From the simulation of the data given in Figure 7, we estimated the rate constants. The lifetimes of the tautomers in EtOH and ACN are 6.5 and 7.2 μs, respectively. These values are similar to those found in nonpolar solvents. The lifetimes of the anions are 60 and 76 μs, respectively.

In addition to the process shown in Figure 8 the anion may be formed from the intermolecularly hydrogen bonded species, but the present result seems to indicate that such a process is not major.

The TSLE spectra of OHAP in deaerated EtOH and ACN at a delay time of 5 μs at room temperature coincide well with the fluorescence spectra of the anions obtained in the alkaline EtOH and ACN solutions as shown in Figure 4. Therefore, the TSLE fluorescence spectra of these systems are also assigned to the anions. However, different from the case of 7HIN, these TSLE spectra were independent of the delay time without showing the fluorescence of the tautomer. A typical example of the decay of the TSLE fluorescence intensity is shown in Figure 7. The log plots of the TSLE fluorescence intensity vs. the delay times give a nearly linear relation at the initial stage of the decay, but at longer delay times the plots seem to deviate from the linearity. The linear portion of the plots gives a lifetime of 50 μs for OHAP in EtOH at room temperature. Temperature dependence of the lifetime gives an activation energy of 3.0 kcal/mol for the decay process of the anion. The lifetime of the OHAP anion in deaerated ACN was estimated to be 32 μs. The fact that the TSLE fluorescence of the tautomer was not observed in OHAP, OHBA, and SAM in polar solvents indicates that the tautomers also do not have metastable states in polar solvents as in nonpolar solvents, although relatively stable anions are formed in the relaxation processes of the excited-state tautomers.

On the basis of these observations, we discuss the process of the anion formation and possible structures of the anions. In the case of 7HIN, the first laser excitation generates the excited-state tautomer which relaxes vertically to the metastable ground-state tautomer. Then the proton is abstracted by the solvents forming the anion. Whether the anion is ion paired or dissociated is not known definitely, but the nearly exponential decay of the anion at the initial stage of the decay may be attributed to the ion paired anion with the dissociated anion contributing to the slower decay at a later time. Though we were not able to detect the ground-state tautomers of OHAP, OHBA, and SAM in polar solvents, the anions are likely to be formed similarly from the ground-state tautomers after they relax from the excited states. The fact that anions formed from the enol tautomers and those formed from the keto forms in the alkaline EtOH have the same absorption spectra means that these anions are identical. The absorption spectra of the anions are blue-shifted from those of the tautomers. The anion structure compatible with those observations may be given by a resonance between structures a and b shown in Figure 8.

IV. Summary and Conclusions

Among 7HIN, OHBA, OHAP, and SAM, only 7HIN shows TSLE fluorescence due to the metastable enol tautomer. The stability of the tautomer is ascribed to a relatively longer O–H···O bond length in 7HIN caused by the five-membered ring formation. Temperature dependence on the lifetime of the tautomer gave an apparent activation energy of 0.93 kcal/mol.

In polar solvents, not only 7HIN but also OHBA, OHAP, and SAM show TSLE fluorescence. In 7HIN the TSLE fluorescences of the tautomer and the anion were detected, but in others only the TSLE fluorescence of the anion was detected. The analysis of the delay time dependence of the TSLE fluorescence reveals that the anion of 7HIN is formed at the expense of the ground-state tautomer.

Acknowledgment. We are grateful to Professor H. Iwamura of the Institute for Molecular Science for the generous gift of 7HIN.

Registry No. 7HIN, 6968-35-0; OHAP, 118-93-4; SAM, 65-45-2.

Chemistry of Acetylene Exposed to Alumina and Alumina-Supported Rhodium Catalysts

D. M. Hanson,*[†] Y. Udagawa, and K. Tohji

Contribution from the Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444, Japan.

Received October 28, 1985

Abstract: Raman spectroscopy and mass analysis of desorption products were used to obtain information about the chemistry of acetylene exposed to alumina, thermally activated alumina, and alumina-supported rhodium catalysts. For the three catalyst systems, the chemistry is similar. High-mass species appear in the mass spectra that are characteristic of polymers containing mixtures of single, double, and triple bonds. For the supported catalyst, the trapping of acetylene trimers correlates with a decrease in the Raman intensity.

