JOURNAL OF CATALYSIS 47, 178–189 (1977)

Calorimetric Studies of Hydrocarbon Adsorption on Metal Films

III. