production due to Auger processes and to dissipation of recoil energy. The relative importance of each of these two modes changes as the density is increased.

Future studies using this system should probably concentrate on the high-density gas-phase region. The low-pressure gas-phase region displays interesting behavior, but the processes which take place in it may be more amenable to study with the use of other techniques such as molecular beams, ion cyclotron resonance spectroscopy, etc. In the solid phase, processes can be studied which would be difficult to study by any other means. These processes are microscopic in nature and include the deposition of small (by nuclear physics standards) amounts of recoil energy in a dense medium, production of transient high local charge in the same, microscopic Auger electron radiolysis, etc. As has been demonstrated,[4] the effects of each are quite different, but it is difficult to vary the conditions under which the processes take place since the experiments are conducted at 77 K. It is difficult or impossible to vary the density, use scavengers, do moderator type experiments, or in general study any two compartment systems. In high-pressure gas-phase studies none of these would be a problem, and thus the microscopic radiolytic processes which take place at condensed-phase densities could be more fully explored. One would like to design a pressure vessel which could withstand on the order of 1000 atm, provide for addition of any gases, and allow for easy retrieval of all the bromine activity in the manner described in the experimental section. Using such an experimental technique, one could more completely explore several high-energy processes which are not easily studied by other methods.

Acknowledgment. We thank the staff who operated the Washington University 52-in. cyclotron for their assistance. J.J.F. was supported by NIH MSTP Grant No. 5-T05-GM02016.

Radical Trapping in a Mass Spectrometer Ion Source. 1

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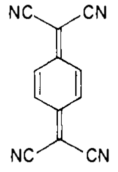
Contribution from E. I. du Pont de Nemours and Company, Inc., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898.

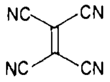
Received November 4, 1980

Abstract: 7,7,8,8-Tetracyanoquinodimethan (TCNQ), tetracyanoethylene (TCNE), and tetracyanopyrazine (TCP) react sufficiently fast with gas-phase carbon-centered radicals that the reaction products dominate the chemical ionization (CI) hydrocarbon reagent gas mass spectrum at high electron emission currents and low partial pressures of TCNQ, TCNE, or TCP. Calculations and radical trapping experiments inside and outside a CI source show that the rate of the TCNQ–radical reaction approaches the diffusion-controlled limit. The radical populations in the CI methane, isobutane, di-*tert*-butyl peroxide, 1-octanol, *n*-octane, and toluene-d_3 plasmas are elucidated, as is the radical population in methane under Townsend discharge conditions. The mechanisms for radical formation under CI conditions are ion fragmentation, hydrogen-atom abstraction from the reagent gas by a radical cation, and ion–electron recombination. Steady-state calculations are given which show the radical concentration under CI conditions can be expected to be much larger than the ion concentration.

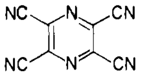
Recently, we reported the first observation of radical addition reactions under chemical ionization (CI) conditions in a mass spectrometer ion source.[1] These gas-phase radical-addition reactions occur between a variety of carbon-centered radicals and 7,7,8,8-tetracyanoquinodimethan (TCNQ), tetracyanoethylene (TCNE), tetracyanopyrazine (TCP), and, to a much lesser extent, hexakis(methoxycarbonyl)trimethylenecyclopropane (**1**) and pentacene (**2**). The measured rate of the TCNE–methyl radical reaction approaches the diffusion-controlled limit and is even faster than methyl radical–radical recombination! The enhanced rate of reaction between carbon-centered radicals and these strong electron acceptors may be the result of charge transfer during a collision or near-collision, leading to gas-phase charge-transfer complexes which rapidly collapse to products.[2] Radical addition to compounds that readily form charge-transfer complexes as electron acceptors are reported to be facile in solution.[3] For example, TCNE[4-7] and TCNQ[5,6] react with radicals by 1,2 or 1,4 and 1,6 addition, respectively.



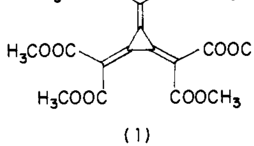
(TCNQ)



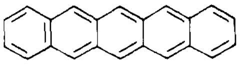
(TCNE)



(TCP)



(1)



(2)

The fast rate of the gas-phase radical-trapping reaction, combined with a higher concentration of radicals than ions in the CI source, as suggested by calculations and experiments, results in radical trapping by TCNQ, TCNE, and TCP being competitive with ionization. Thus, the elemental compositions and the structures[8] of carbon-centered radicals produced in a plasma by ion fragmentation, hydrogen-atom abstraction, and ion–electron recombination can be readily delineated mass spectrometrically.

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

(2) S. W. Benson in "Frontiers of Free Radical Chemistry", W. A. Pryor, Ed., Academic Press, New York, 1980, p 16.

(3) A. A. Kuznetsov, S. N. Novikov, and A. N. Pravednikov, *Akad. Nauk SSSR. Ser. Khim., Isv.*, 297 (1979), and reference cited therein.

(4) S. Kukuzumi, K. Mochida, and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 5961 (1979).

(5) M. Farcasiu and C. S. Russell, *J. Org. Chem.*, **41**, 571 (1976).

(6) D. F. Eaton, *J. Am. Chem. Soc.*, **102**, 3278 (1980).

(7) P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975).

(8) M. A. Rudat and C. N. McEwen, *J. Am. Chem. Soc.*, following paper in this issue.

Additionally, radical isomerizations can be elucidated by using labeling techniques, and factors that affect the radical population in a plasma, such as temperature and pressure, can also be studied.

