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Calorimetric Studies of Hydrocarbon Adsorption on Metal Films

II. Ethylene, Acetylene, Propylene, Methylacetylene and Allene on Molybdenum

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Heats of adsorption of ethylene, acetylene, propylene, methylacetylene, and allene were measured at room temperature in an adsorption calorimeter on molybdenum films deposited in the 10^{-9} Torr region. The initial heats, and the integral heats from zero coverage up to the coverage prevailing at an equilibrium pressure of 2×10^{-5} Torr, are on average (kcal/mole): 69.5 and 63.9 for ethylene; 62.5 and 69.0 for acetylene; 78.4 and 73.2 for propylene; 70.0 and 68.5 for methylacetylene; and 72.6 and 71.5 for allene.

The measured data suggest that alkenes undergo dissociation of the carbon–carbon π-bond and of two C–H bonds, while alkynes are adsorbed with dissociation of two carbon–carbon π-bonds only. Hence, both alkenes and alkynes give surface species of the same basic structure: Mo=(CH)–(CH)=Mo arises from ethylene and acetylene, and Mo=(CH)–C(CH_3)=Mo arises from propylene, methylacetylene, and also allene, which probably first rearranges into methylacetylene and then is adsorbed as such. The hydrogen atoms dissociated from alkenes are not freely mobile on the surface, but are coordinated around the hydrocarbon residue with a heat of adsorption effectively increased by 18 kcal/mole. This interaction between the adsorbed C and H atoms may proceed either directly or via the metal phase.

The suggested difference in the adsorption mechanisms of alkenes and alkynes is corroborated by the energy levels of the molecular orbitals localized on the particular bonds.

I. INTRODUCTION

Little is known about the thermodynamics of adsorption of unsaturated hydrocarbons on metals. Direct calorimetric measurements of Beeck (*1*) with films of Ta, W, Cr, Fe, Ni, and Rh gave for ethylene high initial heats of adsorption, steeply falling with the increasing adsorbed amount. Bond mentioned on p. 281 of his monograph (*2*) the private communication by Wilson that the heat of adsorption of acetylene on a Ni film is initially 66–67 kcal/mole and that it does not change up to a rather high surface coverage. Trapnell (*3*) calculated isosteric heats for the reversibly chemisorbed ethylene and acetylene on Cu and Au films at room temperature, and obtained 20.8 and 18.2 kcal/mole, respectively, for ethylene; and 21 and 19 kcal/mole, respectively, for acetylene. A heat of about 12 kcal/mole for propylene on Pt was mentioned by Trimm and Cooper (*4*). Three and 6 kcal/mole at 298°K, and 16 kcal/mole at 423°K were claimed for ethylene on nickel–alumina catalyst from monitoring the temperature in the catalyst bed upon pulse injection of the gas (*5*).

The main body of information on the strength of bonding of the unsaturated

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hydrocarbons on metals has been inferred from the kinetics and selectivity of their hydrogenation, since the equilibrium surface coverage is assumed to increase with the increasing heat of adsorption and thus to reflect its value. Also the heats of hydrogenation to the next less unsaturated form are believed to parallel the heats of the associative chemisorption. Again, retention times determined by gas chromatography served for estimating the relative strengths of adsorption of hydrocarbons (*6*). From this rather indirect evidence, the following conclusions have been commonly adopted (*2*, *7–11*):

i. Alkynes are more strongly adsorbed than the corresponding alkenes.

ii. Dialkenes are more strongly adsorbed than monoalkenes.

iii. Alkenes are more strongly adsorbed than the corresponding alicylic compounds.

iv. The heat of adsorption of an alkene decreases with the increasing substitution of methyl groups due to stabilization of π-bond by hyperconjugation.

The objective of the present work has been to acquire direct calorimetric data on the adsorption of a series of unsaturated hydrocarbons under comparable conditions on molybdenum which is representative of metals with a high efficiency in cleaving C–C bonds (*12*, *13*), and to use the data to suggest the surface species formed.

II. EXPERIMENTAL METHODS

The experimental technique was the same as in Ref. (*14*), the only exception being the closing of the calorimeter vessel after the film deposition by a magnetically operated ground ball valve, opened only immediately before the inlet of the first dose. The experiments were performed at approximately 295°K.

