyclohexyloxyl radicals (**1**) produced by the thermal decomposition of dicyclohexyl peroxide (**2**) (eq 1). There have been several studies of the chemistry of alkyloxyl and cycloalkyloxyl radicals.[6-11] These studies have shown that at temperatures above about 150 °C β-scission becomes competitive with disproportionation and hydrogen atom transfer processes. Druliner, et al.,[6] using the radical trapping/tandem mass spectrometry method,[4,5] were able to provide a general mechanistic scheme for the fate of cycloalkyloxyl radicals, but the tandem mass spectrometer used for their study had insufficient resolution in the second sector to resolve ions differing by only 1 dalton. Therefore, these authors were unable to follow the fate of a deuterium label during radical isomerization reactions and thus could not distinguish between alternative isomerization pathways.

(1)

2a, R = H
2b, R = D

1a, R = H
1b, R = D

In the study described here, a four-sector tandem mass spectrometer[12] was used to follow the course of cyclohexyloxyl-*1*-d_1 radicals (**1b**) produced by the gas-phase thermal decomposition of dicyclohexyl-α,α'-d_2 peroxide (**2b**). In the four-sector instrument, the resolution was more than adequate to separate ions of trapped radicals differing only in the number of incorporated deuterium atoms and to distinguish fragments of these mass selected ions which differed in mass by only 1 dalton. Thus, in these experiments it was possible to select only ions incorporating one deuterium atom and to determine the position of the deuterium atom in the radical at the time of trapping. The data presented here give a detailed picture of the fate of thermally produced gas-phase cyclohexyloxyl radicals.

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(1) Johnson, C. A. F.; Parker, J. E. *Annu. Rep. Progr. Chem., Sect. C* **1983**, *80*, 237.

(2) Hirota, E. *High-Resolution Spectroscopy of Transient Molecules*; Springer-Verlag: New York, 1985, and references therein cited.

(3) McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 6470.

(4) Rudat, M. A.; McEwen, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 4349.

(5) McEwen, C. N. *Mass Spectrom. Rev.* **1986**, *5*, 521.

(6) Druliner, J. D.; Kitson, F. G.; Rudat, M. A.; Tolman, C. A. *J. Org. Chem.* **1983**, *48*, 4951.

(7) Gray, P.; Williams, A. *J. Chem. Soc.* **1961**, 2620.

(8) Takagi, H.; Washida, N.; Bandow, H.; Okuda, M. *J. Phys. Chem.* **1981**, *85*, 2701.

(9) Gray, P.; Williams, A. *Trans. Faraday Soc.* **1959**, *55*, 760.

(10) Howard, J. A.; Williams, G. H., Ed. *Advances in Free-Radical Chemistry*; Academic Press: New York, 1972; Vol. IV, pp 49–173.

(11) Kochi, J. K., Ed. *Free Radicals*; Wiley: New York, 1973; Vol. II, pp 665–710.

(12) National Institute of Environmental Health Sciences, Research Triangle Park, NC.

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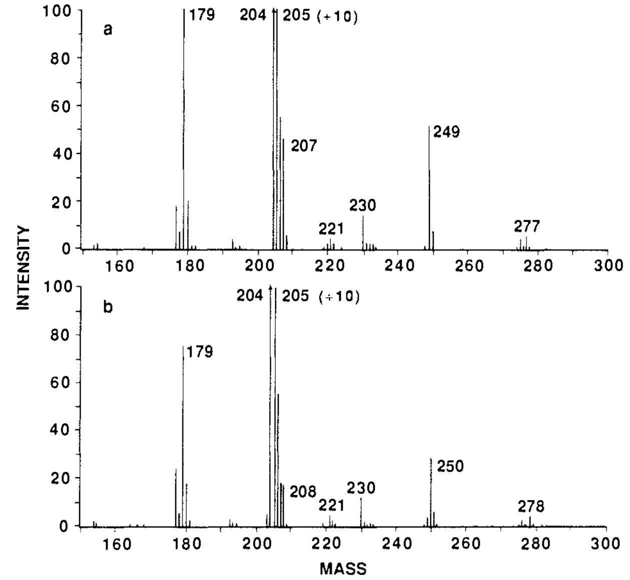
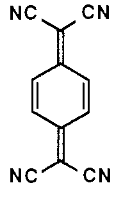


Figure 1. The negative ion TCNQ trapped-radical mass spectrum of (a) **2a** and (b) **2b** normalized to the m/z 205 ion.