The interaction between hydrocarbons and metals and metal oxides is important in many processes of heterogeneous catalysis. We have used Raman spectroscopy and mass analysis of desorption products to obtain information about the chemistry of acetylene exposed to alumina and alumina-supported rhodium catalysts. Our principle interest is to characterize the species that is responsible for the Raman spectrum and to assess whether Raman spectroscopy can serve as a useful probe for chemical species on catalytic surfaces under technologically relevant conditions.

In previous work on these systems, different assignments of similar Raman spectra were made. In one case, the Raman spectrum was assigned to $\sigma_2\pi$-C_2H_2 bonded to supported rhodium with the C–C bond parallel to the surface.[1] In another case, involving acetylene exposed only to alumina, the assignment was to polyacetylene with a mean chain length of about 30 carbons.[2,3]

[†] Permanent address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400.

(1) Parker, W. L.; Siedle, A. R.; Hexter, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 264–266.

(2) Heaviside, J.; Hendra, P. J.; Tsai, P.; Cooney, R. P. *J. Chem. Soc., Faraday Trans. 1* **1978**, 2542–2549.

(3) Tsai, P.; Cooney, R. P.; Heaviside, J.; Hendra, P. J. *Chem. Phys. Lett.* **1978**, *59*, 510–513.

0002-7863/86/1508-3884$01.50/0

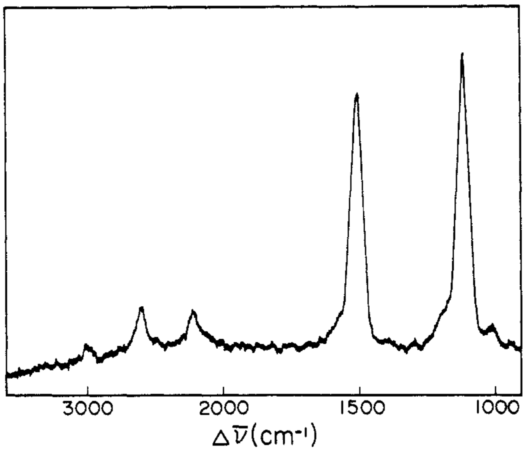


Figure 1. Raman spectrum of alumina-supported rhodium following exposure to acetylene. Note the scale changes at 2000 cm^{-1}.

In contrast, acetylene exposed to a single-crystal Rh(111) surface under ultrahigh-vacuum conditions forms a surface alkylidyne.[4,5]

Experimental Techniques

The Rh/Al_2O_3 catalyst was prepared by mixing powdered γ-alumina with an aqueous solution of either $Rh(NO_3)_3$ or $RhCl_3$, evaporating the solvent by heating, and drying the catalyst at 100 °C overnight. An amount of salt and alumina were mixed to give a final ratio for the Rh/Al_2O_3 catalyst of 10% Rh metal by weight. The salt was reduced to the metal with hydrogen in the Raman cell at a temperature of 150–170 °C. Typically the procedure consisted of degassing the salt-coated alumina until a pressure in the glass vacuum system, which was equipped with an oil diffusion pump and liquid nitrogen traps, of less than 10^{-4} torr was attained with the sample heated to 150–170 °C. Hydrogen gas (200 torr) was introduced at this temperature. After 1 h, the sample cell was evacuated and a second dose of hydrogen was introduced for 1 h. After reduction, the temperature was maintained and the cell was evacuated to a pressure of less than 5×10^{-5} torr. This final degassing step took about 12 h. Acetylene, at pressures ranging from 1 to 400 torr, was admitted to the cell after it had cooled to room temperature. It took a few hours for equilibrium to be established as determined by the increasing intensity of the Raman signal. This equilibration could be hastened by cooling the catalyst with liquid nitrogen. Although the intensity varied, the same Raman bands were obtained independent of the acetylene pressure and whether the catalyst was cooled or not or had previously been exposed to acetylene.