Experimental Section

The radical-trapping compounds used in this study were samples of high purity as determined by electron ionization and $CI(N_2)$ positive and negative ion mass spectrometry. TCNQ, TCNE, and pentacene are available from Aldrich Chemical Co. Research grade methane and isobutane were obtained from Matheson Gas Products, Lyndhurst, NJ. Methane-d_4 (99%) and toluene-α,α,α-d_3 were obtained from Merck and Company Limited, Montreal, Canada. The hydrocarbons used were high-purity samples obtained from Chemical Samples Co., Columbus, OH. Other chemicals were obtained from a Chem Service, Inc. (Media, PA), Lab Assist Kit and were used as received.

Spectra were obtained either with a ZAB-2F mass spectrometer (VG Organic, Altrincham, England) or a 21-491 mass spectrometer (E. I. du Pont de Nemours and Co., Wilmington, DE) equipped with dual EI/CI ion sources. The radical-trapping compounds were introduced into the CI source at rates of ca. 0.1–20 ng/s by evaporation from the solids probe tip directly in the ion source. TCNE was introduced through the gas-chromatograph inlet for some experiments. The radical-precursor compounds were introduced into the CI source at rates of ca. 1–100 μg/s through the heated glass inlet or through the gas chromatograph.

Radical Trapping Outside the Ion Source. TCNQ (20 mg) and di-*tert*-butyl peroxide (30 mg) were in separate sections of a quartz tube which was cooled with liquid nitrogen and evacuated. The evacuated, sealed tube was then placed in an oven and heated to 200 °C for 1 h. The TCNQ reaction products were analyzed by electron-ionization mass spectrometry.

An experiment designed to estimate the rate of the radical-trapping reaction by monitoring the reaction products of competing reactions by gas chromatography was carried out in this manner. A 250-mL glass flask equipped with two stopcocks of Teflon fluorocarbon resin and a high-temperature septum was dried by heating under vacuum. Di-*tert*-butyl peroxide (100 mg) was added to the flask which was heated to 175 °C to deactivate the surface toward radicals. The flask was evacuated and 0.2 atm of N_2 and 7.2 mg of di-*tert*-butyl peroxide were added. The peroxide was decomposed by maintaining the flask at 175 °C for 1 h, and the gaseous products were analyzed for ethane and acetone (see eq 8). This procedure was repeated three times to assure that the amount of ethane produced remained constant (±10%). The effect of TCNE on the amount of ethane produced was determined by adding varying amounts of TCNE (6, 11, and 30 mg) to the flask before the addition of N_2 and 7.2 mg of di-*tert*-butyl peroxide.

The relative amount of ethane produced in each experiment was determined by peak area from the response of an FID detector. The response from the acetone peak was monitored to assure that the amount of methyl radicals produced did not vary by more than 10%. Quantitation of the acetone peak showed that 87 ± 10% of the di-*tert*-butyl peroxide reacted via eq 8 to produce methyl radicals.

The gaseous products were separated on a 2 m Porapak-N GC column temperature programmed from 60–200 °C at 8 °C/min.

Determination of the Minimum Radical Concentration in the CI Source. Known amounts of TCNQ (2–10 μg) were deposited from an acetonitrile solution onto a glass tip which was inserted into the mass spectrometer ion source, using the solids probe. The source conditions were ca. 0.5 torr of methane, 105 °C, and 0.1 or 1.0 mA emission current. The mass spectrometer was scanned every 1.5 s over the mass range 400–50 amu. Data were collected with a VG-Multispec Data System (VG-Data Systems, Altrincham, England). For any single scan in which half of the TCNQ-related ions were from radical reactions, the instantaneous TCNQ concentration was calculated, using the computer-generated total ion current for TCNQ-related ions and the measured flow rate of 100 cm^3/s.

This procedure was carried out in both the positive and negative ion modes, and also with TCNE injected into an HP5700 gas chromatograph interfaced to the ZAB-2F mass spectrometer. If all of the radicals in the source had reacted with TCNQ or TCNE, the concentration of radicals would be one-half the TCNQ or TCNE concentrations for the appropriate scan.

Four-Parameter Factorial Experiment. Mass spectra were obtained and analyzed at all combinations of reasonable low, medium, and high values of methane partial pressure and electron emission, and at low and high source temperatures and partial pressures of TCNE. The methane partial pressures used were 1×10^{-5}, 5×10^{-5}, and 1×10^{-4} torr as measured by a Bayard–Alpert pressure gauge located in the source housing region, at a constant total pressure of 1×10^{-4} torr, which was maintained by using nitrogen gas (corresponding to ca. 0.1, 0.4, and 0.7 torr source pressure). Source temperatures were 100 and 250 °C, and the emission currents were 0.05, 0.5, and 1.0 mA. Low and high values of TCNE partial pressures were obtained by injecting 5 μg of TCNE onto an SP2100 GC column interfaced to the ZAB-2F mass spectrometer and selecting mass spectra from scans at low and high points on the ensuing TCNE total ion current chromatogram. A total of 36 separate experiments were required.

Discharge Study. A Townsend discharge was generated in the CI source at 0.7 torr of methane, using the techniques of Hunt et al.,[9] and maintaining the source at a positive potential relative to the counterelectrode.

Results and Discussion

The negative ion methane chemical ionization mass spectrum of TCNQ contains a series of major ions which correspond to the addition of H, CH_3, and C_2H_5 to TCNQ and these same additions with loss of one or more cyano groups.[1] The positive ion $CI(CH_4)$ spectrum was similar to the negative ion spectrum in that major ions were observed corresponding to addition of H, CH_3, and C_2H_5 with loss of CN and protonation. In addition, a set of ions were observed in the positive ion mode which correspond to addition of H, CH_3, and C_2H_5 plus a proton and an additional hydrogen atom.[1] Accurate mass measurement was used to establish the elemental compositions of the major ions and methane-d_4 was used as a CI reagent gas to ensure that the addition products were originating from the methane plasma.