Experimental Section

The radical trapping technique of Rudat and McEwen[3] was employed to trap carbon-centered radicals produced in a chemical ionization ion source. The radical trapping agent, tetracyanoquinodimethane (TCNQ) (**3**), was continuously evaporated into the ion source from the heated solids probe. The temperature of the probe was determined experimentally by monitoring the $M^{\bullet-}/MH^-$ ratio of TCNQ while radical-producing gases were present (the MH^- ion is the product of a radical trapping reaction [TCNQ + $H^\bullet$]). The ratio of $M^{\bullet-}$ to MH^- was maintained at between 2 and 5. The radical producing gas in these experiments was dicyclohexyl-d_2 peroxide which was leaked into the ion source from a glass reference inlet to give a source pressure of about 0.1 Torr. Argon gas was added to the ion source to give a total pressure of ca. 0.3 Torr. The temperature of the inlet was ca. 100 °C. The ion source temperature was maintained at ca. 200 °C unless otherwise noted. The electron energy was 100 eV, and the filament emission current was maintained as low as feasible (0.1–0.5 mA) to limit ionization induced radicals.[13]



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The mass spectrometer used for this work was a VG Analytical four-sector ZAB-HF of BEEB geometry.[12] A gas collision cell located in the field-free region between the two electric sectors in the MS/MS arrangement was used to collisionally fragment ions that were mass selected using the first mass spectrometer. The resolution of the first mass spectrometer was set to ca. 1500 (10% valley definition). Fragment ions from the collision process were analyzed by the second mass spectrometer operated at about 800 resolution. Helium was supplied to the gas cell at a pressure sufficient to attenuate the main beam by ca. 90%.

The dicyclohexyl-α,α'-d_2 peroxide (**2b**) was prepared by the reaction of KO_2 and cyclohexylmethane sulfonate[14] and was determined to be >90% of the desired product by mass spectrometry. Tetracyanoquinodimethane (**3**) was obtained from Aldrich and used without further purification.

Results and Discussion

The negative ion trapped-radical mass spectra obtained by introducing **2** along with TCNQ into a hot mass spectrometer ion source (ca. 200 °C) are shown in Figure 1. Except for the ions at m/z 204 ($[TCNQ]^{\bullet-}$) and m/z 177 ($[TCNQ - HCN]^-$) and their ^{13}C isotopes, all of the observed ions are trapped radical products.[3] The radicals trapped in these experiments are predominately those produced by the thermal decomposition of **2** (eq 1). The data available in the mass spectra give the mass of the trapped radicals and information concerning the relative abundances of the radicals.

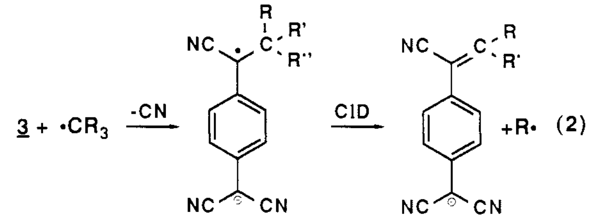
Table I. The CID Spectrum of the m/z 278 Parent (P) Ion Produced by Ionization of the Reaction Products of **2** with TCNQ (**3**) at 210 °C

m/z	presumed fragment ion composition	% intensity[a]
277	$[P - H]^-$	69
263	$[P - CH_3]^-$	8
262	$[P - CH_2D]^-$	2
252	$[P - CN]^-$	18
251	$[P - HCN]^-$	98
250	$[P - CO]^-$?	19
249	$[P - C_2H_5]^-$	10
248	$[P - CDO]^-$	100
235	$[P - C_3H_7]^-$	8
234	$[P - CH_2CDO]^-$	5
233	?	1
221	$[P - C_4H_9]^-$	49
206	$[P - C_5H_{10}D]^-$ and/or $[P - C_3H_6CDO]^-$	3
205	?	5
192	$[P - C_4H_8CDO]^-$	<2

[a] Percent intensity is normalized to largest daughter ion. Daughter ions less than 1% are not reported.