The following gases were used: ethylene puriss. and propylene puriss. (Fluka A. G., Buchs, Switzerland), acetylene purified grade (Matheson Co., East Rutherford, N. J.) methylacetylene research grade (K & K Laboratories, Hollywood, Calif.) and allene CP grade (Koch-Light Labs, Colnbrook, England). Gases filled from a cylinder into a reservoir on the apparatus were subjected before each experiment to repeated freeze–evaporation cycles with pumping off the first and last portions of the vapor phase on evaporation. Admixture of the isomeric compound in the C_3H_4 hydrocarbons was checked by infrared analysis. Allene prepared for dosing contained about 1% of methylacetylene. No allene was detected in methylacetylene.

III. RESULTS

Characteristics of the prepared films are given in Table 1.

A. Adsorption up to n^*

The common feature of the investigated hydrocarbons is that when admitted to the bare film they are rapidly adsorbed to a very low residual pressure. After consumption of n^* micromoles of a hydrocarbon by the film, the equilibrium pressure reaches 2×10^{-5} Torr (1 Torr = 133 N m^{-2}) and becomes detectable with a McLeod manometer. This adsorbed amount referred to 100 mg of film is denoted by N^*. The equilibrium pressure increases when further gas is dosed. Since an analysis of the equilibrium gas phase has not been available in the present study, and because the heat transport between the calorimeter and cold traps via the gas phase becomes appreciable when n^* is exceeded, exact heat determination has been feasible up to n^* only.

Treatment of the calorimetric data was the same as in Part I (*14*). Parameters of the polynomials

$$Q = b_0 + b_1n + b_2n^2 + b_3n^3$$

(Q is the heat evolved by the adsorption of n micromoles) computed to fit best the integral curves, are given in Table 2.

TABLE 1

Characteristics of the Molybdenum Films[a]

Adsorbate	1	2	3	4	5	6	7	8
Ethylene	32	13.3	60	5–6	164	470	15.1	
	33	11.5	60	4–5	195	665	14.8	15.6 ± 0.6
	35	13.8	50	4–5	210	880	16.8	
Propylene	36	14.5	35	1–2	208	823	13.2	
	37	14.9	25	5	168	490	12.8	13.2 ± 0.3
	39	14.5	45	1	204	455	13.7	
Allene	40	13.9	60	5–6	128	765	26.5	
	41	13.9	60	4–5	240	595	23.2	24.2 ± 1.1
	42	8.5	38	5	124	318	22.9	
Methylacetylene	43	11.1	75	4	159	509	22.4	
	44	10.6	52	3–4	133	484	25.1	24.2 ± 0.9
	46	12.0	50	5	161	625	25.0	
Acetylene	56	13.6	83	4	125	802	30.6	30.4 ± 0.1
	59	11.1	70	3	110	469	30.3	

[a] Column: (1) number of the film; (2) film weight (mg); (3) time of the film deposition (min); (4) vacuum during the film deposition (Torr × 10^{-9}); (5) time from the end of film deposition to the first dose (min); (6) time from the end of film deposition to attaining n^* (min); (7) $N^* = n^*/100$ mg of the film (micromoles); (8) average value of N^*.

Differentiation of these fits gave the differential heat vs adsorbed amount curves shown in Fig. 1. The values of b_1 obviously equal the initial differential heats which are on average 62.5, 69.5, 70.0, 72.6, and 78.4 kcal/mole for acetylene, ethylene, methylacetylene, allene, and propylene, respectively. The integral heat between $n = 0$ and

TABLE 2

Results of the Regressional Analysis of the Integral Curves[a]

Adsorbate	Film No.	b_0	s_{b_0}	b_1	$\bar{b}_1$	s_{b_1}	b_2	s_{b_2}	b_3	s_{b_3}	s	A	B	C
Ethylene	32	−1.80	0.18	73.86		0.52	−3.05	0.30	0	0	0.27	0.85	18	65.8
	33	−0.34	0.12	68.12	69.5	0.38	−1.93	0.25	0	0	0.18	0.85	24	63.3
	35	−1.12	0.14	66.66	±1.8	0.18	0	0	0	0	0.48	0.78	32	62.5
Propylene	36	0.02	0.27	74.54	78.4	0.64	0	0	−0.11	0.22	0.66	1	23	73.5
	37	−0.33	0.31	82.29	±1.9	0.52	0	0	−2.53	0.14	0.48	1	16	72.7
	39	−0.81	0.31	78.39		0.51	0	0	−1.15	0.12	0.48	1	15	73.4
Allene	40	−2.32	0.10	70.34	72.6	0.05	0	0	0	0	0.29	1	31	69.7
	41	−1.72	0.29	71.92	±1.6	0.16	0	0	0	0	0.71	1	23	70.3
	42	−1.67	0.32	75.61		0.27	0	0	0	0	0.59	1	14	74.4
Methylacetylene	43	−0.78	0.32	69.86	70.0	0.23	0	0	0	0	0.66	1	18	68.6
	44	−1.69	0.28	71.61	±0.8	0.18	0	0	0	0	0.60	1	18	69.5
	46	−0.74	0.37	68.67		0.22	0	0	0	0	0.89	1	22	67.5
Acetylene	56	−2.66	0.43	62.53		1.01	4.77	0.59	−0.72	0.09	0.76	1	40	69.0