The negative ion results in which H, CH_3, and C_2H_5 add to TCNQ cannot be explained by ion–molecule reactions because negative reagent ions are not produced in a methane plasma and the probability that a positive ion addition to TCNQ will be followed by neutralization and electron capture ionization is too low to be significant. Additionally, the major addition of CH_5^+ and $C_2H_7^+$ to TCNQ cannot be explained by ion–molecule reactions in the positive ion mode. Because of the symmetry of the results in the positive and negative ion spectra, it is unlikely that ion–radical reactions of the types $TCNQH^+ + R\cdot$ and $TCNQ^-\cdot + R\cdot$ account for the major products. Additionally, this kind of reaction has not been previously reported and therefore could only be accounted for in this case if both the positive and negative ion–radical reaction rates were unusually fast and nearly identical, which is unlikely.

A mechanism based on radical addition to neutral TCNQ has been proposed (Scheme I)[1] and accounts for the major products observed in the positive and negative ion spectra. In Scheme I, the carbon-centered radicals present in the CI(methane) plasma (eq 1–4) react by addition to TCNQ with subsequent ionization

$$CH_4 + e^- \rightarrow CH^{+}\cdot \quad (1)$$

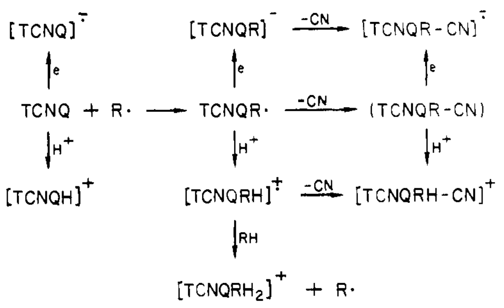
$$CH_4^{+}\cdot \rightarrow CH_3 + H\cdot \quad (2)$$

$$CH_4^{+}\cdot + CH_4 \rightarrow CH_5^+ + \cdot CH_3 \quad (3)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (4)$$

of the TCNQ–radical products. Ionization by protonation, however, produces a radical cation which under CI conditions is observed only in very low abundance. Instead, even-electron ions are formed from the molecular ions by loss of ·CN or by hy-

Scheme I



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[9] D. F. Hunt, C. N. McEwen, and M. T. Harvey, *Anal. Chem.*, **47**, 173 (1975).

Table I. CI(isobutane) Positive- and Negative-Ion Mass Spectra of TCNQ[a]

	% rel intensity[b]		assignment	
m/z	pos	neg	positive ions	negative ions
291	5		$[TCNQ(C_3H_7)_2]H^+$	
263	80		$[TCNQHC_4H_9]H^+$	
261	5	10	$[TCNQC_4H_9]^+$	$[TCNQC_4H_9]^-$
249	100		$[TCNQHC_3H_7]H^+$	
247	50	7	$[TCNQC_3H_7]^+$	$[TCNQC_3H_7]^-$
236	15		$[TCNQC_4H_9 - CN]H^+$	
235		15		$[TCNQC_4H_9 - CN]^{-\cdot}$
222	40		$[TCNQC_3H_7 - CN]H^+$	
221	30	20	$[TCNQHCH_3]H^+$	$[TCNQC_3H_7 - CN]^{-\cdot}$
220	10		$[TCNQCH_3]H^{+\cdot}$?	
219		25		$[TCNQCH_3]^-$
211	3		$[TCNQHC_4H_9 - 2CN]H^+$	
210		10		$[TCNQHC_4H_9 - 2CN]^{-\cdot}$
207	35	2	$[TCNQH_2]H^+$	$[TCNQC_2H_5 - CN]^{-\cdot}$?
206	15		$[TCNQH]H^{+\cdot}$	
205		55		$[TCNQH]^-$
204	20		$[TCNQ]^{+\cdot}$	
197	5		$[TCNQHC_3H_7 - 2CN]H^+$	
196		12		$[TCNQHC_3H_7 - 2CN]^{-\cdot}$
194	80		$[TCNQCH_3 - CN]H^+$	
193		70		$[TCNQCH_3 - CN]^{-\cdot}$
182	25		$[TCNQ(CH_3)_2 - 2CN]H^+$?	
179	60	100	$[TCNQH - CN]H^+$.	$[TCNQH - CN]^{-\cdot}$
168		30		$[TCNQHCH_3 - 2CN]^{-\cdot}$
155	25		$[TCNQH_2 - 2CN]H^+$	
154		30		$[TCNQHCH_3 - 2CN]^{-\cdot}$
141	35		$[TCNQH - C_3N_2]^+$	

[a] Spectra were not obtained under the same ion source conditions. [b] $\geq 2\%$ relative intensity corrected for ^{13}C isotopes.

drogen-atom abstraction from neutral gas molecules.

Mechanisms of Radical Formation. Several mechanisms are available for radical production. Fragmentation of radical cations, as in eq 2, is a common mode of radical formation in mass spectrometry and is expected to account for some of the hydrogen atoms that add to TCNQ in the methane plasma. Hydrogen-atom abstraction from neutral compounds by radical cations of TCNQ (Scheme I) also appears to be a general process for producing (M − 1) radicals under CI conditions. Radical cations produced by the primary ionization of the reagent gas may in some cases abstract hydrogen atoms in a process similar to that given in eq 3.

Trapped radicals are also observed which are produced from ion–electron recombinations. For example, the addition of $\cdot C_2H_5$ to TCNQ in the methane plasma indicates the presence of ethyl radicals which are probably produced via eq 5. In addition, eq

$$C_2H_5^+ + e^- \rightarrow \cdot C_2H_5 \quad (5)$$

$$CH_5^+ + e^- \rightarrow \cdot CH_3 + H_2 \quad (6)$$

$$CH_5^+ + e^- \rightarrow H + CH_4 \quad (7)$$

6 and 7 are methods of forming hydrogen atoms and radicals by ion–electron recombination. Hot radicals produced by high-energy processes such as ion–electron recombination not involving a third body are expected to fragment forming alkenes and smaller radicals. Of interest is the finding that large ions such as the *tert*-butyl reagent ions produced in the CI(isobutane) plasma can be neutralized to the *tert*-butyl radical without subsequent decomposition (Table I). The relative amount of intact radicals reacting with TCNQ is too high to be accounted for by a three-bodied collision mechanism, thus either the radicals survive sufficiently long after two-bodied neutralization or, as seems more likely, ion–wall collisions produce stabilized radicals.