The relative population of the various radical structures in the mass spectrometer ion source is directly reflected in the relative ion abundances of the TCNQ trapped radical products if the rate of radical trapping by TCNQ is equal for all radicals of interest and the ionization efficiencies of the trapped radical products are equal. These criteria have been shown to closely hold for propyl, butyl, and pentyl radicals[13] and are assumed to approximately hold for the radicals discussed here.

$C_6H_{11}O^\bullet$ Radicals. The mass spectra in Figure 1 show that only about 5% of the trapped radicals, excluding hydrogen atoms, correspond to **1** or an isomeric product of **1**. The ions corresponding in mass to the trapped radicals of **1** are observed at m/z 277 in Figure 1a and m/z 278 in Figure 1b (i.e., $[TCNQ - CN + 99]^{\bullet-}$ and $[TCNQ - CN + 100]^{\bullet-}$, respectively). The structures of the trapped radicals can be determined using collision-induced decomposition (CID) of the mass selected $[TCNQ - CN + CR_3]^{\bullet-}$ ions (eq 2) where in this case CR_3 denotes $C_6H_{10}DO^\bullet$ radicals.[4]



(2)

Collisional decomposition of these ions results in preferential loss of the R groups on the $C_6H_{10}DO^\bullet$ radicals.[4] The R groups are different for each $C_6H_{10}DO^\bullet$ radical.

The CID results listed in Table I are produced by trapping $[C_6H_{10}DO]^\bullet$ radicals, mass selecting the $[TCNQ - CN + C_6H_{10}DO]^{\bullet-}$ ions, and collisionally fragmenting these ions. Table I is interpreted by looking at the mass losses from the parent ion beam (m/z 278).[4] Loss of 26 and 27 daltons corresponds to loss of CN and HCN, respectively, from the TCNQ portion of the ion. The large number of remaining ions is from R group losses and shows that several radical structures are trapped by TCNQ. The structures of the trapped radicals are determined by comparing the expected R group losses for all possible radical structures produced by low-energy isomerizations of **1**, with the actual losses listed in Table I. Some of the possible structures are shown in Scheme I along with the masses of the expected R group losses (in parentheses).

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(13) McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4343.
(14) Druliner, J. D. *Synth. Commun.* **1983**, *13*(2), 115.

Scheme I

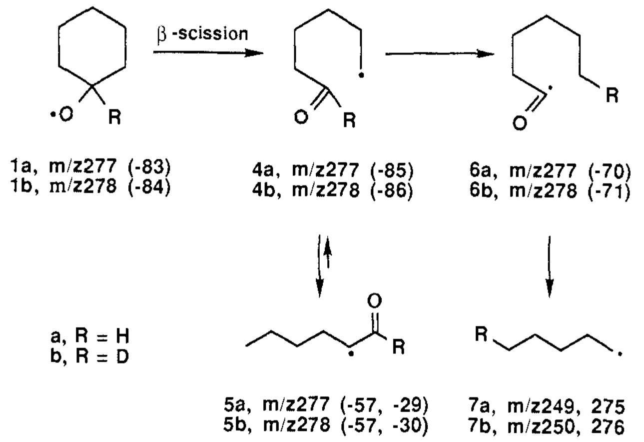
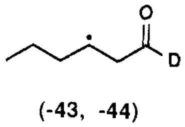


Table I shows no loss of $C_6H_{10}D$ (*m/z* 194); therefore, radical **1** is not trapped. Loss of C_4H_8CDO (*m/z* 192) (**4b**) is observed, but in less than 2% abundance.[15] The most intense ions observed in the CID spectrum, representing ca. 80% of the total ion abundance, are the loss of 30 (*m/z* 248) and 57 (*m/z* 221) daltons from *m/z* 278 and describe structure **5b**. As postulated in Scheme I, radical **5b** is formed from **4b** through a six-membered cyclic (6sp) transition state (notation is that employed by Hardwidge et al. in ref 16). Radical isomerization through cyclic six-membered transition states is known to be fast.[4,16-18]

Other ion losses are also listed in Table I. Losses of 43 (*m/z* 235) and 44 (*m/z* 234) daltons suggest structure **8** which could be formed from **4b** by a 5sp isomerization. Losses of 15 (*m/z* 263) and 72 (*m/z* 206) daltons suggest structure **9** which is formed from **5b** by a 5ss isomerization. These results show that competitive isomerizations are occurring through five- and six-membered cyclic transition states.



