those needed for homogeneous catalytic CO hydrogenation.[2] This conversion presumably requires operation of two steps which might not have been anticipated to proceed this easily: migratory insertion of CO into an oxy-substituted methyl-metal bond, and hydrogenation of an aldehyde intermediate to alcohol. A second reductive elimination pathway yielding the one-carbon product has also been demonstrated. Mechanistic details of hydrogen activation and transfer in these reactions are not yet clear. Radical species have been shown to be involved in hydrogen activation by $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$[31] and may be important in this system also. The possibility that a bimolecular process[32] is involved in product-forming steps is being investigated. Nevertheless, the major features of Scheme I appear to provide a mechanistic model for more complex catalytic systems, especially Fischer-Tropsch-type catalysts for production of alcohols from synthesis gas[2] and hydroformylation catalysts which convert formaldehyde to glycoaldehyde and glycol.[26,33] Studies dealing with other mechanistic aspects of these reactions are also in progress.

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(17) Calcd for $C_{11}H_{11}O_7Mn$: C, 42.58; H, 3.55. Found: C, 42.16; H, 3.44. NMR ($CDCl_3$): δ 1.15 (s, 9 H), 4.70 ppm (s, 2 H). IR (*n*-hexane): 2119 (w), 2052 (w), 2018 (vs), 2001 (s), 1726 cm^{-1} (m).

(18) The reaction has also been carried out successfully in tetrahydrofuran.

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(22) Calcd for $C_{12}H_{11}O_8Mn$: C, 42.60; H, 3.25. Found: C, 42.05; H, 3.25. NMR ($CDCl_3$): δ 1.20 (s, 9 H), 4.70 ppm (s, 2 H). IR (*n*-hexane): 2118 (w), 2059 (w), 2019 (vs), 2007 (s), 1751 (m), 1674 cm^{-1} (m).

(23) The electron-withdrawing effect of a hydroxy or acyloxy substituent is expected to decrease substantially the ability of an alkyl group to undergo CO insertion, based on observations[24] and calculations[25] on migration rate as a function of alkyl group electronegativity. Facile insertion of CO into a metal–α-silyloxybenzyl bond has been reported,[4] but this ligand is electronically and sterically very different from hydroxymethyl. Insertion of CO into a cobalt–hydroxymethyl bond under mild conditions has been postulated as a step in the stoichiometric hydroformylation of formaldehyde.[26]

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(28) Although these results might appear to be inconsistent with those of King and co-workers,[29] who report the observation under somewhat more severe conditions of unreduced acetaldehyde from $(CO)_5MnC(O)CH_3$ and H_2 alone, it should be noted that the acetyl complex may release CO upon reaction with H_2. Small amounts of CO may also have remained in solution from formation in situ of the acetyl complex from $(CO)_5MnCH_3$ and CO.

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Reactions of Vinylcyclopropane Induced by Multiphoton Absorption of Infrared Radiation

Sir:

Over the past few years, the activation of chemical reactions via multiphoton absorption of infrared radiation has been shown to be a fairly general phenomenon in polyatomic molecules.[1] As part of an investigation of applications of this technique to problems in organic reaction dynamics, we report here our work on the CO_2 laser-induced unimolecular reactions of vinylcyclopropane (VCP). From changes in the product distribution as a function of photolysis conditions, we make inferences about the influence of bath gas pressure and structure and laser frequency on the energy distribution in laser-activated reactants. There have been several previous studies of the unimolecular reactions of VCP initiated both thermally[2] and via chemical activation.[3] The product distributions from these studies make an interesting comparison with our work.

Our experiments have been carried out using a grating-tuned Lumonics TEA 101 CO_2 laser tuned to the P(24) line of the 001–100 transition (940.6 cm^{-1}). The beam was focused with a 15-in. ZnSe lens, and the cell was centered 5 cm beyond the focal point. In all cases reported, the laser fluence at the front window of the cell was 5.0 ± 1 J/cm^2.[4] Typically, 250 pulses were delivered to a given sample prior to chemical analysis by gas chromatography or gas chromatography-mass spectrometry (GC-MS), in both cases by direct gas injection. The cell was a Pyrex cylinder 5 cm × 2.5 cm (i.d.) fitted with KCl windows. It was filled to known pressures of materials ranging from 0.02–10 Torr on a vacuum line equipped with an MKS Baratron capacitance manometer. Vinylcyclopropane is prepared by the procedure of Kirmse et al.,[5] and purified by preparative GC prior to use.

When 0.2 Torr of vinylcyclopropane is irradiated under these conditions, the product distribution shown in Table I is obtained. Mass balance is good. The sum of the product yields equals 100 ± 2% of the VCP disappearance. It is interesting to compare this distribution with those obtained in the thermal and chemical activation experiments (Table I). The high cyclopentadiene yields distinguish the laser-activated results from thermal distributions at 362 °C. Although at higher temperatures cyclopentene (**4**) will decompose to cyclopentadiene (**5**) and H_2,[6] the laser results cannot be rationalized by simple