[a] s denotes the standard deviation of the overall fit; s with an index denotes the standard deviation of the coefficient given in the index; $\bar{b}_1$ stands for the mean deviation of the b_1 values; A: n/n^* up to which the fit holds; B; number of doses up to n^*; C: integral heat (kcal/mole) from $n = 0$ to n^*.

$n = n^*$ is on average 63.9, 68.5, 69.0, 71.5, and 73.2 kcal/mole for ethylene, methylacetylene, acetylene, allene, and propylene, respectively.

In Expt 31, not included in Fig. 1, the integral curve for ethylene up to $n/n^* = 0.25$ corresponded slightly better to a mild increase of the differential heat, but this was not reproduced in the three following experiments. The integral curves of ethylene could be expressed by a polynomial up to $n/n^* = 0.85$ only. Description of the entire curve by a more complex expression was abandoned and an approximately linear fall of the differential heat at n/n^* 0.85 was assumed.

The shape of the differential heat curve of acetylene obtained in experiment 56 was confirmed in a further experiment. However, this is not included in Table 2 and Fig. 1, because an adaptation of the calorimeter caused an uncontrolled change in its heat capacity and thereby a shift of the absolute value of the heat obtained.

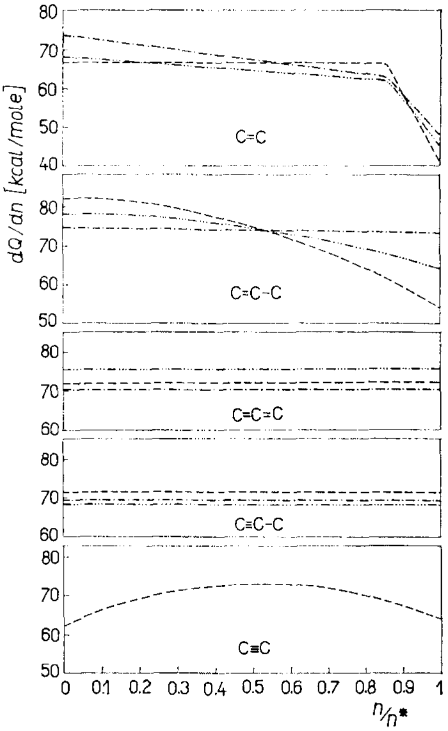


FIG. 1. Differential heat vs adsorbed amount curves obtained by differentiation of the best fit to the integral curves. Ethylene: (–·) Expt 32; (–···) Expt 33; (– –) Expt 35; propylene: (–·) Expt 36; (– –) Expt 37; (–···) Expt 39; allene: (–·) Expt 40; (– –) Expt 41; (–···) Expt 42; methylacetylene: (–·) Expt 43; (– –) Expt 44; (–···) Expt 46; acetylene: (– –) Expt 56.

B. Adsorption at Coverages Exceeding n^*

Some introductory experiments were carried out with the dosing of hydrocarbons after n^* had been reached. In general, the gas uptake proceeded with a more or less progressively falling rate under progressively increasing equilibrium pressure and decreasing heat which, however, amounted in a number of successive doses to tens of kilocalories per mole of the dosed hydrocarbon. With all the five compounds studied, a point was eventually attained at which a further dose caused the equilibrium gas amount over the film to exceed the sum of the added dose plus the preceding equilibrium gas amount. This was encountered with ethylene at approximately 2 n^*, and with the other four hydrocarbons very soon after n^*. An analysis of the gas phase was unfortunately not available. The temperature–time trace did not differ from the usual shape for a rapid heat evolution, with the exception of ethylene which yielded after the dose inlet a fast onset of heat liberation, immediately followed by very slow evolution of a very low heat.

