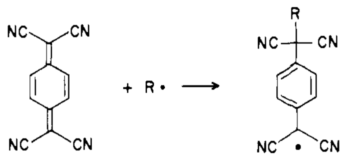
Table V. Positive-Ion CI(isobutane) Mass Spectrum of TCP at Low TCP Partial Pressure and Low- and High-Electron Emission

	% rel int with emission current		
m/z	0.05 mA[a]	1.0 mA[b]	ion assignments[c]
254		18	$[TCPC_4H_9 - CN]C_3H_7^+$
252		15	$[TCPC_4H_9 - CN]C_3H_5^+$
240		15	$[TCPC_3H_7 - CN]C_3H_7^+$
238		20	$[TCPC_3H_7 - CN]C_3H_5^+$
223	20	20	$[TCP]C_3H_7^+$
221	25	25	$[TCP]C_3H_5^+$
212		100	$[TCPC_3H_7 - CN]CH_3^+$ and/or, $[TCPC_4H_9 - CN]H^+$
210		20	$[TCPCH_3 - CN]C_3H_5^+$
207	6		$[TCP]C_2H_3^+$?
198		61	$[TCPH - CN]C_3H_7^+$
196		53	$[TCPH - CN]C_3H_5^+$
195	5		$[TCP]CH_3^+$
194		15	$[TCPC_3H_3 - CN]H^+$
181	100	93	$[TCP]H^+$
171		25	$[TCPH_2 - 2CN]C_3H_5^+$?
170		70	$[TCPCH_3 - CN]H^+$
156		60	$[TCPH - CN]H^+$
128	13		$[TCP - 2CN]^{+\cdot}$
102	15		$[TCP - 2CN - HCN]H^+$

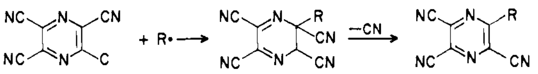
[a] Minimum relative intensity 5%, corrected for ^{13}C isotopes.
[b] Minimum relative intensity 15%, corrected for ^{13}C isotopes.
[c] Ion assignments based on accurate mass measurements. Ion vs. radical addition unknown.

TCP/radical products produced major ions in the methane/TCP plasma at high TCP pressure and suggests that CH_3^+ may react by addition to TCP faster than with methane (eq 4).

The differences in the radical-addition products observed with TCNQ and TCP can be explained by resonance considerations. For TCNQ, addition of a radical produces an aromatic structure from a quinone structure (eq 15). However, TCP loses its aromatic character upon radical addition unless ·CN is lost (eq 16). The loss of a cyanide radical is especially interesting since its heat of formation is 100 kcal/mol as compared to 30 kcal/mol for a methyl radical.[14] Thus for this reaction to be exothermic, assuming the reactants are ground state, the stabilization gained from alkyl-radical replacement of ·CN on TCP must be considerable. Also, ·CN may be lost upon ionization of the TCP/radical product.



(15)



(16)

Conclusion

Radical-trapping reagents have been identified which react by addition and CN substitution with carbon-centered radicals sufficiently fast to provide a means of studying the radical products in a chemical-ionization source. The mechanisms identified for radical production include ion fragmentation, hydrogen-atom abstraction, and ion-electron recombination. Even-electron positive ions can retain their structural integrity during neutralization caused by collisions with the walls.

A variety of compounds produce unique, trapped-radical, mass spectra. The trapped (M − H)· radicals have been observed for nearly all compounds studied and provide a means of identifying the molecular weights of the parent compounds. Hydrogen abstraction by radical cations is believed to be the major source of the (M − H)· radicals for most compounds.

The radical population in the CI source is increased on an absolute basis and relative to the ion concentration by increasing the electron emission. This provides a means of distinguishing ionized trapped-radical products from ionized unreacted species. Changing the method of ionization also changed the relative population of trapped radicals. For example, considerably fewer hydrogen atoms and ethyl radicals were trapped in the methane plasma produced by a DC discharge than in the plasma produced by electron emission from a hot filament, even though the positive-reagent-ion current in the two modes of ionization are very similar.

This new technique provides a means of studying the radical population in a plasma mass spectrometrically and adds a new dimension for studying the fundamental processes occurring in a low-pressure plasma.

Gas-Phase Radical Structures. Radical Trapping. 2

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Abstract: A new mass spectrometric technique for the determination of gas-phase carbon-centered radical structures is reported. Collisional activation (CA) of selected ions resulting from the fast reaction of 7,7,8,8-tetracyanoquinodimethan (TCNQ) with radicals in a chemical ionization ion source provides CA spectra that are dominated by fragmentation of the original radical and are directly interpretable in terms of the radical structure at the time of reaction with TCNQ. The CA spectra from C_1–C_8 alkyl radicals and from radicals generated by hydrogen abstraction from alkanes and ketones are discussed. Five- and six-membered ring intramolecular radical-site rearrangements were observed in those cases in which rearrangement was possible; the calculated rate constant for the five-membered ring rearrangement is estimated to be ca. $10^2\ s^{-1}$, consistent with that reported for thermal radicals. CA spectral parameters have been elucidated, and a method for the quantitation of structural isomers in a radical structure mixture has been developed. This CA technique provides a powerful means by which gas-phase radical structures, radical rearrangements, and mass spectrometric fragmentation mechanisms can be studied.

Various methods have been employed to study the structures and identities of radicals in the gas and liquid phases including photoelectron spectroscopy,[1] electron spin reasonance (ESR) spectroscopy,[2,3] and trapping the radicals with alkenes or other

Table I. RTCA[a] Spectra of C_1-C_4 Radicals

R (precursor)	parent *m/z*	relative intensity, %						
		P − 1	P − 15	P − 27	P − 29	P − 43	P − 57	P − 71
H (cyclopropane)	179^-	100	4	10	6			
CH_3 (cyclopropane)	193^-	100	2	2	7			
C_2H_5 (*sec*-butylamine)	207^-	63	100	13	12	10		
n-C_3H_7 (*n*-butylamine)	221^-	54	9	11	100	6	10	
sec-C_3H_7 (isobutylamine)	221^-	40	100	6	3	9	1	
n-C_4H_9 (*n*-pentylamine)	235^-	47	4	13	12	100	4	6
iso-C_4H_9 (isopentylamine)	235^-	43	9	10	4	100	3	5
sec-C_4H_9 (3,4-dimethylhexane)	235^-	68	59	11	100	5	8	1
t-C_4H_9 (neopentylamine)	235^-	32	100	6	4	2	3	

[a] $[TNCQR - CN]^{-\cdot}$ ions.

traps followed by analysis of the product mixtures by gas chromatography.[4-11] The method most successfully applied to the analysis of gas-phase radical structures and mixtures of radical structures has been the trapping technique, by which intramolecular radical rearrangements have been studied. However, with this method, it is difficult to account for all possible competing reactions, and the analytical problem of analyzing product mixtures in which there may be only minor isomer differences is serious.

In this paper a new mass spectrometric method for the study of gas-phase carbon-centered radical structures is reported which is based on the fast reaction of 7,7,8,8-tetracyanoquinodimethan (TCNQ) with carbon-centered radicals.[12,13] With the use of this method, the exact mass and thus the elemental compositions of the radicals in their TCNQ-trapped forms can be determined prior to the study of their structures. Then, by mass selecting the TCNQ/radical ions of interest and subjecting them to analysis by collisional activation (CA) mass spectrometry,[14,15] the structures of the radicals attached to the TCNQ molecules can be deduced.

The application of the CA technique to certain TCNQ/radical ions (namely, the $[TCNQR - CN]^{-\cdot}$ and $[TCNQRH - 2CN]^{-\cdot}$ ions) produces spectra highly characteristic of the structures of the radicals (R·) attached to the host TCNQ molecule. The direct relationship of the spectra to the structures permits the interpretation of the CA spectra rather than the deduction-by-comparison technique required for most CA studies. This clarity of information permits the unambiguous identification of radical structures, particularly for the shorter-chain carbon-centered radicals. In this paper the interpretation and identification of these spectra are demonstrated, with the nature of the CA technique in this case permitting the quantitative determination of radical structures in isomeric mixtures. In addition, the study of radical rearrangements and the structures of radicals resulting from hydrogen abstraction are discussed.

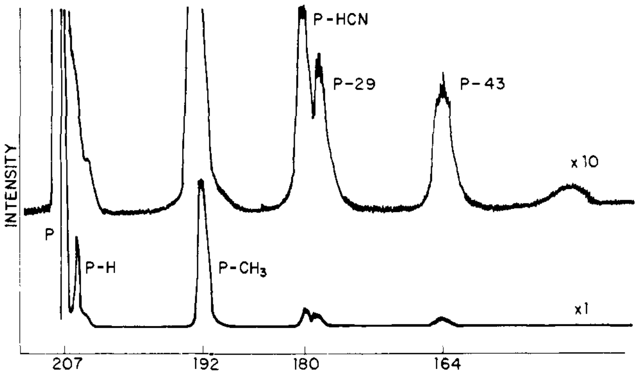


Figure 1. RTCA spectrum of C_2H_5 radicals: negative-ion CA spectrum of $[TCNQC_2H_5 - CN]^{-\cdot}$ ions.

The results presented here were obtained by allowing TCNQ to react with radicals present in a chemical ionization (CI) (high pressure) mass spectrometer ion source, as described in the preceding paper.[13] The trapped gas-phase radicals were those which were present in the source, and which therefore had a finite lifetime before trapping. TCNQ can also be used to trap radicals outside of the mass spectrometer and the products subjected to analysis as described here. This permits the study of other high-radical-density phenomena, using this method.

Experimental Section

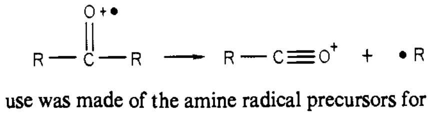
All CA spectra were obtained on a "reverse geometry" double-focusing ZAB-2F mass spectrometer (VG Micromass, Altrincham, England), fitted with a gas collision cell in the second field-free region. The helium pressure in the region near the gas cell as measured by the Bayard–Alpert gauge over a diffusion pump was typically 10^{-7} torr, resulting in a decrease in parent ion intensity of 50–70%. Spectra were obtained by scanning the electrostatic sector (ESA) and obtaining peaks as a function of transmitted ion energy. Typical mass resolution of the parent peaks ($M/\Delta M$) was 1000; the parent ion beam energy was nominally 6 keV.

Typical ion source conditions were: 1 mA emission current, 50 eV electron energy; 150 °C source temperature; 1×10^{-7} torr of TCNQ, $5-10 \times 10^{-6}$ torr of sample, and $1-3 \times 10^{-5}$ torr of N_2 as measured on the Bayard–Alpert pressure gauge on the ion source housing. The total source pressure under these conditions was ca. 0.3 torr.

TCNQ purity was verified by electron ionization and CI(N_2) negative ion mass spectrometry;[13] no other compounds were detected. Samples used as radical precursors were obtained from Aldrich Chemical Co., Tridom Chemical Co. (Hauppauge, N.Y.), and a Chem Service Lab Assist Kit (Media, Pa.) and were used as received.

Radical precursors were generally of two types: amines and ketones. Advantage was taken of the fragmentation mechanisms of the molecular ions of these functional groups:

$$\overset{+\bullet}{H_2N}—CH_2—R \longrightarrow \overset{+}{H_2N}{=}CH_2 + \bullet R \qquad (1)$$



$$R—\overset{O^{+\bullet}}{\overset{\|}{C}}—R \longrightarrow R—C{\equiv}O^+ + \bullet R \qquad (2)$$

Principal use was made of the amine radical precursors for the generation

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(16) For a discussion of the term "critical energy" see A. Maccoli, *Org. Mass Spectrom.*, **15**, 109 (1980).

Table II. RTCA[a] Spectra of C_5–C_8 Radicals

		relative intensity, %								
original R (precursor)	parent m/z	P – 1	P – 15	P – 27	P – 29	P – 43	P – 57	P – 71	P – 85	P – 99
n-C_5H_{11} (*n*-hexylamine)	249^-	78	36	28	9	100	100	6		
t-C_5H_{11} (3,3-dimethylhexane)	249^-	93	63	17	100	7	7			
n-C_6H_{13} (*n*-octylamine)	263^-	87	45	13	15	13	100	6		
n-C_7H_{15} (*n*-octylamine)	277^-	100	35	15	44	14	29	46	6	
sec-C_7H_{15} (2-ethylhexylamine)	277^-	100	43	16	81	17	57	74	9	
n-C_8H_{17} (dodecylamine)	291^-	100	21	17	34	44	38	20	42	9
c-C_6H_{11} ((aminomethyl)cyclohexane)	261^-	100	4	7	4	15	8	4		
c-C_7H_{13} ((aminomethyl)cycloheptane)	275^-	100	10	18	18	7	12	5	2	

[a] $[TCNQR - CN]^{-}\cdot$ ions.

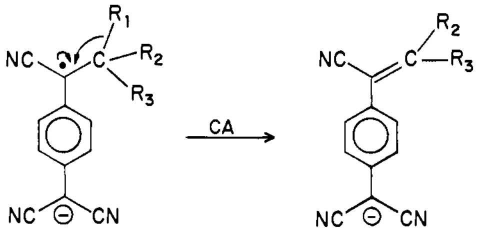
of well-defined radical populations.

Results and Discussion

In order to facilitate discussion of the results, the technique of collisional activation as applied to the $[TNCQR - CN]^{-}\cdot$ ions will be referred to as the RTCA (radical-trapped collisional activation) technique. Therefore, losses of fragments as observed in the CA spectra are losses from the $[TCNQR - CN]^{-}\cdot$ ions that are induced by the CA process, where R is the radical under discussion.

A variety of radicals have been studied by using the RTCA technique, and it will be shown by example and discussion how alkyl radical structures can be readily studied and elucidated with this technique.

C_1–C_4 Radicals Attached to TCNQ. A typical RTCA spectrum is shown in Figure 1 and the RTCA results for C_1–C_4 radicals are summarized in Table I. When various radical isomers were created in the CI plasma, the RTCA spectrum changed in a way consistent with a parent ion structure such as I, which upon collisional activation cleaves the bond α to the original radical site. The radical nature of the anion may strongly direct the site of bond cleavage:



I

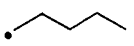
By this mechanism, the structure of the original radical $\cdot CR_1R_2R_3$ can be determined by noting the identity of the lost fragments, R_1, R_2, and R_3. The relative intensities of the losses of R_1, R_2, and R_3 are apparently determined by the critical energy[16] of the reaction, which is influenced to a greater extent by the heats of formation of the radical fragments than by the stability of the new TCNQ product ions formed. For example, in the case of *sec*-butyl radicals, CA-induced α cleavage of the resultant TCNQ anion radical results in the loss of ·H, $\cdot CH_3$, and $\cdot C_2H_5$ radicals. Loss of the more stable $\cdot C_2H_5$ radical is favored over the loss of $\cdot CH_3$ by ca. 1.8:1.