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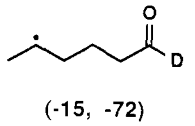

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Pentyl Radicals. The most abundant ions observed in Figure 1 account for ca. 40% of the trapped radical ion current, excluding hydrogen atoms, and correspond to radicals having a mass of 71 daltons ($C_5H_{11}^•$) for structure **2a** and 72 daltons ($C_5H_{10}D^•$) for **2b**. The masses of the radicals are deduced from the ions at *m/z* 275 ($[TCNQ + 71]^-$) and 249 ($[TCNQ - CN + 71]^{•-}$) (Figure 1a) and *m/z* 276 ($[TCNQ + 72]^-$) and 250 ($[TCNQ - CN + 72]^{•-}$) (Figure 1b).

According to Scheme I, primary *n*-pentyl radicals (**7**) are produced by irreversible loss of CO from **6**. Radical **6** in turn is produced from **4** through a seven-membered cyclic isomerization which is in competition with isomerization of **4** to **5** through a six-membered cyclic intermediate. Even though six-membered isomerizations have been shown to be faster than isomerizations through seven-membered intermediates,[4,5,16-18] the product of the seven-membered isomerization (pentyl radicals) dominates the trapped radical spectra (Figure 1).

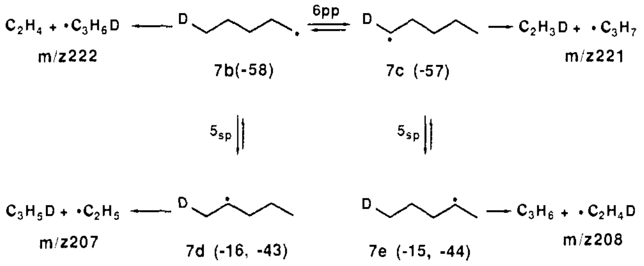
The dominance of the product produced by isomerization through the seven-membered cyclic intermediate suggests that the isomerization reactions are reversible with the exception that production of an acyl radical such as **6** results in loss of CO in a fast irreversible step. Thus, at longer times, radicals such as **7**, which make up the *m/z* 249 and 250 ion current, should increase in abundance at the expense of the radicals that make up the 277/278 ion current (Figure 1). This premise can be tested experimentally by changing the lifetime of the radicals before trapping. Short radical lifetimes favor structures **4**, **5**, **8**, and **9** and thus the *m/z* 278 ion, whereas long lifetimes favor irreversible formation of **6**, and thus the *m/z* 250 ion.

Table II. CID Spectra of the *m/z* 250 Parent (P) Ion Produced by Ionization of the Reaction Products of **2** with TCNQ (**3**) at Three Different Ion Sources

m/z	presumed fragment ion composition	% intensity[a] 210°	240°	265°
249	$[P - H]^-$	260	110	95
248	$[P - D]^-$	12	5	2
235	$[P - CH_3]^-$	83	52	60
234	$[P - CH_2D]^-$	52	29	26
233		4	2	2
224	$[P - CN]^-$	46	27	16
223	$[P - HCN]^-$	129	55	36
222		27	23	14
221	$[P - C_2H_5]^-$?	30	11	7
220	$[P - C_2H_4D]^-$?	16	7	5
219		7	5	4
218		3	2	
207	$[P - C_3H_7]^-$	83	65	75
206	$[P - C_3H_6D]^-$	100	100	100
205		21	9	12
204		6	1	2
193	$[P - C_4H_9]^-$	29	13	5
192	$[P - C_4H_8D]^-$	67	29	15
179	$[P - C_5H_{11}]^-$	4	3	2
178	$[P - C_5H_{10}D]^-$	3	2	2

[a] Intensity normalized to *m/z* 206 daughter ion. Daughter ion intensities below 1% are not reported.