After a few further doses, the phenomenon of the excess increase in the total gas amount over the film disappeared, and further dosing gave the normal pattern of the gas uptake under a progressively decelerating evolution of decreasing heat and progressively increasing equilibrium pressure. When the gas phase over the film was pumped off at this stage and new hydrocarbon doses admitted, the same behavior was observed as before the pumping off: with ethylene, there was adsorption with slow evolution of a very low heat, and with the other four hydrocarbons, fast adsorption liberating an appreciable heat. The evolved heat was in no relation to the equilibrium amount in the gas phase after n^*, but it depended on the magnitude of the dose, and as mentioned, it decreased progressively with the number of admitted doses.

C. Admission of Hydrogen onto the Hydrocarbon Layer

Preliminary results were obtained with admission of hydrogen onto films covered with hydrocarbon amounts exceeding n^* and then subjected to pumping off the equilibrium gas phase. The films precovered with hydrocarbon to a higher extent gave lower and more slowly evolved heat, and their capacity for the uptake of hydrogen was reduced. Continuing hydrogen dosing yielded decreasing heat and increasing equilibrium pressure. After the uptake of a certain amount of hydrogen, its further dosing caused the equilibrium gas amount over the film to exceed the sum of the added dose plus the previous equilibrium gas amount. The corresponding temperature–time trace did not show any departure from the usual shape in a rapid adsorption. The heat effect was low. After a few further doses of hydrogen, this phenomenon disappeared, but the subsequent hydrogen dosing gave only a low heat.

IV. DISCUSSION

A. Adsorption Modes of Unsaturated Hydrocarbons

The heats of adsorption of all the five unsaturated hydrocarbons are close to 70 kcal/mole and depend slightly or not at all on the coverage up to n^*. This is a marked difference from the behavior of cyclopropane on molybdenum, and resembles its behavior on platinum (*14*).

Many conflicting views exist on the nature of the surface species formed in the adsorption of unsaturated hydrocarbons. This is because the structure of these species depends on a variety of factors, such as the electronic structure of the reacting molecule and of the metal surface (*8*, *15–19*), geometry of the two partners (*15*, *18–22*), kind and abundance of other particles on the surface (*19*, *23–26*), temperature (*6*, *24–26*), and other circumstances (*25*, *27*, *28*). The species formed may interconvert and coexist (*16*, *24*). The following modes of chemisorption of unsaturated hydrocarbons on metals are discussed most frequently:

Mode I consisting of splitting off hydrogen atoms with preservation of the multiple bond system in the species attached to the surface by carbon–metal σ-bonding (*2*, *29*). (Reported dissociation of ethylene at room temperature into two C_1 fragments (*30*) has not been observed by others so far.)

Mode IIa resulting from dissociation of one π-bond between the carbon atoms in alkenes or alkynes, and formation of two carbon–metal σ-bonds (*2*, *29*).

Mode IIb occurring when the both π-bonds in alkynes are dissociated and two double bonds with the surface arise.

Mode III representing a mixture of modes I and II, so that for example the structure of adsorbed ethylene is

$$\mathrm{Me{=}(CH){-}(CH){=}Me},$$

or perhaps

$$\mathrm{Me_2{=}(CH){-}(CH){=}Me_2}.$$

Mode IV consisting of the formation of a back-donation bond. Its σ-part arises from the overlap of the filled bonding π-orbital of the hydrocarbon with the empty e_g orbital of the metal atom, and the π-part of the bond is formed by back-donation from a filled nonbonding t_{2g} orbital of the metal into the empty antibonding π^*-orbital of the hydrocarbon, thus reducing the negative charge on the metal. This scheme introduced for explaining the bonding in the metal–alkene and metal–alkyne complexes (*31*, *32*) has been applied to the adsorption on metal surfaces (*7, 8, 10, 16, 33, 34*). Withdrawing of the negative charge to neighboring atoms acting as weak stabilizing ligands was proposed (*17*) instead of the back-donation mechanism mentioned.

Mode V occurring when a hydrogen atom in the α-methyl or α-methylene group of an alkene or alkyne is split off, and a π-allyl species exhibiting electron delocalization is formed, attached by π-bonding to one surface site (*7, 17*).

When trying to employ the experimental results obtained in the present study for formulation of a consistent scheme of the surface species formed under the given conditions, we started with the hypothesis that chemisorption of the studied hydrocarbons involves primarily their multiple bond system without cleavage of the C–C σ-bonds, and that the extent of dissociation of the hydrogen atoms should be considered for each particular compound separately.