As can be seen from a review of Table I and the above CA decomposition mechanism, the C_1 to C_4 alkyl radicals produced CA spectra consistent with their initial structure. The most significant losses from the straight-chain alkyl radical $[TCNQR - CN]^{-}\cdot$ ions were thus H, CH_3, C_2H_5, and C_3H_7 for the trapped $\cdot CH_3$, $\cdot C_2H_5$, *n*-$C_3H_7\cdot$, and *n*-$C_4H_9\cdot$ radicals, respectively. Alternative fragmentation pathways and structures produce very little background.

The only other significant peaks in the RTCA spectra, the loss of 1 amu (H) and 27 amu (HCN), were also the major peaks in the metastable ion spectra. Thus, the major fragmentation pathways observed in the RTCA spectra are confined to the high-energy regime of collisional activation.

The distinct, understandable, and reproducible differences in the RTCA spectra make them directly *interpretable* rather than requiring the use of "standard" spectra for deduction-by-comparision, as has been necessary for most CA studies.

Larger Alkyl Radicals and Radical Rearrangement. The fact that the RTCA technique is an interpretive one is important for understanding the results obtained for radicals of chain length $\geq C_5$. Primary *n*-pentyl radicals initially produced in the source yielded an RTCA spectrum that not only had the expected major loss of $\cdot C_4H_9$ for the primary radical, but also major losses corresponding to $\cdot CH_3$ and $\cdot C_3H_7$ (Table II). Interpretation of the RTCA spectrum by using the postulated fragmentation mechanism and the fact that the parent ion mass corresponded only to the ion $[TCNQC_5H_{11} - CN]^{-}\cdot$ showed that two pentyl radical structures were present in the ion source:



II

III

The 2-pentyl radical III can be produced from the 1-pentyl radical II by a five-membered ring intramolecular hydrogen abstraction,[2] and these results provide direct evidence for its occurrence in the gas phase at a reasonably fast rate. (This rearrangement will be called a 5sp rearrangement (after Hardwidge et al.[6]), indicating the transition state ring size and the rearrangement to a secondary (s) from a primary (p) radical site.) Comparing the intensity of the CA fragment peak corresponding to radical II ($[P - C_4H_9]^-$; P = parent ion = $[TCNQC_5H_{11} - CN]^{-}\cdot$) to those corresponding to III ($[P - C_3H_7]^-$ plus $[P - CH_3]^-$) suggests that most of the trapped radicals had rearranged under these conditions. Thus, in the time available for rearrangement between radical formation and trapping by TCNQ, ca. 77% of the originally primary pentyl radicals that were subsequently trapped underwent intramolecular 5sp isomerization.

When the concentration of TCNQ was raised so that TCNQ became an important factor in determining the lifetimes of the trapped radicals, the RTCA spectrum from the originally primary $\cdot C_5H_{11}$ radicals changed. At a very low concentration of TCNQ in the source, the fraction of $\cdot C_5H_{11}$ radicals trapped as the unrearranged primary species was 23%, and when the TCNQ concentration was increased, the percentage trapped as primary radicals increased to 58% at the highest TCNQ concentration attained. This clearly shows that the radical lifetimes were significantly shortened by the presence of a high concentration of TCNQ.

During the time allowed for radical isomerization[13] (ca. 10^{-2} s) the radicals also have the opportunity to decompose. For those that are sufficiently energetic when formed, decomposition can precede collisional stabilization due to the fast decomposition rates of energetic and chemically activated radicals.[17-20] The radical

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products of these decompositions are evident in the TCNQ trapped radical mass spectra;[13] it is the less energetic or collisionally stabilized radicals that are trapped by TCNQ and studied with collisional activation.

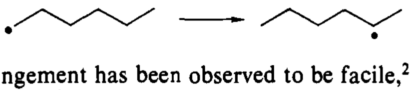
Despite some uncertainties regarding the internal energies of the radicals, the presence of substantial quantities of both II and III at low TCNQ concentrations provides an opportunity to determine and approximate rate constant for the 5sp rearrangement, provided that the radical lifetimes can be estimated. Since a substantial variation of the reported rate constants[4-11] exists, depending on the internal energy of the radicals, it is useful to estimate the rate constant for the 5sp rearrangement by using lifetime concepts discussed in the preceding paper.[13]

Since the rate of formation of the radicals is constant under steady state conditions, the lifetime of the radicals must be determined by the loss mechanisms. The primary loss mechanisms for radicals without TCNQ present are flow from the source, diffusion to the walls, and radical–radical recombination.[12,13] Considering each factor independently, the maximum lifetimes allowed by each are 10^{-2} s, ca. 10^{-3}–10^{-1} s, and 10^{-2} s. If radical destruction at stainless steel walls at 150 °C is inefficient, then radical lifetimes will be limited by flow from the source and radical–radical recombination. Thus, a good estimate of the radical residence times is 10^{-3}–10^{-2} s.