Alumina samples (without rhodium) were prepared by following the same procedure. "Activated" alumina samples[2] were prepared by heating the alumina under vacuum to a temperature of 650 °C, following the exposure to hydrogen at 150–170 °C. After 2 h with the sample at this temperature, the pressure in the vacuum system was 5×10^{-5} torr. The sample then was cooled gradually to 80 K, and acetylene was introduced at a pressure of 375 torr. The sample was allowed to come to room temperature and equilibrate for 1 h. After this "activation" procedure and exposure to acetylene, the white alumina had turned violet. This coloration of alumina after such "activation" has been noted previously.[2]

Raman spectra were obtained with a JEOL Model JRS-400 T spectrometer using a Spectra Physics Model 164 argon ion laser. Typically the laser beam (514.5 nm) was not focused, and slit widths of 1 mm and a laser power of 500 mW were used. The all-glass Raman cell consisted of two flat windows (1 cm × 2 cm), separated by 2 mm, attached to a stopcock and a ground glass or o-ring joint. This arrangement allowed the sample to be prepared under vacuum conditions and then removed to obtain Raman and mass spectra.

The mass spectra, collected up to *m/e* 900, were obtained with a JEOL Model JMS-D300 mass spectrometer equipped with a JMA-2000S data analysis system.

Experimental Results and Discussion

Raman Spectroscopy. The new features appearing in the Raman spectrum of the Rh/Al_2O_3 catalyst following the exposure to acetylene are shown in Figure 1. There are two intense peaks at 1123 ± 2 and 1508 ± 2 cm^{-1} and three corresponding overtone and combination bands. A weak peak at 1010 ± 5 cm^{-1} also is present. This simple spectrum indicates the presence of an ethylene moity. For example, the Raman spectrum of *cis*-1,2-dichloroethylene has two intense bands,[6] one at 1587 cm^{-1} and the other at 1179 cm^{-1}. The unusually strong overtone and combination bands may indicate that the Raman scattering process is resonantly enhanced.[7] Spectra like this one are obtained whether the chloride or the nitrate is used as the starting material. On the other hand, if silica rather than alumina is used as the substrate, the Raman intensity is about 10 times smaller, although the line positions (frequencies) appear to be the same within the experimental uncertainty. The reason for the weaker Raman signal is not clear, but the dependence of the chemical reactivity of supported rhodium on the composition of the support has been documented for other reactions.[8-10] It was not possible to obtain Raman spectra from the alumina samples without rhodium because of the strong fluorescence from these samples.

The Raman spectrum shown in Figure 1 is similar to spectra that have been reported previously for acetylene exposed to Rh/Al_2O_3 and to Al_2O_3 alone. Except for a frequency shift of around 30 cm^{-1}, this spectrum appears to be identical with that reported by Parker et al.,[1] which was assigned to a $\sigma_2\pi$-C_2H_2 adsorbate. That spectrum has intense bands at 1098 and 1476 cm^{-1} for a sample that was prepared under conditions very similar to ours. The only apparent difference is a lower background pressure in the vacuum system, 5×10^{-7} torr. The species producing that spectrum is tightly bound to the surface because the signal intensity and peak positions do not change upon evacuating the cell. In contrast, the Raman signal that we observe drops dramatically upon evacuation at room temperature.

One explanation for these differences is that the surface in our experiment contains adsorbed hydrogen because of the higher vacuum pressure under which the catalyst was prepared. This adsorbed hydrogen may cause the Raman-active species to be less tightly bound to the surface, resulting in a stronger C–C bond and a higher vibrational frequency. The weaker surface bond and the possibility of reacting with the adsorbed hydrogen also may allow the species to desorb near room temperature.

Raman spectra of acetylene adsorbed on γ-alumina "activated" at various temperatures has been reported by Heaviside et al.[2] These spectra also consist of two intense peaks near 1100 and 1500 cm^{-1}. The exact frequencies correlate with the activation temperature. For example, the frequencies we observed with the Rh/Al_2O_3 catalyst correlate with an Al_2O_3 activation temperature of about 750 °C even though our samples were prepared at temperatures no higher than 170 °C. Such spectra and the color of the alumina following exposure to acetylene were attributed to the formation of different polyenes.[2] A chain length of 15 C=C bonds was proposed[3] to explain the color and the vibrational frequencies of 1117 and 1501 cm^{-1}.

