Radiochemical Studies of Chemisorption and Catalysis

XIII. A Mass-Spectrometric Study of the Interaction of Acetylene and Carbon Monoxide with a Rhodium-on-Silica Catalyst

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Mass spectrometry and thermal desorption studies have shown that when acetylene, at pressures of a few Torr at 18°C, interacts with a Rh–SiO_2 catalyst the principal reaction occurring is self-hydrogenation to ethylene and ethane, with ethane as main product. Species which could be thermally desorbed from the surface in the range 36–186°C included benzene, methane, ethylene, ethane, C_3- and C_4-hydrocarbons. Carbon monoxide had the effect of inhibiting self hydrogenation. C_1- to C_6-hydrocarbons could still be recovered by thermal desorption from the surface. Hydrogen, as a probe for surface species, brought ethane into the gas phase after exposure of Rh–SiO_2 to acetylene. Small amounts of C_3-hydrocarbons represented the only other species. A reaction scheme is presented.

INTRODUCTION

In a previous paper *(1)*, we have described the behavior of the radioactively-labeled species present when ^{14}C-carbon monoxide and ^{14}C-acetylene interacted with rhodium on silica or rhodium on alumina catalysts. The identities of the species present and the nature of the reactions occurring could not be deduced from the radioactivity results. We have therefore undertaken a mass-spectrometric study of the same system aimed at elucidating the reactions and changes which were occurring.

EXPERIMENTAL

The experimental procedure was similar to that described in Part XI of this series *(2)*. The catalyst (~1 g), usually 5% rhodium on silica, was dispersed on to the walls of the reaction vessel (capacity, ca. 100 ml), which was connected to an A.E.I. MS 10 mass spectrometer via a Metrosil

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leak. Following activation, as described previously *(2)*, the catalyst was exposed to acetylene under various conditions of pressure, temperature, and time.

After exposure of the catalyst for a given time, the gas-phase material in equilibrium with the surface was analyzed mass spectrometrically, or the gas-phase was removed, and the species which subsequently underwent thermal desorption from the catalyst into the gas-phase were analyzed mass spectrometrically. The thermal desorption technique was the same as described previously *(2)*, except that the desorbed material was condensed into an evacuated vessel cooled in liquid nitrogen before admission to the mass spectrometer.

The effect of hydrogen on the adsorbed species was examined, as was the effect of pretreating the catalyst with carbon monoxide before exposure to acetylene.

RESULTS

Throughout this study, the hydrocarbon spectra were obtained at 15.0 eV in order to minimize the extent of hydrocarbon fragmentation. The spectra presented be-
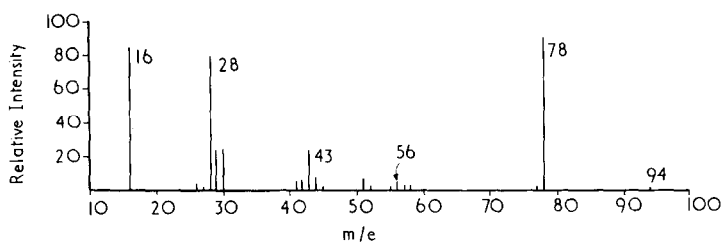
Fig. 1. Catalyst exposed to C_2H_2, 3 Torr for 30 min: desorption at 120°C: pressure 3.4×10^{-4} Torr.

low are the observed spectra, which have not been corrected for fragmentation, but which have been normalized with respect to the largest observed peak. Any corrections which are necessary for fragmentation are referred to in the text.

Unless otherwise stated, all the adsorptions were carried out at 18°C, and the catalyst vessel evacuated at this temperature before the thermal desorption was commenced. The pressures quoted for the desorbed products are those measured in the mass spectrometer by means of an ionization gauge. No attempt has been made to analyze the desorbed products quantitatively, since in the system used the extent of adsorption of acetylene in the different experiments could not be ac-

curately measured, thus rendering quantitative comparisons between experiments impossible.

Products from Desorption after Exposure of $Rh–SiO_2$ to Acetylene

The catalyst was exposed to acetylene at 3 Torr at 18°C for 30 min. The vessel was evacuated and then heated to 120°C for 15 min. Species desorbed gave the spectra shown in Fig. 1. In another experiment, the catalyst was heated in stages to 95°C, to give products with the spectra in Fig. 2.