In solution at 100 °C, it is known that acetophenone primary radicals undergo CO elimination to form benzyl radicals, and that 4-*tert*-butylpyridyl primary radicals isomerize to 4-*i*sobutylpyridyl tertiary radicals at rates of ca. 10^3 s^{-1}.[21] At a source temperature of approximately 100 °C, the TCNQ-trapped radical mass spectrum from acetophenone showed ions corresponding to the addition of benzyl radicals, but none corresponding to acetophenone radicals, and the RTCA spectrum from 4-*tert*-butylpyridyl radicals showed that they had all isomerized to the tertiary isobutyl structure. These experiments lend further support to the calculated lifetime of ca. 10^{-2} s (since gas-phase rates should be similar to solution-phase rates[22]).

Assuming a lifetime of ca. 10^{-2} s together with the fact that $[\mathrm{II}]/[\mathrm{III}] \approx {}^1/_3$, the unimolecular rate equation yields a rate constant for the 5sp rearrangement reaction of ca. 10^2 s^{-1}. This is in substantial agreement with the value given by Endrenyi and LeRoy[4] for thermal radical populations. The much larger rate constants for excited radicals of Hardwidge et al.[6] would yield lifetimes of $\sim 10^{-6}$ s, which is insufficient time for the TCNQ molecules to collide and react with radicals. Since the estimated 5sp rate constant is similar to that reported for thermal radicals and substantially different from that reported for chemically activated radicals, it must be concluded that primarily thermal or near-thermal radicals are trapped by TCNQ.

Continuing the alkyl radical series, the RTCA spectrum of the (originally) primary *n*-hexyl radical showed only two major peaks, corresponding to the loss of $\cdot CH_3$ and $\cdot C_4H_9$. The RTCA technique shows that within the measurement precision of the technique, most of the primary hexyl radicals had rearranged to the 2-hexyl radical via a six-membered-ring intramolecular hydrogen-abstraction reaction (6sp) (Table II).



This rearrangement has been observed to be facile,[2,5,6] and significantly faster than the 5sp rearrangement because of the more energetically favorable transition state.[2] As a result of the extent of conversion in the present experiments, it is not possible to estimate the rate constant of the reaction with any certainty, except to say that it is much faster than the five-membered-ring rearrangement, as observed by Hardwidge et al.,[6] as tabulated by Mintz and LeRoy,[23] and as tabulated and calculated by Babayan and Stepukhovich.[9,24,25]

It is of interest to note that, in contrast to alkyl ions, alkyl radicals do not rearrange by 1,2 or 1,3 hydrogen shifts or methyl shifts. The RTCA data, consistent with previous work using thermal radicals,[2,3,22] shows that in the nonfragmenting C_3–C_6 radicals no such rearrangement occurred on this time scale. Therefore, the RTCA technique is not sampling high-energy radicals, or even radicals that have been later stabilized, but rather it is mostly sampling near-thermal radicals which do not undergo processes requiring a high activation energy.

Considering the available rearrangement processes and their relative rates, it is possible to understand the general features of the RTCA spectra arising from heptyl, octyl, and larger radicals that were originally generated as primary species (Table II). In the case of the heptyl radicals, the 6sp and 7sp isomerizations are faster than the 5sp, and as a consequence the 4-heptyl radical structure was significantly under represented in the RTCA spectrum (loss of C_3H_7). As expected, the 6sp rearrangement seems to be slightly faster than the 7sp isomerization (compare the losses of $C_2H_5 + C_4H_9$ vs. $CH_3 + C_5H_{11}$). For *n*-octyl and larger radicals, the possibility of sequential rearrangements to different secondary sites arises, and apparently contributes, in concert with the 5sp, 6sp, and 7sp rearrangements, to a uniform-appearing RTCA spectrum.

The RTCA spectrum is in marked contrast to the CA spectrum obtained from a genuine *n*-octyl-substituted TCNQ. To ensure that the observed spectra actually arose from radical rearrangements prior to trapping by the TCNQ, as opposed to β, γ, δ, etc., bond scission, authentic samples of *n*-hexyl- and *n*-octyl-substitued TCNQ were subjected to CA analysis. The only fragment ions present were those expected from the CA bond-breaking mechanism outlined above, i.e., $[P - H]^-$ and $[P - HCN]^-$ ions from metastable and CA decomposition, and $[P - C_5H_{11}]^-$ and $[P - C_7H_{15}]^-$ ions from the *n*-hexyl- and *n*-octyl-substituted TCNQ CA fragmentation reactions, respectively. Thus, rearrangements prior to trapping can be observed, independent of possible conflicting effects, and these results further support the α-cleavage mechanism of CA decomposition.