Mass Spectroscopy. In view of these two different assignments of very similar spectra, we used mass spectroscopy to determine whether the chemistry of acetylene exposed to alumina, thermally activated alumina, and alumina-supported rhodium catalysts is similar or different, to determine whether polyenes are formed, and to determine which species correlate with the Raman signal. Samples of these three systems were prepared as described above, and four sets of mass spectra for each sample were obtained. One was the mass spectrum of the ambient gas (acetylene plus reaction products) in equilibrium with the catalyst at a pressure of 200 torr. Another was for the ambient gas reduced to a pressure of 1 torr. The third set consisted of spectra, taken at 1-min intervals, of the gas desorbing from the solid under vacuum at room tem-

---

(4) Dubois, L. H.; Castner, D. G.; Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*, 5234–5240.

(5) Koestner, R. J., Van Hove, M. A.; Somorjai, G. A. *Chem. Technol.* **1983**, *13*, 376–384.

(6) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated* U. S. Dept. of Commerce: Washington, D. C., 1972; Vol. I, NSRD-NBS39.

(7) Behringer, J. In *Raman Spectroscopy: Theory and Practice*; Szymanski, H., Ed.; Plenum: New York, 1967; 168–223.

(8) Solymosi, F.; Tombacz, I.; Kocsis, M. *J. Catal.* **1982**, *75*, 78–93.

(9) Iizuka, T.; Tanaka, Y.; Tanaka, K. *J. Catal.* **1982**, *76*, 1–8.

(10) DelAngel, G. A.; Coq. B.; Ferrat, G.; Figueras, F. *Surf. Sci.* **1985**, *156*, 943.

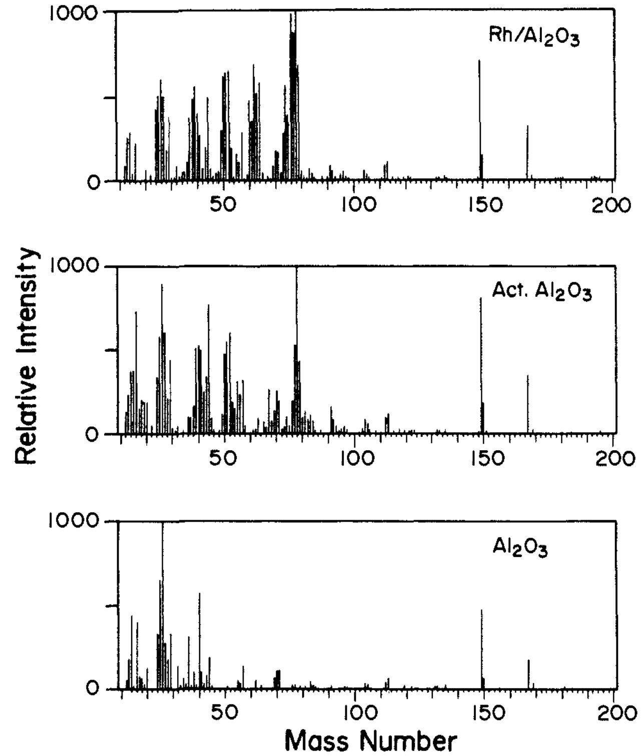


Figure 2. Top: Mass spectrum of the ambient gas, reduced to a pressure of 1 torr, for an alumina-supported rhodium sample. Additional mass peaks at 210 and 279 were observed with relative intensities of 202 and 222, respectively. Middle: Integrated mass spectrum of the thermal desorption from an activated alumina sample. Mass peaks at 210 and 279 had relative intensities of 95 and 146. Bottom: Integrated mass spectrum of the room temperature desorption from an alumina sample. For this situation, the mass peaks at 210 and 279 had relative intensities of 52 and 79.

perature, and the fourth consisted of spectra, taken at 1-min intervals, of the gas desorbing under vacuum while the sample was heated. For purposes of data reduction, only the time integrals of the sequential spectra are reported here.

A spectrum characteristic of each system is shown in Figure 2. The interesting feature is the appearance of high mass fragments that appear in groups characteristic of C_nH_m species. These species apparently result from the "polymerization" of acetylene. The most striking feature is the appearance of masses around 78 with the Rh/Al_2O_3 catalyst. These masses are not found with alumina and only desorb from the activated alumina when it is heated. From the time evolution of the sequential mass spectra, it is clear that several different species contribute to the spectra shown in Figure 2. Positive identification of these species is not possible because of the complexity introduced by the different fragmentation patterns in the mass spectrometer. While some masses that can be associated with polymers consisting purely of single and double or single and triple bond linkages are found in small amounts, e.g., 54 (C_4H_6), 80 (C_6H_8), 106 (C_8H_{10}), and 210 ($C_{16}H_{18}$), or 74 (C_6H_2), 98 (C_8H_2), and 122 ($C_{10}H_2$), the dominant products appear to consist of single, double, and triple bond linkages together.