In contrast with these desorptions at elevated temperatures, when the catalyst was exposed to acetylene, evacuated, and desorption allowed to proceed at room temperature, very little desorption oc-
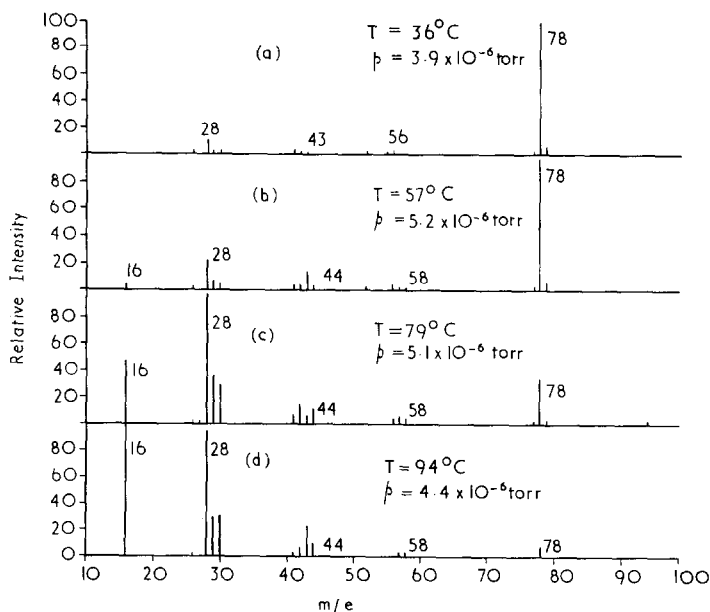
Fig. 2. Desorption into vacuum/liquid nitrogen trap. Catalyst exposed to acetylene at 3 Torr for 30 min at room temperature: evacuated 1 hr, desorption for 15 min.
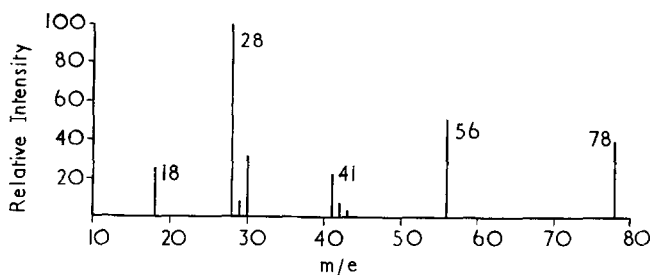
FIG. 3. Desorption into vacuum at room temperature. Exposure C_2H_2 (3 Torr) for 30 min. Pressure of desorbed gas 2.9×10^{-7} Torr.

curred. The spectrum from the desorbed species is shown in Fig. 3: here the total pressure of desorbed material was 2.9×10^{-7} Torr compared with 3.4×10^{-5} and between 3.9 and 5.2×10^{-6} Torr for Fig. 1 and Fig. 2, respectively.

Gas Phase Over Catalyst in the System C_2H_2–*Rh*–*SiO_2*

In some experiments, acetylene was admitted to the catalyst in such amounts that there was a small residual pressure over the catalyst. The gas over the catalyst was analyzed after 30 min and 13 hr; the spectra are shown in Fig. 4.

Acetylene-Support Interaction

The silica support, after treatment in a manner analogous to that used for the Rh–silica catalyst, was exposed to acetylene at a pressure of 4 Torr for 15 min.

Subsequent analysis of the gas phase showed no peaks other than those ascribed to acetylene itself. Similarly, after evacuation and desorption at 78°C, analysis of the desorbed gas revealed no products other than unreacted acetylene. However, when the desorption temperature was increased to 174°C, several products were desorbed from the silica surface (Fig. 5).

CO Pretreatment of Catalyst

Analysis of the gas-phase species formed when acetylene was admitted to a catalyst precovered with carbon monoxide showed a major peak at $m/e = 26$ (acetylene), together with a very small peak at $m/e = 28$, which, from a comparison with ethylene spectra, can be ascribed to carbon monoxide. After evacuation of the catalyst, the products desorbed at 55, 88, and 186°C