Cyclic Radicals. The RTCA spectra of cyclic radicals were relatively simple and lend further support to the single bond cleavage CA mechanism (Table II). The only significant peak in the spectrum was from the loss of H; scission of two bonds, resulting in the loss of $C_{n-1}H_{2n-2}$ from the $[TCNQC_nH_{2n-1} - CN]^{-\cdot}$ ion, did not occur. It is therefore feasible to study noncyclic structures in the presence of cyclic ones of the same molecular weight, since the cyclic structures would only contribute substantially to the metastable ion and $[P - H]^-$ ion signals.

Quantitation of Radical Structure Populations. To quantitate the amounts of the nonfragmenting, acyclic, radical structures detected in the RTCA spectra, a number of criteria must be met: the reactivity with TCNQ of the various isomers of radicals of the same elemental formula must be the same, the collisional activation fragmentation cross-sections for the different $[TCNQR - CN]^{-\cdot}$ ions must be the same, and the CA "branching ratios" or fragmentation pathway factors for competing CA alkyl losses must be reproducible and known. A self-consistent calculational method for assigning the peak intensities to the various structures is also required.

The reactivity of the radicals with TCNQ was checked by using the same partial pressure of radical precursors in a nitrogen CI plasma to generate different propyl, butyl, and pentyl radical structures for reaction with a constant amount of TCNQ at constant temperature and total pressure. The reactivity, as judged from the resulting intensity of the $[TCNQR - CN]^-$, peak, was identical within experimental error for all of the isomers of the various radical species examined. Thus, discriminating reaction rates resulting from the primary, secondary, or tertiary nature of the radicals was eliminated as a source of error. This also shows that the competing radical decomposition pathways do not interfere

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Table III. Fragmentation Pathway Factors[a]

	loss of		
vs. loss of	C_1	C_2	$C_{n\geq 3}$
C_1	1.0	1.85	2.3
C_2	0.54	1.0	1.3
$C_{n\geq 3}$	0.43	0.77	1.0

[a] ±10% relative; read as, e.g., $C_2/C_1 = 1.85$.

with the measurements for isomeric radicals of the same carbon number.

The fragmentation cross-sections of the various methyl, ethyl, propyl, butyl, and pentyl radical structures were determined by comparing the total CA fragment ion intensities at a constant parent ion intensity for the various radical isomers. Thus, for the *sec*-butyl radical, the sum of the $\cdot CH_3$ and $\cdot C_2H_5$ losses was compared to the sums of the fragment losses for each of the other butyl parent ion species. (In order to include the loss of H, the metastable loss of H from TCNQ must be accounted for and subtracted; for ions other than $[TCNQCH_3 - CN]^{-}\cdot$, the H loss from the alkyl group was not significant and was ignored.) For all of the cases examined, including $[TNCQCH_3 - CN]^{-}\cdot$ for which *only* the loss of H occurs, the total fragmentation cross-sections agreed within 10%. Thus, although the loss of H is very disfavored when another fragmentation pathway is available (e.g., the loss of a butyl radical), the CA process provides sufficient energy for fragmentation to be induced by using *some* available pathway.

"Fragmentation pathway factors" are needed to unravel the RTCA spectra since, as discussed above, the loss of the alkyl side chains is dependent upon the critical energy for the reaction, which is in turn dependent upon the stability of the radicals lost in the fragmentation. The ratio of alkyl to H loss cannot be accurately determined, due to the variation of the relative metastable ion contribution to the spectra caused by slight differences in CA gas pressure. However, the *loss ratios* between different alkyl side chains (the "fragmentation pathway factors") were reasonably constant (Table III), and can be used to calculate the contribution of a particular structure to a CA peak intensity. Alternatively, the RTCA spectrum of a particular structure could be predicted by using the fragmentation pathway values.

The calculation of structure populations within a trapped-radical-structure mixture begins with a cataloging of all of the reasonable isomeric structures which may contribute to the RTCA spectrum in question. For each radical structure, the expected fragmentation pathways are noted (i.e., loss of R_1, R_2, and R_3 in I). If a particular structure is the only one that can contribute to a given CA peak, then its contribution to any other CA peaks may be substracted from them by using the fragmentation pathway factors to estimate that contribution. For all remaining structures which simultaneously contribute to one or more CA peaks, simultaneous linear equations must be constructed, taking proper account of the CA losses and fragmentation pathway factors appropriate for each structure. Upon solution of the equations, the total intensity of all of the CA peak contributions must be determined for each structure, and population percentages calculated on that basis. With the use of this method, radical structure percentages quoted in this paper and in the following one[26] have been calculated. Additional information on the calculational methodology is available from the authors.