The mass distribution found for the ambient atmosphere is summarized in Figure 3 and that for the desorbing gases in Figure 4. Where the mass ranges overlap, the species have been assigned arbitrarily to the lower carbon-containing group. The contribution of such species to the data is not significant. The average of the time-integrated spectra obtained at room temperature and that obtained while heating the sample is shown in Figure 4 because these two data sets are similar.

It is clear from these data (Figures 2–4) that similar high-mass species are produced when acetylene is exposed to alumina or alumina-supported rhodium. It also is clear that the order of reactivity in this regard is Rh/Al_2O_3 > activated Al_2O_3 > Al_2O_3. More C_2H_2 is consumed with the Rh/Al_2O_3 catalyst, and the ambient atmosphere is richer in the higher mass products with this catalyst. This trend also is documented in Table I. Table I gives the ratio of high-mass to low-mass species found in the ambient atmosphere at pressures of 200 and 1 torr, obtained by evacuation from the initial pressure of 375 torr. This similarity in reactivity between Al_2O_3 and Rh/Al_2O_3 can be attributed to the Lewis acid properties of both alumina[2] and rhodium. Both can "activate" acetylene in the same way, by lowering the electron density of the C–C bond.

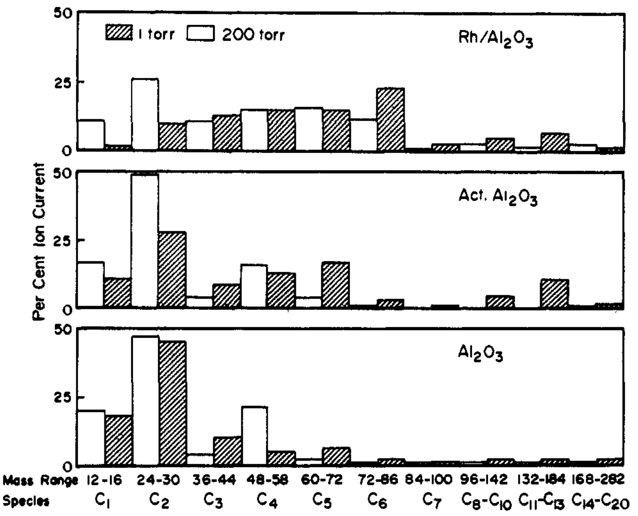


Figure 3. Mass distribution in the mass spectra of the ambient gas in equilibrium with the catalysts at pressures of 200 and 1 torr, obtained by evacuation from the initial pressure of 375 torr.

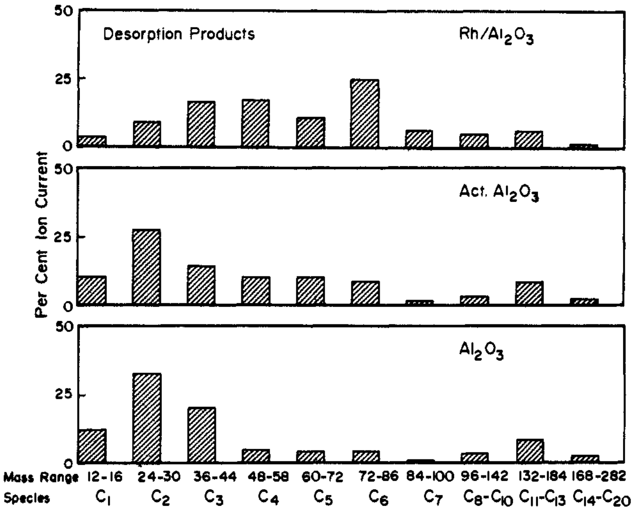


Figure 4. Mass distribution in the mass spectra of the gases desorbing from the catalysts.