This suggestion is supported by the energy levels of the molecular orbitals in the molecules under consideration. The highest occupied molecular orbitals in the unsaturated hydrocarbons have rather high energies and are located on the π-bonds (*35, 36*). The energies of the orbitals located on the σ-bonds between the carbon atoms are much lower. This points to a ready interaction of the π-bonds with a surface, while dissociation of the C–C σ-bonds is difficult (*36*). Furthermore, the energy levels of molecular orbitals located on the C–H bonds in alkenes indicate that dissociation of these bonds is likely (*36*).

Having this in mind, we have adopted a working hypothesis that two C–H bonds are dissociated in the chemisorption of alkenes, while no C–H bonds dissociate in alkynes. Hence, essentially the same surface species arise from alkenes and the corresponding alkynes. This working hypothesis is analyzed in the following sections.

B. Thermochemical Arguments

If the same surface species are formed by alkenes and alkynes, the following thermochemical cycle should hold:

$$\begin{array}{llll} C_2H_{4(g)} \rightarrow C_2H_{2(g)} & + H_{2(g)} & & + Q_1 \\ C_2H_{2(g)} \rightarrow C_2H_{2(ads)} & & & + Q_2 \\ H_{2(g)} \rightarrow 2H_{(ads)} & & & + Q_3 \\ \hline C_2H_{4(g)} \rightarrow C_2H_{2(ads)} & + 2H_{(ads)} & + Q_1 + Q_2 & + Q_3. \end{array}$$

$Q_1 = 41.7$ kcal/mole is the heat of dehydrogenation of ethylene to acetylene (*37*). $Q_2 = 62.5$ and $Q_3 = 30.0$ kcal/mole are the observed initial heats of adsorption of acetylene and hydrogen (*38*), respectively. The heat effect of the cycle amounts then to 50.8 kcal/mole, i.e., 18.7 kcal/mole less than is the mean observed initial heat of adsorption of ethylene. An analogous cycle may be formulated for propylene:

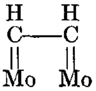
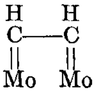
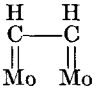
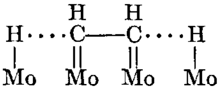
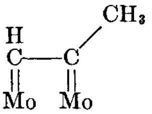
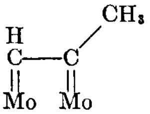
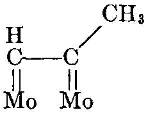
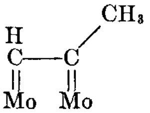
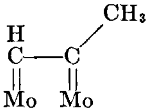
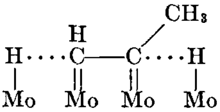
$$\begin{array}{llll} C_3H_{6(g)} \rightarrow C_3H_{4(g)} & + H_{2(g)} & & + Q_1 \\ C_3H_{4(g)} \rightarrow C_3H_{4(ads)} & & & + Q_2 \\ H_{2(g)} \rightarrow 2H_{(ads)} & & & + Q_3 \\ \hline C_3H_{6(g)} \rightarrow C_3H_{4(ads)} & + 2H_{(ads)} & + Q_1 + Q_2 & + Q_3. \end{array}$$

$Q_1 = 39.4$ kcal/mole is the heat of dehydrogenation of methylacetylene to propylene (*37*). $Q_2 = 70.0$ and $Q_3 = 30.0$ kcal/mole are the observed initial heats of adsorption of methylacetylene and of hydrogen (*38*), respectively. Hence, the heat balance of the cycle is 60.6 kcal/mole, i.e., 17.8 kcal/mole less than the observed mean initial heat of adsorption of propylene.

Results of the thermochemical analysis are in both cases consistent with the working hypothesis if it is assumed that the dissociated hydrogen atoms are adsorbed preferentially on sites adjacent to the molybdenum-bonded carbon atoms, and that thereby an additional heat of interaction of about 18 kcal/mole is gained, as compared to independent adsorption of hydrogen and acetylene or methylacetylene. This additional heat may be formally attributed to the adsorption of hydrogen, thereby enhancing effectively the initial heat of adsorption of hydrogen to approximately 48 kcal/mole.

