unimolecular decomposition becomes competitive with further absorption. Collisions with bath gas molecules act primarily to decrease the population of the partially activated reactants, and hence the yield, without appreciably altering the ultimate energy distribution of decomposing molecules. It is this energy distribution which should principally define the partitioning ratio. From the pressure dependence of the cyclopentadiene to cyclopentene ratio, assuming strong collisions,[12] we calculate a total average energy of ~110 kcal/mol for cyclopentene, corresponding to an average of 82 kcal/mol, or ~11 photons in excess of that required to surmount the barrier to cyclopentene, for laser-activated VCP.[13] It appears that the product distributions are mutually consistent with statistical unimolecular rate theory and this total average energy. A more quantitative analysis of the data along these lines using RRKM theory is in progress.

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References and Notes

(1) (a) N. Bloembergen and E. Yablonovitch. *Phys. Today*, **31**, 23–30 (1978); (b) V. S. Letokhov and R. V. Ambartzumian in "Chemical and Biochemical Applications of Lasers", Vol. 3, C. B. Moore, Ed., Academic Press, New York, pp 166–316, 1977; (c) A. M. Ronn, *Sci. Am.*, 240 (5), 114 (1979).
(2) (a) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962); (b) D. G. Retzloff, B. M. Coull, and J. T. Coull, *ibid.*, **74**, 2455 (1970).
(3) (a) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962); (b) P. M. Crane and T. L. Rose, *J. Phys. Chem.*, **79**, 403 (1975).
(4) Laser power was monitored with a Scientech (Model 38-0102) volume-absorbing calorimeter. The laser pulse consisted of an initial spike (~100-ns fwhm) with a lower intensity tail out to 700 ns (Laser Precision kT-1510 pyroelectric detector). The fraction of laser light absorbed was too low to measure (*i.e.*, <5%) and therefore no attempt was made to measure energy absorbed per pulse.
(5) W. Kirmse, B. G. von Bülow, and H. Schepp, *Justus Liebigs Ann. Chem.*, **691**, 41 (1966).
(6) D. W. Vanas and W. D. Walters, *J. Am. Chem. Soc.*, **70**, 4053 (1948).
(7) (a) W. C. Danen, W. D. Munslow, and D. W. Setser, *J. Am. Chem. Soc.*, **99**, 6961 (1977); (b) D. Gutman, W. Braun, and W. Tsang, *J. Chem. Phys.*, **67**, 4291 (1977).
(8) Number of pulses was 250 at 5 ± 1 J/cm^2. Product composition (ethylene and acetic acid from ethyl acetate) was determined by gas chromatography.
(9) A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954).
(10) The *cis*-1,3-pentadiene yield has not been measured in these experiments.
(11) W. Tsang, J. A. Walker, W. Braun, and J. T. Herron, *Chem. Phys. Lett.*, **59**, 487 (1978).
(12) $\omega = 1.3 \times 10^7$ Torr^{-1} s^{-1} based on collision diameters of 5.2 and 5.8 Å for vinylcyclopropane and pentane, respectively.
(13) Using quantum RRK theory one predicts that a decrease of an order of magnitude in the rate of decomposition due to a decrease in the energy of activated VCP from 82 to 70 kcal/mol should lead to a change in the product ratio (k_4:($k_1 + k_2$)) of approximately a factor of 3.
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William E. Farneth,* Marcus W. Thomsen, Mark A. Berg[14]
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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Fast Radical Reactions in a Mass Spectrometer Ion Source: Radical Addition to 7,7,8,8-Tetracyanoquinodimethane[1]

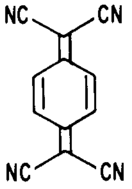
Sir:

7,7,8,8-Tetracyanoquinodimethane[2] (TCNQ, **1**) reacts with the hydrocarbon reagent gas plasma in a chemical ionization (CI) source, apparently by an unusually fast radical addition reaction prior to ionization. The predominance of the ionized radical-addition products relative to the TCNQ molecular ion suggests that the radical concentration greatly exceeds the reagent ion and thermal electron concentrations, and that the rate of the radical addition reaction approaches the diffusion controlled rate. These are the first radical addition reactions to be reported under chemical ionization conditions.