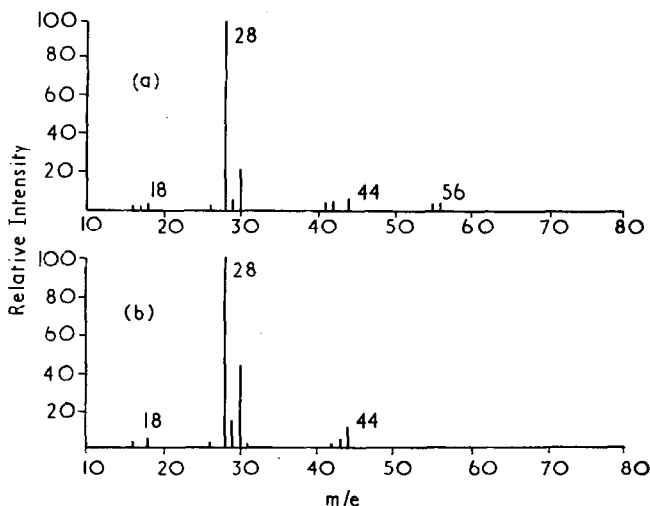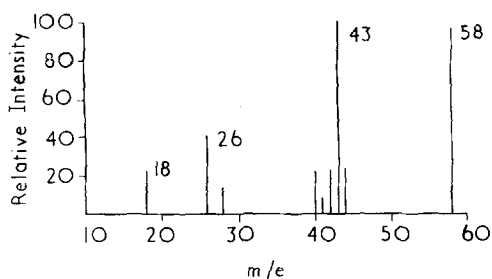FIG. 4. Gas phase over catalyst: 3 Torr C_2H_2 for (a) 30 min (b) 13 hr.

FIG. 5. Silica support exposed to C_2H_2 (4 Torr) for 15 min: evacuated and products desorbed at 174°C (pressure 2.4×10^{-7} Torr).

gave the spectra shown in Fig. 6(a), (b), and (c), respectively.

Hydrogen Reaction with Adsorbed Species

After exposure of the catalyst at 18°C to acetylene (4 Torr) and evacuation of the reaction vessel for 60 min, hydrogen was admitted to a pressure of 15 Torr. Gas phase species removed by hydrogen were examined after 5 min and, after further addition of hydrogen to 15 Torr, again after 65 min. The results are shown in Fig. 7(a and b). Without further addition of hydrogen, the catalyst vessel was heated to 47 and 84°C. The desorbed products were condensed at 77°K and analyzed, Fig. 7 (c and d).

DISCUSSION

When acetylene is admitted to a Rh–SiO_2 catalyst in such quantities that a gas-phase pressure exists over the catalyst, the principal reaction which occurs is self-hydrogenation (Fig. 3). Only minor amounts of methane and C_3-hydrocarbons are produced. The self-hydrogenation proceeds to the extent of producing ethane as the main product. The growth of ethane with respect to ethylene can be seen in Fig. 4 (a and b), where the contact times were 30 min and 13 hr. The m/e 28:30 ratio after 30 min was 4.4:1, indicating the presence of ethylene in the gas-phase, and after 13 hr was 2.3:1. This latter value was close to that for pure ethane at 2.32:1.

The radiochemical studies of the C_2H_2–Rh–SiO_2 system (1) showed that the adsorption of acetylene occurred in two well
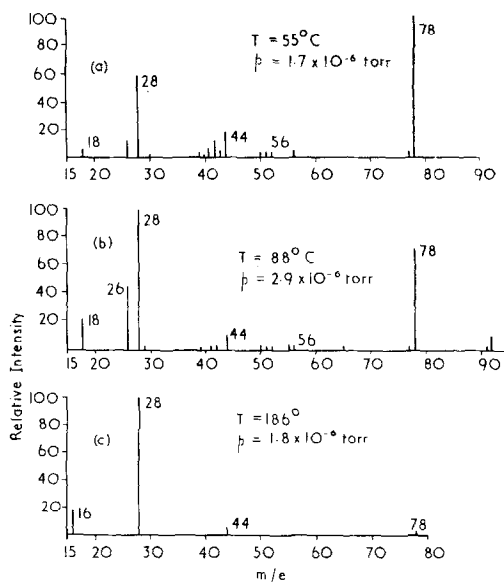

FIG. 6. Catalyst exposed to CO (6 Torr) for 5 min; followed by C_2H_2 (8 Torr) for 6 min and then evacuated for 1 hr.

defined stages; a fast initial stage (primary region) and a slower secondary stage. Furthermore, these studies showed that the effect of evacuation was to remove the secondary material. Thus the results for thermal desorption apply to species involved in primary adsorption upon the metal.