Reactions of TCNQ with Thermally Produced Radicals. In support of the mechanism proposed in Scheme I, it was shown that TCNQ reacts with gas-phase methyl radicals produced during the thermal decomposition of di-*tert*-butyl peroxide (Table II, eq 8). (Interestingly, no products were observed corresponding to

$$[(CH_3)_3C\text{–}O]_2 \xrightarrow{\Delta} [2(CH_3)_3C\text{–}O\cdot] \rightarrow 2\cdot CH_3 + 2(CH_3)_2CO \quad (8)$$

tert-butoxy radicals reacting with TCNQ.) However, demonstrating that gas-phase radicals react with TCNQ is not sufficient justification for Scheme I. The reaction must also be rapid enough to occur during the lifetime of TCNQ in the CI source. In practice, the product of the radical–neutral rate constant and the radical concentration must approach the product of the ion–molecule rate constant and the ion concentration.

The rate constant for the reaction of methyl radicals with TCNE was determined by comparing the rate of methyl radical recombination for which a value is known with the rate of methyl radical addition to TCNE. (TCNE was used in this experiment because of its lower heat of vaporization relative to TCNQ.) Ethane, produced from the recombination of methyl radicals, was determined quantitatively by gas chromatography in the presence and absence of TCNE. Addition of 0.55 mol of TCNE per mol of methyl radicals (as determined by the amount of acetone produced during the thermal decomposition of di-*tert*-butyl peroxide, eq 8) reduced the ethane concentration by ca. 65% relative to an identical experiment without addition of TCNE. A 1:1 molar ratio of TCNE to methyl radicals resulted in approximately a ninefold reduction in the ethane concentration and a 3:1 molar ratio gave ca. 100 times less ethane than the experiment run without addition of TCNE. The major nongaseous products of the reaction as determined by GC/MS and accurate mass measurement were $CH_3C(CN)_2CH(CN)_2$ and $CH_3CH(CN)_2$.

These data show that the rate of methyl radical reaction with TCNE is approximately three times faster than methyl radical recombination or ca. 10^{-10} cm^3 s^{-1}! Thus, the methyl radical–TCNE reaction is only about an order of magnitude slower than most ion–molecule reaction rates.

Calculations Supporting a High Radical Concentration in the CI Source. Further support for Scheme I comes from calculations designed to predict the ion and radical concentrations in the CI source. Siegel calculated the ion and electron concentrations in a CI source[10] based on the assumptions that the CI plasma fits

Table II. Electron-Impact Mass Spectrum of the Products Produced from the Gas-Phase Reaction of TCNQ and the Thermal-Decomposition Products of Di-*tert*-butyl Peroxide

m/z	% rel int[a]	ion assignment	*m/z*	% rel int[a]	ion assignment
263	5	$[TCNQHC_4H_9]H^+$	192	30	$[TCNQCH_3 - HCN]^{+b}$
248	12	$[TCNQHC_3H_7]^{+\cdot b}$	179	12	$[TCNQH - CN]^{+\cdot}$
235	20	$[TCNQ(CH_3)_2]H^{+b}$	178	15	$[TCNQH - HCN]^+$
234	100	$[TCNQ(CH_3)_2]^{+\cdot b}$	177	20	$[TCNQ - HCN]^{+\cdot}$
221	5	$[TCNQHCH_3]H^+$	166	15	$[TCNQHCH_3 - 2HCN]^+$
220	80	$[TCNQHCH_3]^{+\cdot b}$	165	35	$[TCNQCH_3 - 2HCN]^{+\cdot}$
219	20	$[TCNQCH_3]^{+b}$	155	55	$[TCNQCH_3 - C(CN)_2]^{+\cdot b}$
208	5	$[TCNQ(CH_3)_2 - CN]^+$	152	10	$[TCNQ - 2CN]^{+\cdot}$
207	40	$[TCNQ(CH_3)_2 - HCN]^{+b}$	141	25	$[TCNQ - C(CN)_2]^{+b}$
206	15	$[TCNQH_2]^{+\cdot}$	129	12	
204	75	$[TCNQ]^{+\cdot}$	69	30	

[a] Minimum intensity 5%; corrected for ^{13}C isotopes. [b] Assignment based on accurate mass measurement.

Langmuir's definition (i.e., $>10^8$ ions/cm^3)[11] and that steady-state and ambipolar diffusion[12] conditions exist in the source. This approach appears to produce a reasonable picture of conditions present in a tight CI source and is used here to calculate the relative concentrations of ions and radicals under a fixed set of CI source conditions.

The equation Siegal derived[10] for the positive reagent ion concentration in the absence of sample molecules (assuming steady state conditions) includes the production of ions by electron ionization and their loss by flow from the source, diffusion to the walls, and ion–electron recombination (eq 9, where S = the

$$\frac{d[I^+]}{dt} = S - \frac{F}{V}[I^+] - \frac{Da}{r_0^2}[I^+] - \alpha_r[I^+][e^-] = 0 \qquad (9)$$

primary ion production rate, $-(F/V)[I^+]$ = the loss of ions I^+ by flow F from volume V, $-(Da/r_0^2)[I^+]$ = the loss of I^+ by ambipolar diffusion, D_a, to the walls of the source having radius r_0, and $-\alpha_r[I^+][e^-]$ = loss of I^+ by ion–electron recombination; $[I^+] = [e^-]$ by the condition of ambipolar diffusion in the absence of negative-charge carriers other than electrons). The steady-state reagent-ion concentration in the CI plasma is calculated to be 3×10^{10} ions/cm^3, using the values for the constants reported by Siegel.[10] According to eq 9, 80–90% of the reagent ions initially produced in the CI source are lost by ion–electron recombination and less than 1% is lost by flow from the source.