TABLE 3

Suggested Structure of the Surface Species

Compound	Sites required	Basic skeleton of the surface species	Hydrogen atoms localized on adjacent sites	Complete surface complex	Number of free hydrogen atoms on the surface
Acetylene	2		0		0
Ethylene	4		2		0
Methylacetylene	2 + screening		0		0
Allene	2 +screening		0		0
Propylene	4 + screening		2		0

The interaction might be due to perturbation of the adjacent metal atoms by an increase in their electron density resulting from the accumulation of positive charge on the adsorbed carbon atom, which leads to a stronger adsorption of hydrogen on the electron-enriched metal atoms. This suggestion is virtually the same as that proposed earlier by Rooney and Webb (*17*). Another explanation may lie in a direct lateral interaction between the adsorbed carbon atom in the hydrocarbon residue and the dissociated hydrogen atoms. The experimental results do not allow us to decide which alternative is more likely. In either case, however, the net effect is a restriction of the surface mobility of the dissociated hydrogen atoms, which are more or less localized in the vicinity of the adsorbed hydrocarbon species.

The arguments outlined suggest that all five unsaturated hydrocarbons yield under the given conditions the same basic pattern of surface species, as sketched in Table 3.

A word of caution should be given on the proposed mode of adsorption of propylene. In only one experiment the heat of adsorption of propylene was constant, while in two other experiments it was falling with coverage, in contrast to the other unsaturated hydrocarbons. Furthermore, the initial heat of propylene is rather high. Hence a question arises as to whether the suggested mode of adsorption of propylene is the only one operative under the given conditions. Fragmentation of propylene in some extent appears to be possible (*36*).

Heats of formation and hydrogenation of allene are 1.6 kcal/mole higher than the heats of methylacetylene (*37*). In good accord with this, the initial and integral heats of adsorption of allene are 2.6 and 3.0 kcal/mole, respectively, higher than the heats of methylacetylene. Thus thermochemical data are consistent with the view that allene and methylacetylene are adsorbed as the same species. This can be tentatively explained by suggesting that allene first rearranges into the isomeric methylacetylene and then is adsorbed as such. Further evidence on this point is desirable.

C. Magnitude of N^* for the Particular Hydrocarbons

As mentioned in Sec. III, n^* denotes the amount adsorbed when a residual pressure of 2×10^{-5} Torr is detected over a film. This quantity referred to 100 mg of the film is given by N^*. The film weight is taken to be proportional to the accessible surface area (*39*). The doses admitted after N^* liberated heats which gradually decreased, but still amounted to several tens of kilocalories per mole, thus indicating that further chemisorption occurred. The mass-spectrometric measurements of Merta (*12*, *13*) with cyclopropane and propylene on metal films have shown that the rise of the equilibrium pressure after N^* is due entirely to the formation of saturated hydrocarbons by self-hydrogenation. Only considerably later do the feed hydrocarbons also appear in the gas phase. Assuming an analogous behavior of the unsaturated hydrocarbons under study, we may expect that they yield approximately the same degree of surface coverage at N^*, and that this coverage is not much lower than an effective monolayer.

Provided this is valid, it would be possible to estimate the relative number of sites involved in the adsorption of the individual hydrocarbons from the ratio of the respective values of N^*. N^* of ethylene and of propylene are approximately half the values for acetylene and methylacetylene, respectively (Table 1). Consequently, monoalkenes appear to occupy twice as many sites as alkynes. The most natural interpretation is that acetylene needs 2 sites, while ethylene needs 4 sites, two of them being occupied by the dissociated hydrogen atoms. This is in accord with the outcome of the thermochemical analysis. The values of N^* for the C_3 hydrocarbons, which are somewhat lower than for the C_2 hydrocarbons, can be accounted for again in terms of a 2-site requirement of methylacetylene and a 4-site requirement of propylene, provided the methyl group is not chemisorbed itself, but effectively blocks the access to x sites. The ratio of N^* for acetylene and methylacetylene is inversely proportional to the number of occupied sites: $N_{C_3H_4}^*/N_{C_2H_2}^* = 2/(2 + x)$. Inserting from Table 1, we get $x \approx 0.5$. Similarly we can write $N_{C_3H_6}^*/N_{C_2H_4}^* = 4/(4 + x)$, and by insertion from Table 1 we obtain again $x \approx 0.5$. Allene has the same N^* as methylacetylene. This is in line with the above-mentioned tentative proposal that allene first isomerizes into methylacetylene and then is adsorbed as such.

The agreement of conclusions based on the values of N^+ and on the thermochemical analysis of initial heats of adsorption suggests that the structures of species formed do not change substantially up to n^+.