Table I. Ratio of High-Mass (>30) to Low-Mass (<30) Species

pressure, torr	Al_2O_3	activated Al_2O_3	Rh/Al_2O_3
200	0.5	0.4	1.7
1	0.5	1.5	6.5

Given that a number of different chemical species appear to be present under these conditions, the question arises as to the species responsible for the Raman spectrum. Is it an "ethylene-like" adsorbate,[1] a C_{30} polyene,[3] or some other possibility? To answer this question we trapped the desorption products accompanying a decrease in the Raman signal. This trapping experiment was done by cooling the sample below 200 K and then slowly raising the temperature with the sample under vacuum. The desorption products were trapped in different liquid nitrogen traps for different temperature ranges. During this period, the intensity of the Raman signal was monitored. The results of the experiment are summarized in Figure 5. The Raman bands at

Table II. Fragmentation Patterns of Acetylene Trimers[a]

	mass peak						
compnd	79	78	77	52	51	50	39
benzene	60	1000	190	160	150	110	100
1,5-hexadien-3-yne	60	1000	260	590	440	320	210
1,3-hexadien-5-yne	60	1000	230	410	300	270	210
2,4-hexadiyne	60	1000	160	350	500	290	120
1,5-hexadiyne	53	890	360	580	480	400	1000

[a] *Eight Peak Index of Mass Spectra*; Mass Spectrometry Data Center, Royal Society of Chemistry, The University, Nottingham, UK, 1983.

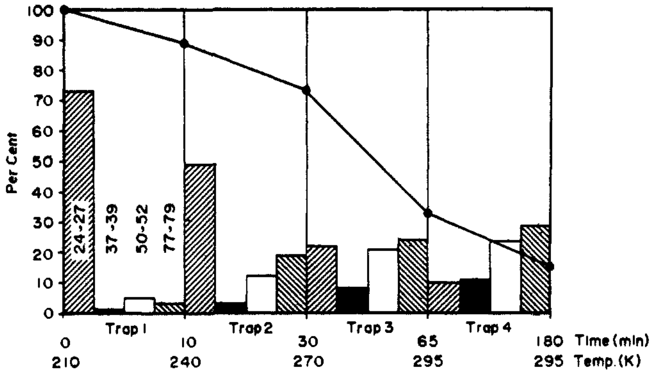


Figure 5. Results of the temperature-programmed desorption experiment. The line graph shows the change in the Raman intensity, and the bar graph shows the accompanying changes in the mass distribution appearing in the mass spectra of the desorption products.

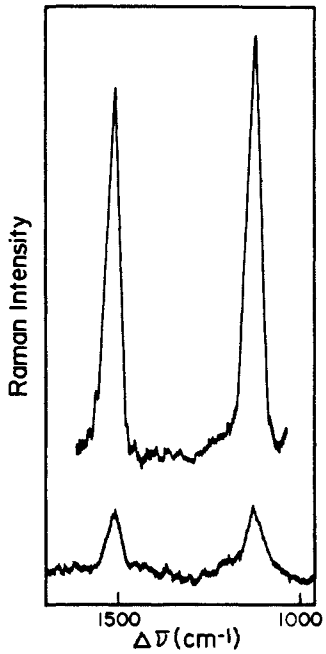


Figure 6. Raman spectra at the beginning and end of the temperature-programmed desorption experiment.

the beginning and end of the experiment are shown in Figure 6, and the mass spectra obtained from traps 1 and 3 are shown in Figure 7.

The desorption products below 240 K were caught in trap 1. The Raman signal began to decrease around 210 K. Trap 2 was used between 240 and 270 K. During this interval the Raman signal decreased from about 90% to 75% of its initial value. The greatest change in the Raman signal came between 270 and 295 K. The desorption products during this interval were caught in trap 3. The Raman signal then continued to decrease gradually and was monitored for another 2 h with the sample at 295 K. During this period trap 4 was used.

As shown in Figure 5, the dramatic decrease in the Raman intensity (Figure 6) correlates with the trapping of species that produce three mass groups, corresponding to C_3, C_4, and C_6, in the mass spectrometer. No higher masses were detected in this experiment. The drop in Raman intensity does not correlate with the trapping of C_2 or high-mass polyene species.