A similar equation can be derived to calculate the steady-state radical population in a CI plasma. The equation similarly takes into account radical production, which should be about twice the production rate for ions (note eq 1–7), and radical losses by flow from the source, diffusion to the walls, and radical–radical recombination (eq 10, where $S_{R\cdot}$ = the primary rate of radical production, and $-k_r[R\cdot]^2$ = the loss of radicals by recombination). Loss of radicals by ionization is not expected to be important and is not included as a loss mechanism.

$$\frac{d[R\cdot]}{dt} = S_{R\cdot} - \frac{F}{V}[R\cdot] - \frac{\kappa D}{r_0^2}[R\cdot] - k_r[R\cdot]^2 = 0 \qquad (10)$$

Again with the use of the numerical values from Siegel's work[10] where applicable and the known rate of methyl radical recombination ($k_r = 4 \times 10^{-11}$ cm^3 s^{-1}),[13] it is found that the radical concentration is strongly dependent on the reactivity (κ) of the radicals with the source walls. For the case in which every collision with the wall results in loss of the radical ($\kappa = 1$), the radical concentration, $[R\cdot]$, is calculated to ca. 2.3×10^{11} radicals/cm^3, and when radicals seldom react on collision with the wall ($\kappa \ll 1$), $[R\cdot] \simeq 2.5 \times 10^{12}$ radicals/cm^3. Thus, the radical concentration in the CI (methane) source is 7–80 times higher than the ion concentration! These values together with the fast methyl radical–TCNE rate determined above give strong support for Scheme I.

The equations for estimating the ion and radical concentrations further suggest that the radical population will be considerably more dependent than the ion concentration on the primary rate of formation of ions and radicals and thus on the electron-emission current. This is because ion–electron recombination is sufficiently fast to be a major loss mechanism for the ions whereas radical–radical recombination, which is considerably slower, is not an important loss mechanism except at very high radical concentrations. Experimental results confirm this prediction.

The Minimum Radical Concentration in the CI Source. Support for the calculated results can be obtained experimentally by determining the minimum radical concentration in the CI(methane) plasma. This was done by introducing a known amount of TCNQ into the CI source and calculating its "instantaneous" concentration, at various points on the total ion current (TIC) curve, from the TCNQ-related TIC profile and the measured flow from the CI source of 100 cm^3/s. For the spectrum in which equal amounts of reacted and unreacted ionized TCNQ were observed, the concentration of radicals was equal to half of the TCNQ concentration if all of the radicals reacted, assuming that reacted and unreacted TCNQ have equal ionization efficiencies.

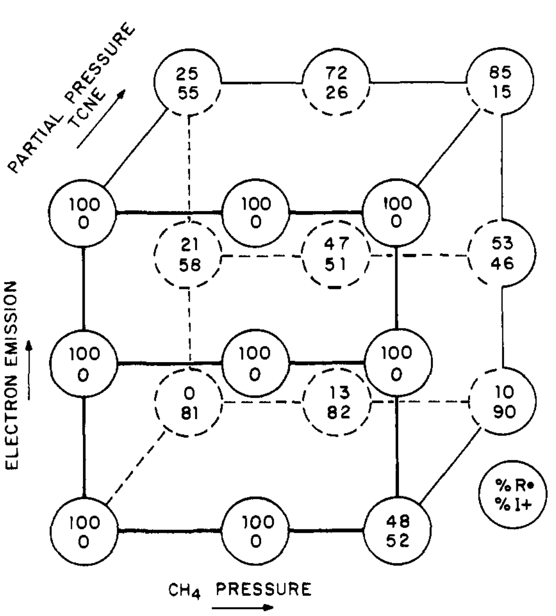

Figure 1. Factorial experiment showing the relationship between unreacted and radical reacted TCNE as a function of CI source methane pressure, TCNE concentration, and emission current.

At low TCNQ concentration in the source, as determined by the TIC profile, essentially all of the TCNQ had reacted with radicals, and at high TCNQ concentration, near the top of the TIC curve, a majority of the TCNQ was unreacted. At 0.05 mA emission current (ca. 2–3 μA delivered electron current), half of the TCNQ had reacted with radicals when the concentration of TCNQ in the source was ca. 10^{12} molecules/cm^3. The concentration of TCNQ in the source was ca. 10^{13} molecules/cm^3 when half of the TCNQ had reacted with radicals at the increased emission current setting of 1.0 mA (ca. 50–60 μA delivered). Thus, the minimum radical concentration in the CI(methane) plasma at 0.05 mA emission current is ca. 5×10^{11} and at 1.0 mA emission current is ca. 5×10^{12} radicals/cm^3. These values are consistent with the calculated results.

Similar results were obtained in the positive and negative ion modes and in similar experiments, using known amounts of TCNE injected into a gas chromatograph interfaced to the mass spectrometer.

Factors That Affect the Radical Population in the CI Source. Because the CI(methane) spectra of TCNQ and TCNE varied considerably under different experimental conditions, and because the calculations for determining the radical concentration predicted a strong dependence of the radical concentration on the electron emission current, a four-parameter randomized factorial experiment was conducted to assess the relative importance of pressure, temperature, TCNE concentration, and electron-emission current on the production and capture of radicals in the CI source. Mass spectra were taken and evaluated at reasonable high, middle, and low combinations of these parameters. TCNE was chosen because it could be easily and reproducibly introduced through the gas chromatograph inlet. It was assumed that reacted and unreacted TCNE are ionized with equal efficiency.