Scheme II



It has been established that the lifetime of radicals in a chemical ionization source can be changed by altering the concentration of TCNQ (**3**) in the source.[4] High concentrations of TCNQ result in fast trapping of radicals and short radical lifetimes, whereas, low TCNQ concentrations result in slow trapping and longer lifetimes for radicals. In these experiments, high TCNQ concentrations gave a larger *m/z* 278/250 ratio than low TCNQ concentrations. Thus, longer radical lifetime favors the formation of **6** at the expense of the radicals that make up the *m/z* 278 ions, supporting the above premise.

Scheme I suggests that only primary *n*-pentyl radicals are produced by the decomposition of **6**, but CID of the $[TCNQ - CN + C_5H_{10}D]^•$ ion shows that both primary and secondary pentyl radicals are trapped. Table II shows the CID spectra of the mass selected *m/z* 250 ions for three ion source temperatures. As in the decomposition of the *m/z* 278 ions, loss of 26 and 27 daltons represents loss of CN and HCN. The remaining fragment ions in the CID spectra are from loss of R groups (eq 2) and suggests a mixture of structures. Most of the major ions in the spectra are accounted for by the structures shown in Scheme II. The expected neutral losses from each of these pentyl radicals are shown in parentheses. Loss of 58 daltons (*m/z* 193) for the parent *m/z* 250 ion indicates loss of $^•C_4H_8D$ from **7b**. Loss of 57 daltons is explained if **7b** isomerizes through a cyclic six-membered transition state (6pp isomerization) to produce **7c**. The losses of

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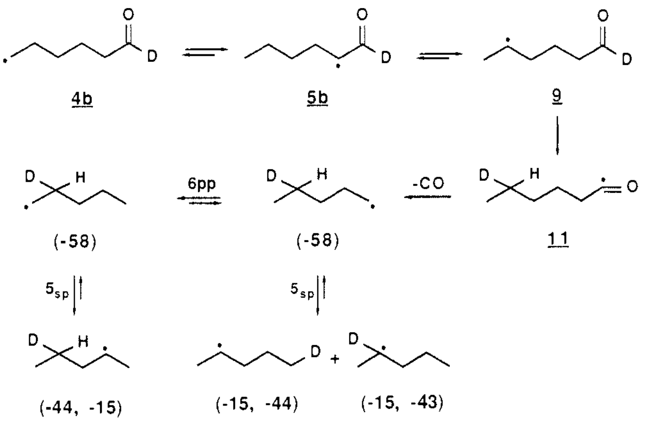
(15) For a discussion on the direct relationship of CID ion current and relative abundances of radicals in the mass spectrometer ion source, see ref 4.

(16) Hardwidge, E. A.; Larson, C. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1970**, *92*, 3278.

(17) McEwen, C. N.; Rudat, M. A. In *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley: New York, 1983, Chapter 20.

(18) Watkins, K. W.; Ostreko, L. A. *J. Phys. Chem.* **1969**, *73*, 2080.

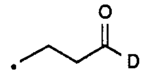
Scheme III



15 (m/z 235) and 44 (m/z 206), and 16 (m/z 234) and 43 (m/z 207) daltons are from the two 2-pentyl radicals, **7e** and **7d**, respectively, produced by a 5sp isomerization of the isomeric primary pentyl radicals **7b** and **7c**.

Comparison of the CID spectra of the mass selected m/z 250 ions at different ion source temperatures (Table II) shows that increasing the temperature favors the formation of the secondary pentyl radicals. Thus, the ratio of trapped primary to trapped secondary pentyl radicals goes from 0.30 at 210 °C to 0.17 at 240° to 0.08 at 265°. This is interpreted to mean the reaction is kinetically controlled and that increasing the ion source temperature enhances the rate of isomerization. Therefore, the initially formed pentyl radicals have a primary structure as suggested in Scheme I.