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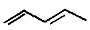
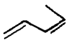
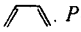
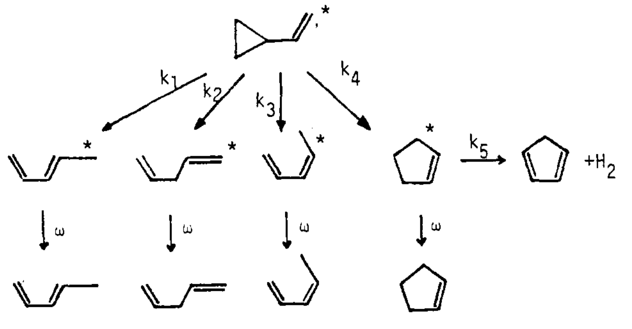
Table I. Product Distributions from Vinylcyclopropane Decomposition

activation method	product distribution					ref
	 **1**	 **2**	 **3**	 **4**	 **5**	
(1) CO_2 laser 5 J/cm^2, 940 cm^{-1} (0.2 Torr)	8	4	4	32	52	this work[a]
(2) $:CH_2$ + , P_{total} = 200 Torr	21	28[b]	23[b]	26	2	3b
(3) $:CH_2$ + , P_{total} = ~10 Torr	27	27[b]	21[b]	12	12	3b
(4) thermal, 362.5 °C, ~10 Torr	1.6	1.2	1.2	96		2a

[a] GC peak areas uncorrected for detector response. [b] Uncorrected for small amount arising directly from C–H insertion by $:CH_2$.

Scheme I



heating. If cyclopentadiene resulted from indiscriminate thermal activation at a temperature high enough to induce **4** → **5**, the ratio of [**5**]:[**4**] should increase with the number of pulses. This is not observed. In fact, within experimental error, the entire product distribution is independent of the number of pulses over the first 25% of reaction (~250 pulses). Collisional activation of cyclopentene, therefore, appears not to be a factor in defining the overall product yield.

Collisional activation in general can be ruled out in another way using a mixture of two potentially reactive gases, one of which preferentially absorbs radiation at the incident laser frequency.[7] We have used mixtures of ethyl acetate and VCP, both of which absorb in the CO_2 laser region. Irradiation of a 1:1 mixture at a total pressure of 0.2 Torr[8] leads to essentially selective decomposition of the absorbing species. When the laser is resonant with EtOAc absorption (1047 cm^{-1}) a selectivity factor (% EtOAc/% VCP decomposed) of (35 ± 3):1 is observed. At 940 cm^{-1} where VCP absorbs, this ratio is 1:(30 ± 3). These results are clearly incompatible with intermolecular energy randomization. Using the known Arrhenius parameters,[3b,9] thermal reactivity ratios would be expected to vary from ~2 to 0.1 over a temperature range of 300-5000 K. A thermal mechanism, therefore, clearly cannot account for the crossover from highly selective VCP decomposition to ethyl acetate decomposition with irradiation frequency and, in fact, cannot rationalize the magnitude of the selectivity factor in either case.

As in chemical activation experiments, cyclopentadiene can arise via loss of H_2 from cyclopentene formed as one of four products in the initial partitioning of activated VCP. This further reaction of "hot cyclopentene" (k_5) occurs on a time scale competitive with collisional deactivation (ω) (Scheme I). When bath gases are added to the photolysis vessel, the total product yield rapidly decreases as shown for added pentane in Figure 1. However, the only substantial change in the product distribution is a sharp decline in the ratio of cyclopentadiene to cyclopentene. The VCP partitioning ratio k_4:(k_1 + k_2), where the sum of cyclopentadiene and cyclopentene yields represents k_4, is virtually unchanged (Figure 2).[10] In chemical activation experiments, pressure increases similarly lead to changes in the relative amounts of cyclopentadiene and cyclopentene, without significantly altering the k_4:(k_1 + k_2) ratio (see Table I). The VCP partitioning ratio k_4:(k_1 + k_2) is larger in our experiments than in chemical activation. This suggests a lower average energy for decomposing VCP activated by multiphoton absorption than for chemical activation (111.1 kcal/mol).[3b]

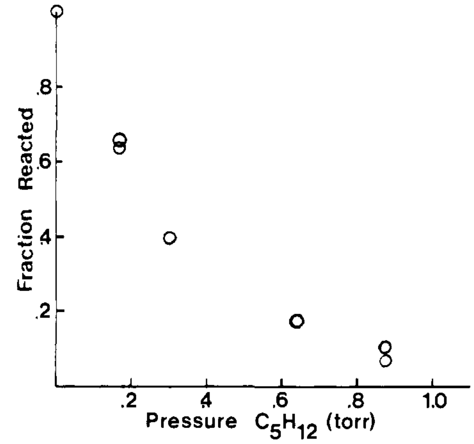


Figure 1. Fraction of vinylcyclopropane decomposed after 250 pulses as a function of pentane pressure. Values are normalized to the yield for no added pentane.

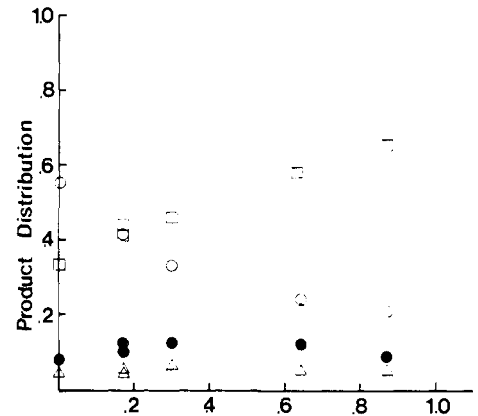


Figure 2. Pressure dependence of the product mixture from vinylcyclopropane photolysis. Yields are given as fraction of total products.

The insensitivity of the product ratio to pressure, even over more than an order of magnitude change in the yield, is consistent with the idea of a two-stage absorption process of the type recently suggested by Braun et al.[11] In this model, there is a bottleneck in the activation sequence at low excitation energies. After reaching the quasi-continuum, subsequent absorptions proceed rapidly to total excitation levels at which 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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(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.

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

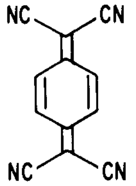
Sir:

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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