Figure 1, for desorption at 120°C, showed that the adsorbed species produced methane, ethylene, ethane, C_3- and C_4-hydrocarbons, and benzene. When the desorption was performed in stages, at a series of increasing temperatures, the following pattern emerged:

36°C, benzene was the major product: there was little self-hydrogenation.
57°C, evidence for increased self-hydrogenation.
79°C, benzene production insignificant: extensive self-hydrogenation.
94°C, self-hydrogenation and methane production now dominant.

Study of desorption into vacuum at room temperature (Fig. 3), showed that only a small amount of desorption took place, but all the processes, self-hydrogenation to
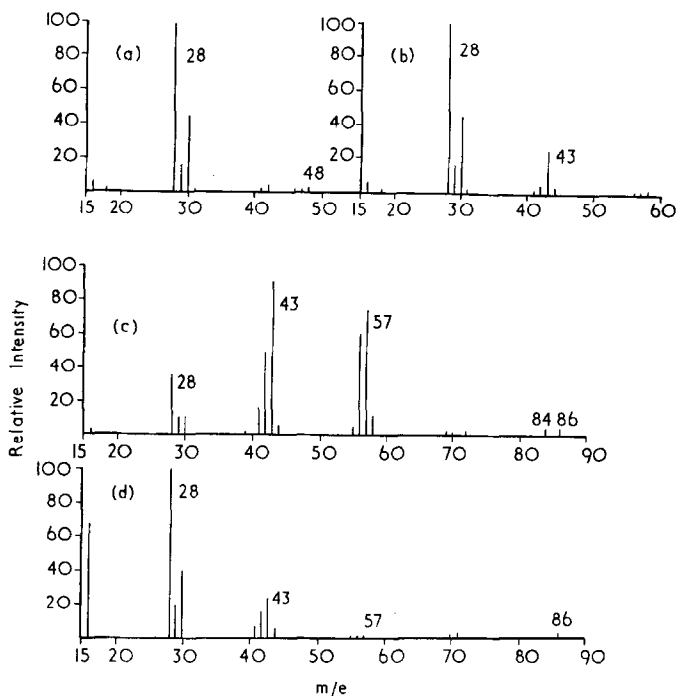
FIG. 7. Effect of hydrogen on acetylene-precovered surface (a) shows spectrum of gas phase after 5 min, (b) gas phase after 65 min, room temperature. (c) Products desorbed at 47°C, pressure 0.82 × 10⁻⁵ Torr and (d) desorbed at 84°C, pressure 1.1 × 10⁻⁵ Torr.

ethylene and ethane, and production of C_3- and C_4-hydrocarbons and benzene were all occurring.

When acetylene was introduced to the support material alone, the acetylene was unchanged. Only small amounts of gas could subsequently be recovered by thermal desorption. This consisted, up to 78°C, of acetylene; only on raising the temperature to 174°C did small amounts of ethylene, C_3- and C_4-species appear. Benzene was absent. These experiments confirm our view that the quite different results reported for rhodium on silica should be ascribed to interactions with the metal.

Carbon monoxide has been used specifically as a detector of metal sites for supported catalysts (3). The object of its use in this study was to find out which of the reactions previously mentioned was influenced by its presence. It had been established in the radioactivity study that pretreatment of the surface with carbon monoxide caused the elimination of the primary adsorption stage for acetylene, al-

though secondary adsorption remained unaffected (1).

The effect of carbon monoxide pretreatment was to stop the self-hydrogenation observed when the gas-phase above the catalyst was examined. Self-hydrogenation in the absence of CO can be seen clearly in Fig. 4.

When the gas-phase was removed by evacuation and the nature of adsorbed species from thermal desorption examined, it can be seen in Fig. 6(a) that benzene was present in considerable amounts. C_3- and C_4-hydrocarbons were also present, and some self-hydrogenation had occurred since some ethylene was also observed. The comparable result for an unpoisoned catalyst is shown in Fig. 2(b). The production of ethylene and methane becomes increasingly important at higher temperatures [Fig. 6(b) and (c)].