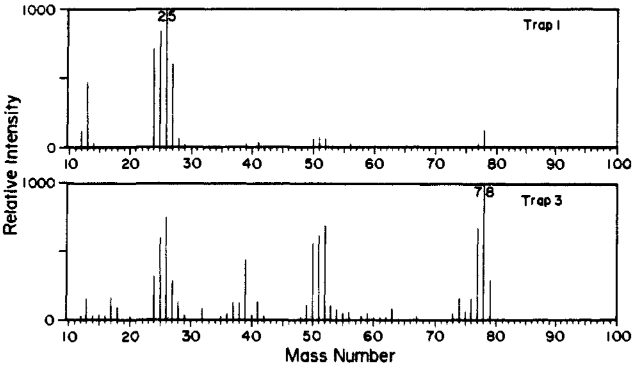


Figure 7. Mass spectra of the desorption products in traps 1 and 3 obtained in the temperature-programmed desorption experiment.

More specifically, Figure 7 shows that the drop in the intensity of the Raman spectrum correlates with the appearance of mass peaks 78, 77, 52, 51, 50, and 39 in the mass spectrum. As shown in Table II, these mass peaks all are characteristic of the fragmentation pattern of acetylene trimers in the mass spectrometer. Except for benzene, these trimers contain one or more triple bonds, which should produce an intense Raman band around[11] 2100–2200 cm^{-1}. Two considerations reconcile the absence of such a band in the Raman spectrum with the mass data. Raman scattering by the vibrational mode involving the triple bond may not be enhanced. The enhancement may only involve the part of the molecule directly coupled to rhodium atoms. It also is possible that the triple bond or the trimer only forms as the species desorbs from the surface.

Figure 6 shows that the Raman intensity has not vanished at the end of this experiment. Some species producing a Raman signal remain on the surface. Two observations support the view that these are the same species that desorbed below 295 K: First, the maxima in the Raman spectra shown in Figure 6 occur at the same positions. Second, these same mass groups continue to desorb as the sample is heated. The fact that the same species desorb over a wide temperature range indicates that a particular species is associated with a range of surface binding energies, and hence with different binding sites on the inhomogeneous surfaces present in this supported catalyst system. Different binding sites also can produce the weak structure (shoulders) in the Raman spectrum.

Conclusions

The objectives of this work were to characterize the species responsible for the Raman spectrum obtained after exposing an alumina-supported rhodium catalyst to acetylene at pressures of 1–400 torr and to assess whether Raman spectroscopy can serve as a useful probe of chemical species on catalytic surfaces under technologically relevant conditions. Specifically, in view of previous work, we were interested in learning whether the chemistry of acetylene exposed to alumina, thermally activated alumina, and alumina-supported rhodium catalysts is similar or different, whether large polyenes are formed from the acetylene, and which chemical species correlate with the Raman signal.

---

[11] Melveger, A. J.; Baughman, R. H. *J. Polymn. Sci., Polym. Phys. Ed.* **1973**, *11*, 603–619.

We found that the chemistry of acetylene exposed to these three catalysts is similar. high-mass C_nH_m species appear in the mass spectra that are characteristic of polymers containing mixtures of single, double, and triple bonds. The formation of large polymers, with only single and double bonds, does not appear to be very significant. The dramatic decrease in the Raman intensity correlates with desorption products producing mass spectra characteristic of acetylene trimers. It therefore appears that a trimer species may be responsible for the Raman spectrum.

This correlation of the Raman signal with a trimer appears to conflict with previous assignments of such a spectrum to a $\sigma_2\pi$-C_2H_2 rhodium-bonded moity or to a C_{30} polyene. Since our experimental conditions differ from those used in the previous work, a higher background pressure in one case and the presence of Rh on the alumina in the other, it is possible that different species produce similar Raman spectra in the three cases. On the other hand, it is not clear why the difference in background pressure should have a dramatic chemical effect for the high acetylene pressures being used. Also, the chemistry of acetylene exposed to thermally activated Al_2O_3 and to Rh/Al_2O_3 is similar, and the formation of polyenes on Al_2O_3 or Rh/Al_2O_3 appears not to be very significant. We therefore prefer to think that the same chemical species is responsible for the Raman spectra in the three cases. Differences in the observed frequencies can be attributed to differences in the binding site and strength of binding caused by differences in the experimental conditions.[12] More characteristics of the surface-bound species are needed, however, for a positive identification.