Table I. Methane Negative Ion Chemical Ionization Mass Spectra of TCNQ at 0.5- and 0.05-mA Emission Currents

m/z	ion	% total ion current[a] 0.5 mA	0.05 mA
247	$MC_3H_7^-$	0.1	
245	$MC_3H_5^-$	0.1	0.1
233	$MC_2H_5^-$	0.4	0.2
221	$[MC_3H_7 - CN]^{-\cdot}$	0.3	0.1
220		0.5	0.2
219	MCH_3^-	1.7	1.0
218		0.4	0.2
207	$[MC_2H_5 - CN]^{-\cdot}$	3.4	4.7
205	MH^-	6.5	7.0
204	$M^{-\cdot}$	4.0	25.2
193	$[MCH_3 - CN]^{-\cdot}$	10.0	7.8
182	$[MHC_2H_5 - 2CN]^{-\cdot}$	0.2	0.1
180		1.2	2.8
179	$[MH - CN]^{-\cdot}$	46.0	33.6
168	$[MHCH_3 - 2CN]^{-\cdot}$	1.7	1.1
154	$[MH_2 - 2CN]^{-\cdot}$	7.0	3.8
141	$[MH - C(CN)_2]^{-\cdot}$	0.3	0.1
79	$(CN)_2CCH_3^-$	0.1	
65	$(CN)_2CH^-$	0.2	
26	CN^-	3.6	2.8

[a] Corrected for ^{13}C isotopes. Minimum abundance reported, 0.1%. Source temperature 180 °C, source pressure ~0.6 Torr. M = TCNQ.



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The negative ion electron attachment spectrum of TCNQ contains ions at *m/z* 204 ($M^{-\cdot}$, 94%) and 177 ($[M - HCN]^-$, 4%) when nitrogen gas is used as the medium for enhancing the thermal electron concentration. Substituting methane for nitrogen gives the much more complex spectra shown in Table I.

The major ions are from the addition of H, CH_3, and C_2H_5 to TCNQ and the same additions with loss of one or more cyanide groups, as confirmed by accurate mass measurement. Substituting methane-d_4 for methane establishes that these species are generated from the methane plasma. The observed ion products cannot be the result of the ion-molecule reactions, since H^-, CH_3^-, and $C_2H_5^-$ ions are not present in the methane plasma.

A similar set of ions is observed in the CI (methane) positive ion spectrum (Table II). A mechanism postulating a common radical addition reaction for the positive and negative ion results is proposed in Scheme I. The positive ion results are especially interesting in that the radical cation, produced by radical addition to TCNQ and subsequent protonation, is sufficiently reactive to abstract a hydrogen atom from methane. Ions are also observed in the positive and negative ion spectra which correspond to reaction of two radicals with a single TCNQ molecule. These multiple-radical reaction products increase in abundance relative to the single-radical addition products at low TCNQ concentration and as the conditions in the ion source are varied to favor radical production.

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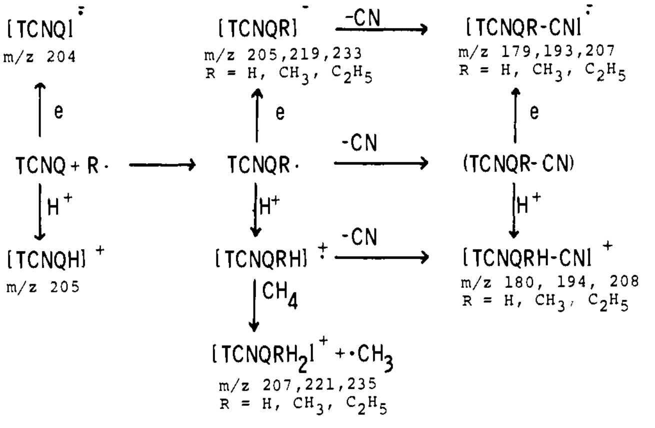
Table II. Methane Chemical Ionization Mass Spectrum of TCNQ

m/z	ions	% TIC[a]	*m/z*	ions	% TIC[a]
275	$[M + 71]^+$	0.3	208	$[MHC_2H_5 - CN]^+$	1.7
263	$MH_2C_4H_9^+$	0.5	207	MH_3^+	30.0
261	$MC_4H_9^+$	0.5	206	MH_2^+	1.5
249	$MH_2C_3H_7^+$	1.5	205	MH^+	3.8
247	$MH_2C_3H_5^+$	2.5	196		0.7
235	$MH_2C_2H_5^+$	5.8	194	$[MHCH_3 - CN]^+$	5.8
234	$MHC_2H_5^+$	0.5	183	$[MH_2C_2H_5 - 2CN]^+$	0.5
233	$MC_2H_5^+$	0.6	182		5.3
222	$[MHC_3H_7 - CN]^+$	0.9	180	$[MH_2 - CN]^+$	8.3
221	$MH_2CH_3^+$	3.8	169	$[MH_2CH_3 - 2CN]^+$	1.2
220	$[MHC_3H_5 - CN]^+$	0.8	157	$[MH_2CH_3 - C(CN)_2]^+$	1.2
210		1.2	155	$[MH_3 - 2CN]^+$	2.7

[a] Percent total ion current corrected for ^{13}C isotopes. Minimum abundance reported, 0.3%. Emission current 0.2 mA, source temperature 160 °C, source pressure ~0.6 Torr. M = TCNQ.

Scheme I



Support for a radical mechanism comes from an extension of calculations reported by Siegel for determining ion concentrations in a chemical ionization ion source.[3] The basic premise is that ions, thermal electrons, and radicals are produced in the reagent gas plasma by processes such as those shown in eq 1–4,[4] but the major loss mechanisms differ for

$$CH_4 + e^- \longrightarrow CH_4^{+\cdot} + 2e^- \qquad (1)$$

$$CH_4^{+\cdot} \longrightarrow CH_3^+ + \underline{H} \qquad (2)$$

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + \underline{\cdot CH_3} \qquad (3)$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (4)$$

radicals and ions. The loss processes for all reactive species include flow from the source and diffusion to the walls. Additionally, ions, electrons, and radicals are lost through ion–electron and radical–radical recombinations with the dominant loss mechanisms for the ions and electrons being ion–electron recombination and, to a lesser extent, diffusion to the walls; both of these processes produce radicals. Thus, if the primary electron current is increased, more positive ions and thermal electrons are produced, but this gain is mostly offset by the radical-producing mechanisms. On the other hand, radicals are expected to be less reactive with the wall surface than ions, and radical–radical recombination is considerably slower than ion–electron recombination (~10^{-11} vs. 10^{-7} cm^3/(molecule s)),[3,5] so that increasing the electron flux increases the radical population without a compensating loss mechanism. Therefore, increasing the primary electron current is an effective way of increasing the radical vs. the ion and thermal electron concentrations. As shown in Table I, the intensities of the ionized radical products increase relative to the molecular anion of TCNQ when the emission current, and thereby the electron flux in the ion source, is increased. This evidence provides a strong argument for the proposed radical reaction mechanism.

Alkyl radicals produced by hydrocarbon gases other than methane can also be trapped by TCNQ. The presence and sometimes the structures of these radicals can now be determined by mass spectrometry. For example, **a** series of $[TCNQC_4H_9 - CN]^{-\cdot}$ ions produced by the reaction of TCNQ with $\cdot C_4H_9$ radicals from isobutane, 3,4-dimethylhexane, and *n*-octane were studied on a reverse geometry double-focusing mass spectrometer using mass-analyzed collisional activation (CA) mass spectrometry.[6,7] The major loss process observed in the CA spectra is cleavage of the alkyl portion of the $(TCNQR - CN)^{-\cdot}$ ion at the bond α to the original radical site. Thus, the $[TCNQC_4H_9 - CN]^{-\cdot}$ ions produced in the CI (N_2-*n*-octane-TCNQ) plasma lose predominately $\cdot C_3H_7$ upon collision with a neutral gas in the field-free region between the magnetic and electric sectors of the mass spectrometer, indicating a primary structure for the butyl radical produced by reaction 5. Similarly, the $[TCNQC_4H_9 - CN]^{-\cdot}$ ions from the CI (N_2-3,4-dimethylhexane-TCNQ) plasma lose $\cdot CH_3$ and $\cdot C_2H_5$, indicating a secondary butyl structure; the same ions produced from the CI (isobutane-TCNQ) plasma lose $\cdot CH_3$ suggesting a tertiary structure for the butyl radicals trapped by TCNQ in the isobutane plasma.

$$[n\text{-}C_8H_{18}]^{+\cdot} \rightarrow C_4H_9^+ + \cdot C_4H_9 \qquad (5)$$

Other compounds found to react in a similar way with alkyl radicals, but to a lesser extent than TCNQ, are tetracyanoethylene, tetracyanopyrazine, and pentacene. Radical addition reactions are not observed with tetracene, anthracene, perylene, *p*-quinone, or 1,3-butadiene, presumably because the rate of radical addition to these compounds is too slow to be observed under the conditions employed in the CI source.