The striking difference in the carbon monoxide preadsorption experiments was the inhibition of self-hydrogenation, and there are at least two interpretations of the

evidence presented about what was happening on the surface. We knew from the radiochemical work that acetylene could displace 40% of adsorbed carbon monoxide. Thus, if the surface was heterogeneous (4, 5), then carbon monoxide could have poisoned the self-hydrogenation sites, from which it was not displaced by acetylene. Benzene production could then be ascribed to those sites on which carbon monoxide replaced acetylene.
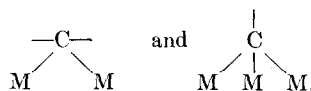
If the surface was homogeneous, then random displacement of carbon monoxide by acetylene would have led to a surface distribution of species in which there were few sites for uptake of hydrogen produced by the dissociative adsorption of acetylene: hence self-hydrogenation would have been inhibited. In this situation, associatively-bonded or π-bonded acetylene molecules might still have met to produce benzene.

We have used hydrogen as a probe for surface species in that it might bring into the gas phase the precursors of the various products discussed above. In these experiments, a surface was exposed to acetylene for 4 min at room temperature. The gas phase was then removed, and hydrogen admitted. This brought ethane into the gas phase [Fig. 7(a) and (b)]: in these, the m/e 28:30 ratios were 2.3:1 and 2.1:1 (cf. ethane 2.32:1). Small amounts of C₃-hydrocarbons constituted the only other species. Heating the surface to 47°C [Fig. 7 (c)], produced C₃- and C₄- species, although at 84°C the C₄-species evidently underwent breakdown to ethane.

The absence of C₆-hydrocarbons as desorption products from experiments involving the addition of molecular hydrogen, indicates that, under conditions where surface hydrogen coverages are relatively high, polymerization to aromatic species does not occur.

From the foregoing discussion, it is evident that, to a large extent, the surface species which are precursors to the thermally desorbed hydrocarbons are formed by dissociative adsorption. Similar observations have been made in infrared spectroscopic studies of hydrocarbons adsorbed on supported metals (6), although no spe-

cific studies using supported rhodium catalysts appear to have been reported. Nevertheless, it is worthwhile considering some of the results obtained from infrared studies in an attempt to gain further insight into the surface processes which were occurring. The situation is summarized succinctly by Avery (6): he states that hydrogenation of an adsorbed olefin led to adsorbed species, which could be successively hydrogenated and dehydrogenated by the mere addition and evacuation of hydrogen. Furthermore, for linear olefins, it is observed that a fraction of the species produced on initial hydrogenation was easily desorbed, leaving a strongly chemisorbed species. From such studies (7), it has been concluded that these strongly adsorbed species involved the formation of carbon–metal multiple bonds, e.g.,

$$ \overset{\displaystyle -C-}{\underset{\displaystyle M \qquad M}{\diagup \quad \diagdown}} \quad \text{and} \quad \overset{\displaystyle C}{\underset{\displaystyle M \quad M \quad M.}{\diagup \; | \; \diagdown}} $$

The results obtained from the radiochemical studies (1), together with those presented in this paper, are explicable in terms of the following reaction scheme (A); in it, we consider the nature and reactivity of the various adsorbed species.

The adsorption isotherm for acetylene showed a steep primary region followed by a less steep secondary region. Since neither alumina nor silica showed any adsorption approaching that observed in the secondary region on the supported metal catalyst, we rule out the possibility that the secondary adsorption process corresponded to physical adsorption. We believe that the secondary adsorption corresponded to a relatively weakly chemisorbed species such as [A] or [B]. The mass spectrometric results show that, in the primary adsorption region, there was considerable self-hydrogenation to ethane and ethylene. Furthermore, ethane was the major product. This suggests that there is extensive dissociation of acetylene to yield species such as [D], [F], and [G], together with surface hydrogen: this hydrogen may react with primary or secondary adsorbed species to yield ethylene and ethane. The observation
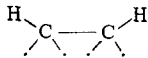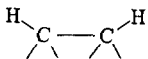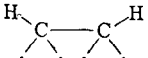
HC≡CH (gas)

[A]   or   [B]

[C]   [D]

- H / +H

Polymers ← +C₂H₂ ← [E]   [F]   [G]

+H / - H

[J]   [H]   C₂H₄ (gas)

+H / -H   +H / - H
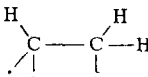
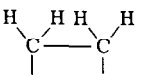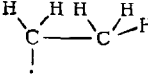[K]   +H → C₂H₆ (gas)

Reaction-1-A
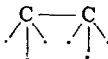
that ethane was the major self-hydrogenation product, even in the presence of gas-phase acetylene, suggests that its formation involves species [E], [J], and [K], rather than [E], [H], and [K]. We draw this conclusion since [H] represents an associatively-bonded ethylene, which by comparison with studies of the rhodium-catalyzed hydrogenation of acetylene (8), might be expected to be desorbed rather than react further to form ethane. The formation of α,α-diadsorbed species such as [J] is not unexpected, since studies of rhodium-catalyzed hydrocarbon-deuterium exchange reaction (9) have shown the ability of this metal to form α,α-diadsorbed species.