Because of the simplicity of the Raman spectrum and the complexity of the mass spectra that we obtained (see Figure 2), the general use of Raman spectroscopy by itself as a surface-sensitive probe under these experimental conditions appears to be limited. The experimental conditions produce several chemical species, and additional data are needed to correlate particular species with Raman spectra that are observed. On the other hand, an enhancement of the Raman scattering may selectively reveal chemically significant intermediates on the surface.

Acknowledgment. Professor A. Ueno of Toyohashi University of Technology is gratefully acknowledged for his assistance and advice.

Registry No. C_2H_2, 74-86-2; Al_2O_3, 1344-28-1; Rh, 7440-16-6.

---

[12] α-Alumina was used in the work reported in ref 1. R. M. Hexter, private communication.

Carbanion Rearrangements. Collision-Induced Dissociations of the Enolate Ion of Heptan-4-one

Michael B. Stringer,[†] John H. Bowie,*[†] and John L. Holmes[‡]

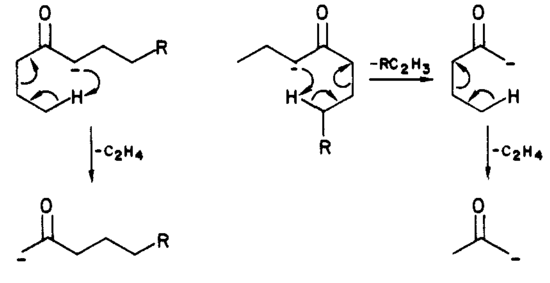
Contribution from the Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia 5001, and Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4, Canada. *Received November 26, 1985*

Abstract: The mechanisms of formation of the major negative ions produced in the collision-induced fragmentations of the enolate ion of heptan-4-one have been studied by using a series of D- and ^{13}C-labeled compounds. H atom loss is specific, involving position 3 (relative to the enolate position, 5). Methane elimination, the most abundant collision-generated fragment ion, largely involves the 1(7)CH_3 group together with a hydrogen atom from C-3(5). It was concluded from ^{13}C and D isotope effects that this reaction is stepwise with two kinetically significant steps. A minor methane loss (ca. 10%) involves H from C-6(2). C_2H_4 loss is also an important process, occurring for the most part (>90%) by loss of the ethyl group with a concomitant γ-hydrogen transfer to the anionic carbon or to oxygen, producing the $CH_3CH_2CH_2COCH_2^-$ and $CH_3CH_2CHC(OH)CH_2^-$ anions. Again, isotope effects show that the reaction must be stepwise. An unusual minor C_2H_4 loss is also observed involving specifically the elimination of a C2, C3 ethene unit, a reaction which must involve a methyl migration. Other decompositions are as follows: Loss of H_2 proceeds by two mechanisms, the first involving the 5 and 6 positions and the second the 1 and 2 positions. Elimination of $C_2H_5^\bullet$ is specific, producing $^\bullet CH_2COCH^-C_2H_5$. Loss of C_3H_8 occurs by two mechanisms, viz., loss of C_3H_7 from positions 5, 6, and 7 together with a hydrogen from position 3, with the second loss involving the methyl and ethyl groups at positions 1 and 6, 7, respectively.

In the past decade there have been significant advances in the analytical applications of negative ion mass spectrometry, particularly in the areas of negative ion chemical ionization and fast atom bombardment.[1] These "soft ionization" techniques often give molecular weight information, but in general, negative ions fragment but little and so, in many cases, fragment ions which in principle could yield structural information are absent from the spectra. Collision-induced dissociation of polyatomic negative ions can often provide this structural information.[1,2] In addition, fundamental information concerning ion behavior may be obtained from such studies.[1,3]

Enolate negative ions may be produced from alkyl ketones by reaction with HO^- in a chemical ionization source.[4] Collision-induced fragmentations of such enolate ions have been explored in several laboratories.[5-9] The acetone enolate ion eliminates methane to yield C_2HO^- while the corresponding ion from

Scheme I



[†] University of Adelaide.

[‡] University of Ottawa.

[1] Bowie, J. H. *Mass Spectrom. Rev.* **1984**, *3*, 161.

0002-7863/86/1508-3888$01.50/0