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References and Notes

(1) Presented in part at the Second Conference on Negative Ion Chemical Ionization Mass Spectrometry, University of North Carolina, Chapel Hill, N.C., March 22–23, 1979.
(2) (a) D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **82**, 6408 (1960); (b) D. S. Acker and W. R. Hertler, *ibid.*, **84**, 3370 (1962).
(3) M. W. Siegel in "Mass Spectrometry", "Practical Spectroscopy Series", Vol. 3, Part B, C. Merritt, Jr., and C. N. McEwen, Eds., Marcel Dekker, New York, Chapter 4, in press.
(4) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966); F. H. Field and M. S. B. Munson, *ibid.*, **87**, 3289 (1965).
(5) J. Alistair Kerr in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 1.

(6) F. W. McLafferty, P. F. Bente, III, R. Kornfeld, S.-C. Tsai, and I. Howe, *J. Am. Chem. Soc.*, **95**, 2120 (1973).
(7) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.

Charles N. McEwen,* Martin A. Rudat
E. I. du Pont de Nemours & Company
Central Research & Development Department
Experimental Station, Wilmington, Delaware 19898

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Dioxygen Complexes of Rhodium Porphyrins

Sir:

A previous communication reported on the preparation of a paramagnetic ($S = {}^1\!/_2$) complex formulated as rhodium(II) tetraphenylporphyrin (Rh^{II}TPP).[1] The report that this apparently low spin (d^7) rhodium(II) complex failed to form a dioxygen complex seemed anomalous in view of the fact that dioxygen complex formation is a general feature of low spin d^7 cobalt(II) complexes such as Co^{II}TPP.[2-5] Furthermore, the limited observations available on authentic Rh(II) species such as $Rh(NH_3)_4{}^{2+}$ indicates that dioxygen complex formation is an important feature of Rh(II) chemistry.[6] We report herein on the reaction of $(RhOEP)_2$ (OEP = octaethylporphyrin) with molecular oxygen to form RhOEP(O_2) and on a reexamination of the complex previously formulated as Rh^{II}TPP.

$(RhOEP)_2$ has recently been prepared from the hydrido complex RhOEP(H).[7] We have modified this procedure by recognizing that RhOEP(H) can be easily photolyzed in toluene solution to quantitatively produce $(RhOEP)_2$ and H_2. $(RhOEP)_2$ reacts rapidly with NO to form RhOEP(NO) (ν_{NO} 1630 cm^{-1}) in analogy to cobalt(II) porphyrins (ν_{NO}-(CoTPP(NO)) 1690 cm^{-1}).[2,8] When dry oxygen is allowed to slowly diffuse into a cold toluene solution (−80 °C) of $(RhOEP)_2$, electronic spectral changes occur (Figure 1) accompanied by the appearance of an EPR spectrum ($\langle g \rangle = 2.032$). Freezing this toluene solution (−160 °C) results in an EPR spectrum with three g values ($g_1 = 2.100$, $g_2 = 2.010$, $g_3 = 1.988$) characteristic of an end-on coordinated dioxygen species similar to HO_2 and CoTPP(O_2)[2,3] (Figure 2). The dioxygen complex is formulated as RhOEP(O_2) and described as a Rh(III) complex. RhOEP(O_2) forms 1:1 complexes with donor molecules such as trialkylphosphines and phosphites as evidenced by the ^{31}P hyperfine splitting in the EPR (Figure 2). These EPR observations on RhOEP(O_2) species closely parallel results for CoTPP(O_2) complexes[2,9] (Table I, Figure 2).

Table I. EPR Parameters for Dioxygen Complexes of Rhodium(II) and Cobalt(II) Porphyrins[a]

complex	g_1	g_2	g_3	$\langle g \rangle$
RhOEP(O_2)	2.100	2.010	1.988	2.030
RhTPP(O_2)	2.084	2.025	1.993	2.033
CoTPP(O_2)(pyridine)[6b,c]	2.072	2.003	2.003	2.026
RhOEP(O_2)-(piperidine)	2.094	2.010	1.996	2.031
RhOEP[$(BuO)_3P$]-(O_2)	2.084 (22)[c]	2.004 (22)[c]	2.000 (24)[d]	2.032 (23.7)[d]
CoTPP[$(BuO)_3P$]-(O_2)[e]				2.016 (31.4)[d]

[a] g values are ±0.001. [b] Reference 3. [c] Reference 6. [d] Values in parentheses are the ^{31}P hyperfine coupling constants in gauss. [e] Reference 9.

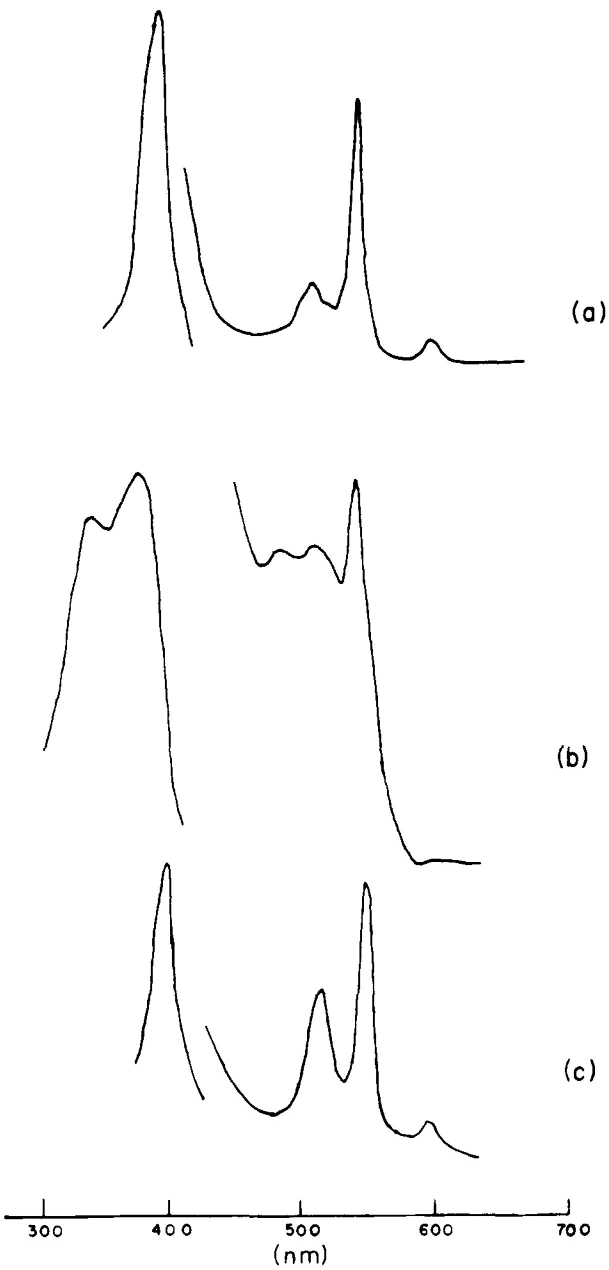

Figure 1. Electronic spectra in toluene solution: (a) RhOEP(H), (b) $(RhOEP)_2$, (c) RhOEP(O_2).

When toluene is pumped off at low temperatures (−20 °C) from a solution of RhOEP(O_2), the resulting solid is predominantly RhOEP(O_2). IR spectra of this solid shows a new band centered at 1075 cm^{-1} which, although partially obscured by ligand bands, is tentatively assigned to the ν_{O-O} stretching frequency in RhOEP(O_2). The ν_{O-O} stretching frequency in an analogous cobalt(II)-dioxygen complex appears at 1137 cm^{-1}.[10]

When solutions of RhOEP(O_2) are warmed to 20 °C the EPR signal diminishes in intensity and eventually disappears. The presence of donor molecules accelerates this process. The resulting diamagnetic complex has electronic and ^{1}H NMR spectra characteristic of a Rh^{III}OEP species and is tentatively formulated as the μ-peroxo complex $(RhOEP)_2O_2$. Bridging peroxo complexes of cobalt(III) and rhodium(III) have been characterized previously.[11,12] The ν_{O-O} band was not observed in the IR of this μ-peroxo complex which is consistent with a centrosymmetric bridging peroxide.[13]

The EPR g values for RhOEP(O_2) are virtually identical

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