The abundances of the trapped isomeric pentyl radicals are all considerably different. The relative abundances are **7e** > **7d** > **7b** > **7c** (Table II). The differences are much greater than would be expected if a deuterium isotope effect was responsible. Initially, it was thought that the differences in abundances were related to contamination of the m/z 250 ion current by trapped radicals other than the isomeric pentyl radicals. For example, a radical having structure **10** trapped by TCNQ would have a mass of 250 daltons, and the R group lost in the CID spectrum would have a mass of 58 daltons. If the mass selected m/z 250 ion current was partially composed of trapped **10**, it could account for the enhanced ratio observed for the loss of 58 relative to 57 daltons and make **7b** appear to be in greater abundance than **7c**. Radical **10** could be produced by β-scission of **4b**. However, high resolution mass spectrometric measurements showed only one peak at m/z 250.



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Scheme III shows another possible explanation for the differences in abundances for the neutral losses from the m/z 250 negative ions. In this scenario, **9** isomerizes to **11** through a cyclic six-membered transition state. Loss of CO from **11** produces a primary pentyl radical with the deuterium on C-4. Equivalent isomerizations to those shown in Scheme II produce radicals that give the neutral losses noted in parentheses in Scheme III from CID of $[\mathrm{TCNQ} - \mathrm{CN} + C_5H_{10}D]^{\bullet -}$ ions. Enhanced losses of 58, 44, and 15 daltons relative to 57, 43, and 16 daltons would be expected from this series of isomerizations and would explain the apparent differences in abundance of the trapped pentyl radicals (Table II).

Ethyl and Propyl Radicals. About 35% of the trapped radicals, again excluding hydrogen atoms, have a mass of 29 daltons (m/z 207) in Figure 1a, whereas in Figure 1b, 16% have this mass. Additionally, Figure 1b shows about 20% of the trapped radicals have a mass of 30 daltons (m/z 208). The m/z 207 ion in Figure 1a and the approximately equal abundance of the sum of the m/z 207 and 208 ions in Figure 1b can be accounted for by postulating isomerization of the initially formed primary *n*-pentyl radicals to secondary 2-pentyl radicals followed by β-scission which produces ethyl radicals and propene (Scheme II).[17] Mass measurement of the ions at m/z 207 shows that the most probable elemental composition is $[\mathrm{TCNQ} - \mathrm{CN} + C_2H_5]^-$. β-Scission of 2-pentyl radicals to produce ethyl radicals has been reported.[19]

The approximately equal abundance of trapped $^{\bullet}C_2H_5$ (m/z 207) and $^{\bullet}C_2H_4D$ (m/z 208) radicals in Figure 1b is explained if primary-to-primary isomerization through a 6pp process, and subsequent but slower isomerization through a 5sp process, is fast relative to fragmentation (Scheme II). Under these conditions, **7d** and **7e** would be produced in approximately equal abundance. The slight enhancement of the m/z 208 ion in Figure 1b relative to the m/z 207 ion supports the mechanism proposed in Scheme III where two of the three 2-pentyl radicals fragment to give $^{\bullet}C_2H_4D$ radicals.

β-Scission of primary *n*-pentyl radicals is expected to produce propyl radicals (Sheme II).[17] Figure 1, a and b, shows only a small ion current at m/z 221 and 222, the expected masses for ions from TCNQ trapped propyl radicals. Accurate mass measurement shows that most of the ion current observed at m/z 221 does not correspond to $[\mathrm{TCNQ} - \mathrm{CN} + C_3H_7]^{\bullet -}$ ions.

The above scenario suggests that thermal decomposition of **2** leads to 1-pentyl radicals (**7a** and **7b**, Scheme I, and **7c**, Scheme II) that subsequently isomerize to 2-pentyl radicals (**7d** and **7e**, Scheme II) before β-scission. Under the conditions of these experiments, β-scission of primary pentyl radicals is apparently slow relative to isomerization. This result is in contrast to results obtained for primary *n*-pentyl radicals produced in a chemical ionization source by fragmentation of the radical cations of amines (eq 3) or ketones (eq 4) in which abundant ions corresponding to trapped ethyl and propyl radicals are observed.[17] Thus, β-scission of 1-pentyl radicals apparently competes with isomerization and β-scission of 2-pentyl radicals when sufficient internal energy is available.

$$\mathrm{RCH_2NH_2}^{\bullet +} \rightarrow \mathrm{R}^{\bullet} + \mathrm{CH_2{=}NH_2}^{+} \quad (3)$$

$$\mathrm{RCOR}^{\bullet +} \rightarrow \mathrm{R}^{\bullet} + \mathrm{RCO}^{+} \quad (4)$$

These isomerization results are rationalized by assuming that β-scission of 1-pentyl radicals require more energy than is required for β-scission of the 2-pentyl radicals. In support of this hypothesis are results that show essentially no fragmentation of thermally produced pentyl radicals below ca. 200 °C and that at ion source temperatures above ca. 250°, abundant ethyl and propyl radicals are trapped. As the source temperature is raised, the variety of radical structures observed increases along with a considerably increased abundance of hydrogen atoms, presumably produced by β-scission processes.