It appears worthwhile to note that N^* for acetylene is by a mere 9% lower than the 33.0 μmoles of hydrogen needed in the experiments (*38*) by a 100 mg molybdenum film to arrive at an equilibrium pressure of 2×10^{-5} Torr. One hydrogen molecule requires two adsorption sites. Hence, the close values of N^* for hydrogen and acetylene lend additional support to the suggested two-site adsorption of acetylene. An implication of this approach, however, is that N^* is spent in both cases for reaching essentially the same degree of surface coverage, i.e., essentially the same number of surface sites is occupied by the hydrocarbon and by hydrogen when the equilibrium pressure is 2×10^{-5} Torr. It is not easy to understand why this should be so. As mentioned, there are some hints that a high degree of surface coverage may exist at N^*. Furthermore, some evidence has been obtained that hydrogen can be adsorbed on the same sites as ethylene (*5*) and methane (*40*). In any event, the outcome of the outlined possibility as to how to interpret the experimental values of N^* fits very well into the consistent pattern of the adsorption mechanisms deduced by the thermochemical and quantum chemical arguments.

D. Supporting Evidence

It has been briefly mentioned above that the energy levels of the occupied molecular orbitals localized on the particular bonds can be correlated with the susceptibility of these bonds to perturbation by a surface. This is analyzed in detail elsewhere (*36*). In summary, localization of the highest occupied molecular orbitals on the π-bonds of the unsaturated hydrocarbons indicates that these bonds interact preferentially with a surface. Further, the markedly lower energy of the occupied molecular orbitals located on the C–H bonds in alkynes compared to alkenes suggests that the C–H bonds in the former compounds are less reactive towards a surface.

Contradictory conclusions in the voluminous literature on the nature of hydrocarbon surface species makes referring to reported results in favor of one or another adsorption mode somewhat problematic. Without giving a critical survey, we will just mention that the structures of adsorbed acetylene and ethylene proposed in the present study are in agreement with recent electron spectroscopic (*41*, *42*), magnetic (*43*), and some other studies (*16*).

E. Estimate of the Carbon–Molybdenum Bond Strength

Heats of adsorption may be approximately taken equal to the difference in the enthalpies of the bonds broken and formed in the chemisorption process, including the contributions of weak van der Waals interactions of those groups which are not directly chemisorbed, if any:

$$\text{heat of adsorption} = -\Sigma\Delta H_{\text{bonds broken}} + \Sigma\Delta H_{\text{bonds formed}} + \Sigma\Delta H_{\text{vdW}}.$$

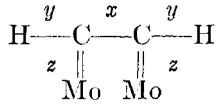
Hence the enthalpy of the adsorption bonds of the assumed surface species [which is not very different from the energy of these bonds (*44*)] can be estimated, provided we can assess the enthalpy or energy of the particular bonds involved in the adsorption process. This is impeded by the uncertainty in the partitioning of the total energy of binding of a molecule into the energies of separate bonds, notably if a multiple carbon–carbon bond is involved (*44–53*), and further by the unknown effect of the external bonding of the species upon their intramolecular bond energies.

A significant perturbation of the gas phase molecular orbitals upon chemisorption has been proved with the back-donation bonding of CO (*34*, *54*). The equilibrium geometry and electron energy state of unsaturated hydrocarbons coordinated to metal atoms in organometallic complexes may strikingly differ from those in the ground state (*55–63*). This indicates that the energies of bonds in gaseous and chemisorbed molecules in general differ.

The true bond enthalpies in hydrocarbon molecules are rather uncertain, if available at all. Therefore, it is advantageous to resort to the bond energy terms, which are additive quantities assigned to the bonds in a molecule in such a way that their sum equates to the experimental heat of atomization, i.e., the total binding enthalpy of the molecule. A remarkably comprehensive and consistent set of such quantities for molecules in their ground states is represented by the Laidler bond energy terms recommended by Cox and Pilcher (*50*).