The total TCNE–trapped-radical-ion current increased at high emission, high TCNE concentration, and high methane pressure, but as can be seen from Figure 1, the relative abundance of ionized TCNE–radical products compared to ionized unreacted TCNE increased dramatically as the concentration of TCNE was reduced, and as the electron-emission current was increased. As the TCNE

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(10) M. W. Siegel in "Practical Spectroscopy Series", Vol. 3, Part B, C. Merritt, Jr., and C. N. McEwen, Eds., Marcel Dekker, New York, 1980, Chapter 4.

(11) I. Langmuir, *Phys. Rev.*, **33**, 954 (1929).

(12) Under ambipolar diffusion all charge carriers diffuse at the same velocity.

(13) J. Alistair Kerr in "Free Radicals", Vol. 1, J. K. Kochi, Ed., John Wiley & Sons, New York, 1973, Chapter 1.

concentration was increased, a point was reached where most of the available radicals were trapped and further increases in the TCNE concentration only enhanced the ratio of unreacted to reacted TCNE. Multiple radical reactions with TCNE were observed to increase at high electron-emission current and low TCNE pressure.

Other less pronounced effects were observed in these experiments. For example, increasing the methane pressure increased the ratio of $TCNECH_3$ to TCNEH products. One explanation is that higher methane pressure enhances the bimolecular reaction in eq 3 relative to the unimolecular decomposition of CH_4^+ in eq 2. On the other hand, increasing the temperature increased the TCNEH addition product relative to the $TCNECH_3$ product. The temperature effect, which was more pronounced than the pressure effect, may be due to an increase in the unimolecular decomposition in eq 2 at higher temperature or to an increased rate of radical decomposition. It might also be related to eq 6 and 7 where eq 6 is 1 kcal/mol more exothermic than eq 7.[14]

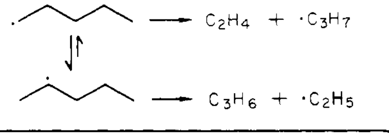
Radical Reactions in a CI Source

The utility of the radical-trapping reaction for determining the carbon-centered radicals produced under ionization conditions is demonstrated in the following examples. However, as noted in the preceding section, ion-source conditions and the amount of radical-trapping reagent in the source can affect relative ion intensities and alter the radical-reaction products. Thus, the spectra presented here are for a typical set of source conditions and may differ dramatically under other conditions.

CI Mass Spectra of TCNQ. The positive- and negative-ion methane CI mass spectra of TCNQ have been reported,[1] and show addition to TCNQ of the radicals produced in the methane plasma. Other hydrocarbon reagent gases also produce radicals that react with TCNQ under CI conditions. The mechanism of radical addition and subsequent ionization is the same as that with the methane plasma. For example, the CI(isobutane) negative-ion mass spectrum of TCNQ shows the radical content of the isobutane plasma to consist primarily of ·H, $\cdot CH_3$, $\cdot C_3H_7$, and $\cdot C_4H_9$ radicals (Table I). Isobutane, like methane and other hydrocarbon gases, does not produce negative reagent ions, so that ion–molecule reactions are not important in the negative-ion mode.

The positive-ion CI(isobutane) mass spectrum of TCNQ also shows the presence of ·H, $\cdot CH_3$, $\cdot C_3H_7$, and $\cdot C_4H_9$ radicals. Protonation of the radical/TCNQ addition products produces a radical cation which, as in the methane case, either loses ·CN or abstracts a hydrogen atom from its surroundings. Also present are $[TCNQC_4H_9]^+$ and $[TCNQC_3H_7]^+$ ions produced by ion–molecule reactions. At low source pressure, electron-impact and charge-exchange ionization of the $TCNQC_4H_9\cdot$ and $TCNQC_3H_7\cdot$ radical products could also produce $[TCNQC_4H_9]^+$ and $[TCNQC_3H_7]^+$ even-electron ions.

TCNQ also reacts with carbon-centered radicals from a variety of organic compounds such as ketones, amines, esters, and nitriles. For example, the CI(N_2/*n*-hexylamine/TCNQ) negative-ion mass spectrum taken at a source temperature of 185 °C contains major ions corresponding to reaction of ethyl and propyl radicals with TCNQ in about equal abundance (100% peaks). Less abundant ions are observed which correspond to reaction of H· (50%), $\cdot CH_3$ (50%), $\cdot C_4H_9$ (5%), and $\cdot C_5H_{11}$ (20%) radicals with TCNQ. It is assumed that primary pentyl radicals produced by the decomposition of *n*-hexylamine molecular ions are the major radical species initially present in the source (ca. 90% of the *n*-hexylamine total ion current is from $[M^{+\cdot} - \cdot C_5H_{11}]^+$ ions). Most of the primary pentyl radicals have sufficient energy to decompose via eq 11, producing propyl radicals, or isomerize to the secondary pentyl radical and decompose via eq 12, producing ethyl radicals. Increasing the source temperature increases and then decreases the $\cdot CH_3$ radical products while the H·/TCNQ products increase in abundance until at 225 °C they dominate the CI(N_2/*n*-hexylamine/TCNQ) mass spectrum. Thus, increasing the thermal energy dramatically increases radical decompositions.