Conclusion

Mass spectrometry combined with radical trapping was used to follow the radical products produced during the vapor phase thermolysis of dicyclohexyl-α,α′-d_2 peroxide (**2b**). The course of the radical reactions is shown in Schemes I–III. At the lowest temperature of these experiments, the only fragmentation reactions observed are β-scission of cyclohexyloxyl-*1*-d_1 radicals (**1b**), loss of CO from acyl radicals (**6b** and **11**), and hydrogen atom loss. Increasing the ion source temperature first increases the abundance of ethyl radicals produced by β-scission of the 2-pentyl radicals, and then at higher temperatures increases the abundance of propyl radicals produced by β-scission of 1-pentyl radicals. Higher source temperature also considerably increases the hydrogen atoms trapped in the source and increases the variety of radicals that are trapped. The ratio of secondary to primary pentyl radicals also increases at higher ion source temperatures.

Increasing the lifetime of the radicals by decreasing the TCNQ concentration in the ion source results in an increase in the $^{\bullet}C_5H_{10}R$ radicals relative to the $^{\bullet}C_5H_{10}CRO$ radicals. This in-

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(19) McEwen, C. N.; Druliner, J. D.; Harvan, D. J. Presented at the 33rd ASMS Conference on Mass Spectrometry and Allied Topics, San Diego, CA, May 31, 1985.

crease at longer radical lifetimes was interpreted to mean that isomerizations leading to acyl radicals are irreversible.

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Registry No. 1a, 3384-35-8; **2a**, 1785-68-8; **2b**, 117439-41-5; **3**, 1518-16-7; cyclohexyl methanesulfonate, 16156-56-2.

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^{125}Te Solid-State NMR Spectra and Secondary Bonding Arrangements for Some Salts of the Trimethyltelluronium and Triphenyltelluronium Cations[†]

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Abstract: The preparation of several salts of the Me_3Te^+ and Ph_3Te^+ cations is reported along with ^{125}Te static and CP/MAS solid-state NMR spectra of the Me_3Te^+ salts and ^{125}Te CP/MAS spectra of the Ph_3Te^+ salts. In addition, crystal structures of the salts $Me_3Te^+Cl^-\cdot H_2O$ (**1**), $Me_3Te^+I^-$ (**2**), $Me_3Te^+NO_3^-$ (**3**), $Ph_3Te^+NO_3^-$ (**4**), $Ph_3Te^+Cl^-\cdot{}^1/_2CHCl_3$ (**5**), and $(Ph_3Te)_2SO_4\cdot 5H_2O$ (**6**) have been determined to help in the interpretation of some of the above spectra. It is shown that secondary bonding interactions with the anions have significant and substantial influence on the geometries of the cations and their crystal packings and on the resulting NMR spectra in terms of the tellurium shielding tensors and isotropic chemical shifts and in the presence of long-range spin $^1/_2$ to spin $^3/_2$ couplings. These couplings are indicative of long-range covalent interactions between the anions and cations in this series of compounds. In particular, the ^{125}Te CP/MAS spectrum of $Me_3Te^+Cl^-\cdot H_2O$ consists of a septet due to coupling to two equivalent chlorine atoms. In the case of **4** and **5** the presence of 4 and 2 crystallographically independent Te atoms is confirmed in the NMR spectra. Crystal data for each compound: **1**, orthorhombic, space group *Pbcm*, $a = 6.432$ (1) Å, $b = 11.413$ (2) Å, $c = 10.070$ (2) Å; **2**, monoclinic, space group $P2_1/n$, $a = 7.115$ (1) Å, $b = 9.673$ (2) Å, $c = 11.324$ (3) Å, $\beta = 107.72$ (2)°; **3**, monoclinic, space group $P2_1/n$, $a = 6.862$ (2) Å, $b = 11.105$ (1) Å, $c = 9.608$ (1) Å, $\beta = 94.96$ (2)°; **4**, triclinic, space group $P\bar{1}$, $a = 12.368$ (2) Å, $b = 14.755$ (2) Å, $c = 19.573$ (3) Å, $\alpha = 84.54$ (1)°, $\beta = 72.37$ (1)°, $\gamma = 76.77$ (1)°; **5**, triclinic, space group $P\bar{1}$, $a = 11.813$ (1) Å, $b = 12.909$ (1) Å, $c = 13.167$ (2) Å, $\alpha = 77.91$ (1)°, $\beta = 66.86$ (1)°, $\gamma = 82.18$ (1)°; and **6**, monoclinic, space group $P2_1/n$, $a = 11.495$ (4) Å, $b = 24.730$ (5) Å, $c = 25.386$ (5) Å, $\beta = 94.21$ (3)°.