Radicals Produced by Hydrogen Abstraction. Radicals corresponding to the molecular weight minus one [(M − 1)·] were observed in significant abundance in the TCNQ CI mass spectra of most compounds studied,[13] and some were also studied by using the RTCA technique to determine their structures. Table IV contains a summary of the RTCA spectra observed for a variety of alkanes, ketones, and amines. The (M − 1)· radicals are probably produced by abstraction reactions of radical cations with neutral molecules,[13] since hydrogen abstraction by radicals is not expected to be a significant process in this system because of the slow rate of those reactions.[2,3,22] Another possible source of (M − 1)· radicals is the neutralization of $(M - 1)^+$ ions. Since $(M - 1)^+$ ions can rearrange by mechanisms not available to (M − 1)· radicals (e.g., 1,2 hydride shifts), some information about the hydrogen abstraction probabilities and the relative importance of $(M - 1)^+$ neutralization vs. hydrogen abstraction pathways for (M − 1)· radical production can be obtained.

Hydrogen abstraction by *radicals* from alkanes has been shown to heavily favor tertiary and secondary sites[2] (tertiary:secondary:primary = 40:5:1), and in acids, sites α to the carbonyl are preferred by 87:1.[2] The hydrogen abstraction reactivity order may be the same for abstraction by radical cations compared to abstraction by radicals, but the energetics of the reaction and thus the absolute ratios may differ substantially.

In the simple case of propane, the RTCA spectrum of the (M − 1)· radicals indicated a mixture of primary and secondary sites, in the ratio 28:72. If no propyl ions contributed to the (M − 1)· radical population, then the secondary hydrogens were favored in the abstraction by 7.7:1, on a per-atom basis. In this case, the neutralized ion and direct radical formation mechanisms cannot be distinguished because the same structure is expected for each.

For the *n*-butane case, the presence of any tertiary butyl (M − 1)· radicals would require the prior formation of $(M - 1)^+$ ions, since the butyl radicals trapped by TCNQ do not rearrange, vide infra. With the use of the calculational method outlined above for determining the amount of primary, secondary, and tertiary structures present in the RTCA spectrum, the result is 16:78:6, respectively. If neutralized ions are assumed not to contribute to the primary and secondary sites, the abstraction ratio on a per-atom basis is 7.3:1.

For *n*-pentane, the calculated distribution of structures present in the RTCA spectrum is: primary:i-pentyl:3-pentyl:tertiary 18:50:29:3. The expectation that the two secondary sites (2-pentyl and 3-pentyl) should be populated statistically 2:1 is verified within experimental error for this determination. Use of a variety of partial-pressure conditions of *n*-pentane and nitrogen gas in a somewhat higher pressure CI source than used above resulted in a consistent set of data having a mean ratio of these structures of 18:48:24:10. Thus, under the latter conditions the presence of a small amount of tertiary pentyl radicals is suggested, and the 2:1 statistical distribution of secondary sites is maintained. For these two sets of data, if the possibility of $(M - 1)^+$ neutralized ion contributions to the secondary and primary radicals is again ignored, the secondary:primary abstraction ratio is about 4:1 on a per-atom basis.

In the case of *n*-hexane, the calculated ratios for the 2-hexyl, 3-hexyl, tertiary 3-methyl-3-pentyl, and the sum of the tertiary 2-methyl-2-pentyl and 2,3-dimethyl-2-butyl radicals were 43:30:23:4. No primary *n*-hexyl was left, within experimental error. However, the uneven distribution of the two secondary sites suggest that some primary hexyl radicals were formed and rearranged prior to trapping to the preferred 2-hexyl structure (ca. 13% of the total), in contrast to the pentyl case, in which the statistical distribution of secondary sites indicates that no rearrangement of primary radicals took place. In this case, the lower-energy six-membered-ring transition state did not provide an insurmountable barrier to rearrangement of the thermal primary radical. The presence of 27% tertiary structures suggests that many of the (M − 1)· radicals originated as ions.

Considering the (M − 1)· radicals from the ketones, the RTCA spectra are sometimes ambiguous in that CO and C_2H_4 have the same nominal mass. However, for the smaller ketones rearrangement is not a problem and neither is the mass ambiguity. In the case of 2-pentanone, for example, hydrogen abstraction occurred at secondary sites and was approximately equally distributed betwen the two secondary locations, as determined by comparing the sums of the intensities of the complementary losses in the RTCA spectrum ($[P - 43]^- + [P - 29]^-$ vs. $[P - 57]^- + [P - 15]^-$). The favoritism for the secondary sites is consistent with the hydrogen-abstraction reactivity order mentioned above,

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[26] C. N. McEwen and M. A. Rudat, *J. Am. Chem. Soc.*, following paper in this issue.