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Because of the general reactivity of TCNQ with carbon-centered radicals, this trapping technique can be used to obtain mass spectra of the radicals produced from compounds eluting from a GC column into the CI source. In the negative ion mode, with ca. 0.3 torr of N_2 and a small amount of TCNQ continuously evaporated into the source, the radicals formed from compounds that are normally transparent to electron attachment can readily be studied. For example, Figure 2 shows the total negative-ion-current chromatogram (from which the background TCNQ ion current has been subtracted) for a mixture of 2-octanone, 1-octanol, 2,5-dimethylphenol, 2,4-dimethylaniline, naphthalene, *n*-dodecane, and *n*-tridecane. Each compound gave a unique TCNQ–radical negative-ion spectrum in which ions corresponding to $[TCNQ(M - 1)]^-$ and/or $[TCNQ(M - 1) - CN]^{-\cdot}$ were observed. Interestingly, naphthalene, 2,4-dimethylaniline, and 2,5-dimethylphenol produced major peaks corresponding to the addition of methyl radicals to TCNQ. For 2,5-dimethylphenol and 2,4-dimethylaniline this corresponds with the loss of CH_3 from the molecular ions to form the largest fragment ions in the EI spectra. However, methyl loss comprises an insignificant fragmentation pathway in the electron ionization of naphthalene.

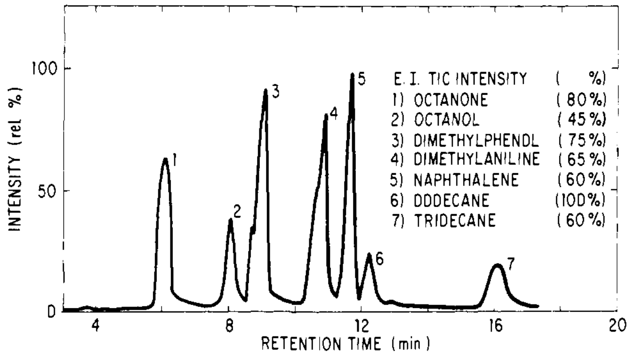

Figure 2. Total CI(N_2, TCNQ) negative-ion-current chromatogram (TCNQ background substracted) for a mixture of compounds injected into a gas chromatograph interfaced to a mass spectrometer. The total ion current (TIC) relative intensities for electron ionization of the same mixture are indicated for comparison.

Reasonably intense TCNQ–radical spectra were obtained with ca. 50 ng/GC component. This represents rather low sensitivity in GC/MS terms, but interestingly the molecular weight of 1-octanol could be deduced from the TCNQ–radical spectrum whereas the molecular ion was not present in the electron-impact spectrum (Table III).

H/D Scrambling. In some cases H/D scrambling can be studied by using the radical-trapping technique. For example, toluene-d_3 upon electron impact or charge exchange loses hydrogen (or deuterium) atoms to produce even-electron $[C_7(H,D)_7]^+$ ions. Hydrogen/deuterium-atom addition to TCNQ was in the expected ratio (62/38) for complete randomization of the hydrogen and deuterium in the toluene-d_3 molecular ions before fragmentation. If complete scrambling is occurring in the toluene-d_3 molecular ions, then no H/D isotope effect is observed in the H/D loss (assuming no inverse effect in the TCNQ/H/D trapping reaction). Addition of $\cdot C_7(H,D)_7$ radicals to TCNQ showed that two and three deuteriums were incorporated into these radicals, but not in the ratio expected for complete scrambling in the molecular ions. The results suggest that some of the $\cdot C_7(H,D)_7$ radicals were produced by deuterium atom loss from the unscrambled toluene-d_3; this is explained by assuming two mechanisms for the formation of $\cdot C_7(H,D)_7$ radicals. The first involves ionization of toluene-d_3 followed by H/D scrambling in the molecular ions and fragmentation to form hydrogen and deuterium atoms and $[C_7(H,D)_7]^+$ ions. These $C_7(H,D)_7^+$ ions, which contain two or three

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[14] J. L. Franklin, J. D. Dillard, H. M. Rosenstock, Y. T. Herron, K. Draxl, and F. M. Fields, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **26** (1969).

Table III. CI(N_2/TCNQ) Negative-Ion Mass Spectrum of 1-Octanol (Molecular Weight = 130)

m/z	% rel int[a]	ion assignment	m/z	% rel int[a]	ion assignment
307	2	$[TCNQ(M-1)-CN]^{-\cdot}$	230	3	$[TCNQCN]^-$
277	4	$[TCNQC_7H_{15}-CN]^{-\cdot}$	221	12	$[TCNQC_3H_7-CN]^{-\cdot}$
263	1	$[TCNQC_6H_{13}-CN]^{-\cdot}$	219	25	$[TCNQCH_3]^-$
261	2	$[TCNQC_4H_9]^-$	207	14	$[TCNQC_2H_5-CN]^{-\cdot}$
259	1	$[TCNQC_4H_7]^-$	205	35	$[TCNQH]^-$
249	3	$[TCNQC_5H_{11}-CN]^{-\cdot}$	204	5	$[TCNQ]^-$
247	7	$[TCNQC_3H_7]^-$	193	10	$[TCNQCH_3-CN]^{-\cdot}$
245	2	$[TCNQC_3H_5]^-$	192	7	$[TCNQCH_3-HCN]^-$?
235	5	$[TCNQC_4H_9-CN]^{-\cdot}$	179	100	$[TCNQH-CN]^{-\cdot}$
233	1	$[TCNQC_2H_5]^-$	154	8	$[TCNQH_2-2CN]^{-\cdot}$

[a] Minimum intensity 1%, corrected for ^{13}C isotopes.

Table IV. Positive-Ion Low-Voltage Townsend-Discharge CI(CH_4) Spectrum of TCNQ

m/z	% rel int[a]	ion assignment	m/z	% rel int[a]	ion assignment
249	8	?	180	4	$[TCNQH-CN]H^+$
221	37	$[TCNQHCH_3]H^+$	169	5	$[TCNQHCH_3-2CN]H^+$
207	5	$[TCNQH_2]H^+$	57	50	$C_4H_9^+$
205	23	$[TCNQ]H^+$	41	300	$C_3H_5^+$
196	8	?	29	1000	$C_2H_5^+$
194	50	$[TCNQCH_3-CN]H^+$	19	300	H_3O^+
182	7	$[TCNQHC_2H_5-2CN]^{+\cdot}$?	17	500	CH_5^+

[a] Minimum peak intensity 0.3% of m/z 29+ intensity; corrected for ^{13}C isotopes.