A large number of triorganochalcogenium salts $R_3M^+X^-$ have been prepared and many of their structures have been determined.[2] In all cases the cation is trigonal pyramidal with a lone pair completing the tetrahedron, that is an AX_3E geometry. Virtually all of these structures contain weak directed interactions or secondary bonds[3] between the chalcogen atoms and atoms in the anions. These secondary bonds, M···Y, are frequently considerably shorter than the sum of the van der Waals radii of the interacting atoms[4] and form roughly opposite the primary bonds to give AX_3YE, AX_3Y_2E, or, most commonly, AX_3Y_3E geometries. Some evidence for the charge transfer involved in these interactions has been claimed in deformation density maps for Me_2TeCl_2 (an $AX_4Y'_2E$ geometry).[5] Secondary bonding in structures containing the related MX_3^+ cations (M = S, Se, or Te; X = F, Cl, Br, or I) has recently been reviewed.[6]

The acquisition of nuclear magnetic resonance spectra of solids has become increasingly facile in recent years with the development of techniques such as cross-polarization (CP) and magic-angle spinning (MAS).[7] It was hoped that the solid-state ^{125}Te NMR spectra of some R_3Te^+ salts could be obtained and that these spectra would reflect changes in the secondary bonding environments of the Te nuclei. Compounds of the Me_3Te^+ cation were examined first since methyl group rotation usually provides efficient ^{1}H relaxation and therefore short recycle times in the ^{125}Te CP experiment. A preliminary communication describing the acquisition of some solid-state ^{125}Te NMR spectra has already appeared.[8]

Experimental Section

Materials. Me_3TeI was prepared by addition of a slight excess of MeI to Me_2Te (Strem) in CCl_4 solution followed by filtration of the white solid product; Me_3TeBr by distilling an excess of MeBr (Matheson) onto neat Me_2Te and evaporating off the excess MeBr from the resulting white powder; Me_3TeCl by stirring an aqueous solution of Me_3TeI with a n excess of AgCl powder for 1 h, filtering the AgCl/AgI residue, and evaporating the solvent; and Me_3TeNO_3 by mixing stoichiometric aqueous solutions of Me_3TeI and $AgNO_3$, filtering the AgI precipitate, and evaporating the solvent. Crystals of Me_3TeI and $Me_3TeCl\cdot H_2O$ were obtained by slow evaporation of aqueous solutions and Me_3TeNO_3 was obtained by slow evaporation of an CH_3CN solution. Crystals of $Ph_3TeCl\cdot{}^1/_2CHCl_3$ suitable for X-ray diffraction were prepared by dissolving Ph_3TeCl (Organometallics) in $CHCl_3$ and slowly evaporating the solvent, and Ph_3TeNO_3 was prepared by mixing stoichiometric aqueous solutions of Ph_3TeCl and $AgNO_3$, filtering off the AgCl precipitate, and slowly evaporating the solvent. $(Ph_3Te)_2Hg_2Cl_6$ was prepared as previously described.[9] Crystals of $(Ph_3Te)_2SO_4\cdot 5H_2O$ were prepared by

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