Table IV. RTCA[a] Spectra of (M – H) Radicals

R (precursor)	parent *m/z*	relative intensity, %									other fragments
		P – 1	P – 15	P – 27	P – 29	P – 43	P – 57	P – 71	P – 85	P – 99	
C_3H_7 (propane)	221^-	69	100	15	40	7					
C_4H_9 (*n*-butane)	235^-	100	39	31	59	19	4				
C_5H_{11} (*n*-pentane)	249^-	70	48	24	86	100	52	4			
C_6H_{13} (*n*-hexane)	263^-	100	52	25	61	48	71	5			
C_7H_{15} (*n*-heptane)	277^-	100	45	15	57	32	37	48	4		
C_8H_{17} (*n*-octane)	266^-	100	13	2	19	20	19	9	15	1	
C_8H_{17} (3-methylheptane)	291^-	100	19	10	36	5	28	11	21	1	
C_8H_{17} (2,3-dimethylhexane)	291^-	100	29	10	7	10	3	40	20	3	
C_8H_{17} (2,2,4-trimethylpentane)	291^-	100	50	15	4	9	39	40	2	46	
C_3H_5 (cyclopropane)	219^-	100	1	100	1						
C_6H_{11} (cyclohexane)	261^-	100	37	8	15	32	18	3			
C_8H_{15} (cyclooctane)	289^-	100	11	7	12	5	5	6	10	1	
C_5H_9O (2-pentanone)	263^-	100	14	46	32	79	94	35	5		P – 17, 10 P – 18, 10
$C_6H_{11}O$ (2-hexanone)	252^-	100	16	10	26	79	66	42	16	3	
$C_7H_{13}O$ (2-heptanone)	291^-	100	17	41	30	48	44	14	18	2	
$C_7H_{13}O$ (4-heptanone)	291^-	94	7	31	32	2	5	100	34	2	
$C_8H_{15}O$ (2-octanone)	305^-	100	20	27	15	62	16	17	6		
$C_9H_{17}O$ (2,6-dimethyl-4-heptanone)	319^-	100	20	46	17	77	9	9	46	27	
$C_{11}H_{21}O$ (6-undecanone)	322^-	12	7	18	9	34	5	7	5	65	P – 113, 15
$C_4H_{10}N$ (*n*-butylamine)	250^-	100	31	48	13	24	4				P – 28, 24 P – 44, 50 P – 55, 29 P – 69, 50
$C_4H_{10}N$ (isobutylamine)	250^-	100	29	43	6	30	25	8			P – 28, 26 P – 56, 46 P – 58, 25 P – 83, 47
C_7H_{13} (3-heptene)	275^-	100	86	11				11			P – 30, 88 P – 44, 32 P – 59, 11

[a] [TCNQR – CN]$^{-\cdot}$ ions.

tertiary > secondary > primary, and with that found for the alkanes. When the chain length was increased, the sites α and β to the carbonyl were favored over other secondary sites for abstraction. In 4-heptanone the α site was apparently more reactive than the β site, consistent with the hydrogen-abstraction reactivity of radicals with acids.[2] In the only ketone case in which a tertiary hydrogen was present, 2,6-dimethyl-4-heptanone, the secondary site α to the carbonyl was apparently favored over the tertiary site by about 2.5:1, suggesting a nearly statistical division of the abstracted hydrogens between the secondary and tertiary sites, and a reactivity order tertiary $\approx$ secondary $\gg$ primary.

Use of TCP for RTCA Spectra. Tetracyanopyrazine (TCP) is another effective radical trap in the CI source;[12,13] the [TCPR – CN]$^{-\cdot}$ ions were investigated for their usefulness in determining radical structures. Fragmentation patterns were very similar to those found with TCNQ, except for some variations in the relative amounts of rearranged vs. unrearranged trapped radicals. TCNQ is favored for use in most RTCA studies because of its high reactivity with radicals and the greater extent of experience with its use in these studies.

Conclusion

A new method utilizing TCNQ as a radical trap followed by collisional activation mass spectrometry has been successfully applied to the determination of carbon-centered radical structures. The dominance in the TCNQ/trapped-radical anion CA spectra of ions produced from the fragmentation of the attached radicals permits unambiguous determination of the precursor radical structures, and thereby the study of radical rearrangements. Additionally, radicals formed by hydrogen abstraction were found to be amenable to study, and the relative importance of different abstraction sites was determined. For compounds of unknown structure, it should be possible to obtain structural information from the (M – H)· RTCA spectra.

In addition to extending this technique to the study of the structures of radical fragments lost during the ionization of molecules of interest, it should also be possible to study the structures of carbon-centered radicals in other high-radical-density environments, using TCNQ or the more volatile TCP. The future discovery of other radical traps which offer analytical capabilities similar to those found for TCNQ may provide structural information about gas- or liquid-phase oxy-, nitrogen-, or metal-centered radicals. In the meantime, the RTCA technique should find broad applicability in labeling studies, structure determinations, fragmentation studies, and radical rearrangement studies. Its application to the study of ion structures and rearrangements by studying the structures of neutralized ions is presented in the following paper.[26]