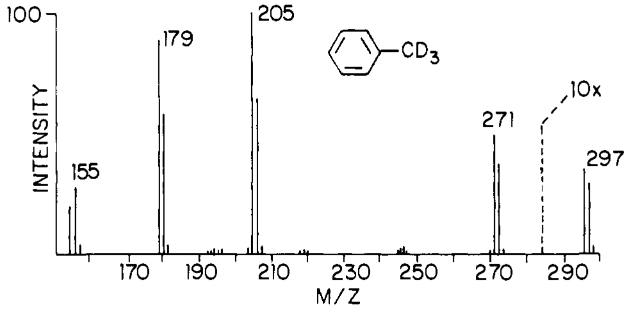


Figure 3. CI(N_2/TCNQ) spectrum of toluene-d_3 above m/z 150.

deuterium atoms, capture electrons to become radicals and are trapped by TCNQ. Additional $\cdot C_7H_5D_2$ radicals are also produced by deuterium abstraction from toluene-d_3 (eq 13). Thus, if H/D

$$[TCNQRH]^{+\cdot} + PhCD_3 \rightarrow [TCNQRHD]^+ + PhCD_2\cdot \quad (13)$$

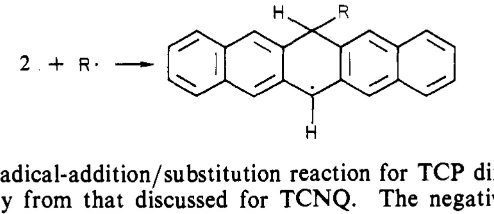
abstraction occurs predominantly on the methyl group, then the concentration of $\cdot C_7H_5D_2$ radicals in which deuterium scrambling has not occurred should be enhanced (Figure 3). The difference in the observed ratio of $271^-/272^-$ and $297^-/298^-$ relative to the expected ratio (38/62) yields a contribution of 20–25% resulting from deuterium abstraction from the toluene-d_3 CD_3 group.

Identification of Radicals Produced in an Electrical Discharge. Radicals produced by using ionization methods other than primary electron bombardment can also be trapped and analyzed mass spectrometrically. For example, the population of radicals produced and trapped by TCNQ in a Townsend discharge,[9] using methane as the discharge and CI reagent gas, was significantly different than that when electron bombardment with 100 eV electrons was used for ionization and radical production (Table IV). The major difference was that methyl radical addition products dominated the spectrum from the low-current Townsend discharge. Hydrogen-atom and ethyl-radical addition products were minor. A significant but unidentified positive ion was observed at m/z 249. Under higher current discharge conditions, hydrogen-atom addition increased slightly.

The methane-reagent-ion currents produced by the filament and discharge modes of operation were very similar. Assuming similar mechanisms of reagent-ion formation (i.e., eq 1–4), it is not readily apparent why the populations of the various radical species should be different; nor is it apparent how a difference in the internal energy of the radicals produced by the two ionization processes could yield the observed results.

Other Compounds Found To React with Radicals in the CI Source. Only a few compounds were found that react sufficiently fast with radicals that identifiable radical-addition/substitution products were observed in the mass spectra. Of the compounds found to react with the carbon-centered radicals in the CI plasma, TCNQ, tetrafluoro-TCNQ (TCNQ-4F), dihydro-TCNQ (TCNQ-2H), TCNE, and TCP all contain four cyano groups. Pentacene (**2**) and possibly hexakis(methoxycarbonyl)trimethylenecyclopropane (**1**) also appeared to react with radicals in the CI source, but with a considerably lower reaction rate than was observed for the cyano compounds.

The radical-addition/substitution products observed for these compounds show structure-related differences. For example, TCNQ and TCNE have similar structural features and produced similar radical-addition mass spectra, with the exception that for TCNE the radical-addition products were less prominent in the negative-ion CI spectrum compared to the positive-ion spectrum. This is explicable if radical addition to TCNE significantly reduces the electron capture cross-section of this molecule by interrupting a significant part of the resonance stabilization of the negative charge. A similar and more dramatic decrease in radical-addition products occurred for **2** in the negative-ion mode. Carbon-centered radical addition to **2** interrupts the five-ring conjugation (eq 14) and apparently reduces the ability of the product to capture or stabilize a negative charge.



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The radical-addition/substitution reaction for TCP differed markedly from that discussed for TCNQ. The negative-ion methane and isobutane spectra of TCP show major ions from alkyl-related substitution for CN, but only very weak ions which may be interpreted as radical addition followed by electron capture. The positive-ion TCP isobutane (Table V) and methane CI spectra had intense peaks which are probably ion addition to TCP, but the major ions observed correspond to ionization of the products produced by radical substitution for CN. Ionization is predominantly by alkyl-ion addition rather than protonation as confirmed by accurate mass measurement. Addition of CH_3^+ to TCP and

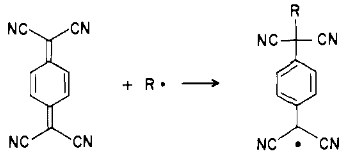
Table V. Positive-Ion CI(isobutane) Mass Spectrum of TCP at Low TCP Partial Pressure and Low- and High-Electron Emission

	% 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.



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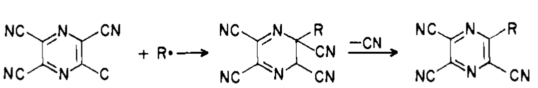

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Conclusion

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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Received November 4, 1980

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

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