Reaction scheme (A) also allows an interpretation of the differences observed between the adsorption of acetylene and ethylene on supported rhodium catalysts.

In particular, we refer to the higher degree to which the surface was covered with strongly adsorbed species from acetylene rather than from ethylene (10), and the more extensive self-hydrogenation observed with acetylene than with ethylene (2). If, as we believe, species [D], [F], and [G] are strongly adsorbed species, then it is apparent that these species are more readily formed from acetylene than from ethylene; formation of these species from ethylene would have involved more extensive dissociation.

Similarly, in terms of scheme (A), we can now comment further on the results obtained in the radiochemical studies (1, 10) when carbon monoxide was used either as a "pre-adsorbed poison" or as a displacing gas for adsorbed ethylene or adsorbed acetylene. Since the adsorption of carbon monoxide occurs on the metal alone (11),

TABLE 1

Observation	Interpretation
CO-precovered Rh	Displacing species
Displacement by acetylene: 40% removal	[structure: H₂C₂ acetylene-type adsorbed species, H—C—C—H]
Displacement by ethylene: ~ NIL	C₂H₄ unable to form [structure: H—C—C—H] for dissociation to [structure: H above C] hindered by CO
C₂H₂-precovered Rh	Surface largely covered by
Displacement by CO: ~ NIL	[structure: H—C—C—H] and [structure: C—C]
C₂H₄-precovered Rh	Possible displacement of
Displacement by CO: significant	[structures: H₂C—C—H ; H₂C—CH₂ ; H C—C—H] with [structure: H]

we are only concerned with the primary adsorbed species. The situation can best be seen in Table 1.

Two features of interest emerge from our proposals. First, formation of C — C is
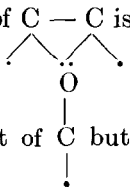
likely to result in displacement of C but
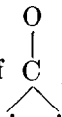
not of C ; hence the displacement of only

40% CO by acetylene (1, cf. 12). Second, we suggest that when acetylene displaces carbon monoxide, the displacing species is [C], rather than [D] or [F]. Carbon monoxide inhibits the dissociation of adsorbed acetylene, since the degree of self-hydrogenation of acetylene was greatly diminished [see Fig. 6(b)]: thus, the formation of hydrogen-deficient surface species is unlikely in the early stages of acetylene adsorption on carbon monoxide precovered surfaces. Further, the formation of benzene, which is favored on hydrogen-deficient surfaces, is still formed in the presence of adsorbed carbon monoxide.

Lastly, we consider the formation of polymers from adsorbed acetylene. The results show that under all conditions C_3- and C_4-hydrocarbons were desorbed from the surface. Similar observations have been made during the hydrogenation of acetylene over alumina-supported rhodium catalysts (8). We believe that these polymeric species arise by reaction between gas-phase acetylene and partially dehydrogenated residues such as species [E] in reaction scheme (A), p. 384.
The C_3 yield could arise either by reaction between acetylene and C_1 residues on the surface, such as species [G], or by the interaction of two acetylene molecules with species of the type [C] or [E] to give an adsorbed C_6-species which undergoes hy-
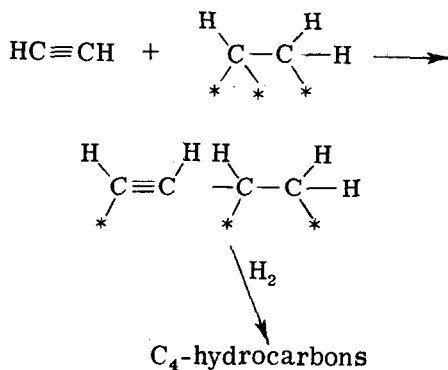
C_4-hydrocarbons

drogenolysis before appearing in the gasphase. From the results presented above, it is not possible to deduce which of these mechanisms is correct, although the absence of any C_6-hydrocarbons, other than benzene, in the thermally desorbed products may indicate that the former of the two postulates is more likely.

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