The recommended Laidler parameters for gaseous acetylene are (kcal/mole):

C–H, 104.19; C≡C, 183.28. The adsorbed species may be depicted as



$$\overset{y}{H{-}}\!\!\!\!\underset{\underset{Mo}{z\,\|}}{C}\overset{x}{-}\underset{\underset{Mo}{\|\,z}}{C}\!\!\!\!\overset{y}{-H}$$

where x, y, and z stand for the Laidler parameters of the particular bonds. Taking 62.5 kcal/mole for the initial heat of adsorption of acetylene, we have

$$z = 62.5/2 + (183.3 - x)/2 + (104.19 - y).$$

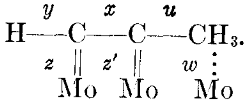
The parameter x is probably not very different from the 85.48 assigned to the C–C bond in saturated hydrocarbons. It might, however, be somewhat increased due to the neighboring double bonds, or reduced by some lengthening of the C–C bond to permit a more perpendicular directioning of the C=Mo bonds to the surface. Suppose that x lies between 80 and 95. The C–H bond parameter is likely to be lower in the adsorbed species compared to gaseous acetylene on account of a change in the bond order of the carbon atoms. Recommended values for

$$=\!C{-}H,\quad =\!\overset{|}{C}{-}H,\quad \text{and}\quad -\underset{|}{\overset{|}{C}}{-}H$$

are 104.19, 100.53, and 96.53, respectively. Hence, z may lie between 80 and 90. Choosing arbitrarily $x = 85.5$ and $y = 100.5$, we obtain $z = 83.8$.

With ethylene, $z = 84.3$, provided 100.5 is chosen for y and 76.1 for the H–Mo bond ($30 + 18 = 48$ kcal/mole is taken for the effective heat of adsorption of the H atoms localized around the C–Mo bond). The disagreement of 0.5 compared to z obtained with acetylene may be due to a small misfit in the Laidler parameters for acetylene and ethylene, and to the employment of an approximate value for the extra interaction energy of hydrogen.

With methylacetylene and propylene, the van der Waals interaction of the CH_3 group with the surface should be taken into account. The recommended Laidler parameters for methylacetylene are: ≡C–H, 104.19; –C≡C– 183.28; ≡C–C, 94.60; and C–H in CH_3, 98.19. The adsorbed species with the marked Laidler parameters of the bonds can be sketched as



$$\overset{y}{H{-}}\!\!\!\!\underset{\underset{Mo}{z\,\|}}{C}\overset{x}{-}\underset{\underset{Mo}{z'\,\|}}{C}\overset{u}{-}\underset{\underset{Mo}{w\,\vdots}}{CH_3}.$$

Taking the initial heat of adsorption of methylacetylene to be 70.0 kcal/mole, and assuming that the C–H bonds in the CH_3 group are unchanged, we obtain

$$z + z' + w = 70.0 + (183.28 + 94.60 - x - u) + (104.19 - y).$$

As for u, values from 85.48 (single bonds neighboring) to 90.07 (vicinal double bond) should be considered. Choosing $x = 85.5$, $y = 100.5$, and consequently $u = 90.1$, we obtain $z + z' + w = 176.0$. Assuming further $z = z' = 83.8$, the van der Waals interaction of the CH_3 group with the surface amounts to 8.4 kcal/mole. The difference of the initial heats of methylacetylene and acetylene adsorption gives $70.0 - 62.5 = 7.5$ kcal/mole for the combined effect of the van der Waals interaction of the CH_3 group and the changes in the intramolecular bond strengths. Similarly, the difference of the initial heats of the propylene and ethylene adsorption gives 8.9 kcal/mole for the combined effect.

No Mo–Mo bond splitting has been considered. Should it be taken into account, $\frac{1}{6}$ of the heat of vaporization (*64*), or 28.4 kcal/mole (*65*) were used.

Let us still mention for the sake of comparison that Bond (*66*), assuming associative two-point adsorption of acetylene and ethylene, estimated the carbon–nickel bond energy to be 57 kcal/mole; Winfield (*67*) obtained 54 kcal/mole. The mean dissociation energy of the back-donation bond between benzene and molybdenum in $(C_6H_6)_2Mo$ is 50.7 ± 2 kcal/mole (*68*), and for the molybdenum–carbonyl bond in $Mo(CO)_6$, 36.3 ± 0.5 kcal/mole (*68*) and 36 kcal/mole (*69*) were reported. Heats of formation of dimolybdenum carbide Mo_2C and of monoatomic gaseous carbon are −11.0 and +171.3 kcal/mole (*70*), respectively. Hence, 91 kcal/mole is obtained for the Mo–C energy in Mo_2C.

F. Adsorption after N*, and Interaction with Hydrogen

Several speculative explanations of the results obtained can be constructed. However, complexity of the problems precludes a meaningful discussion until analysis of the gas phase is available.

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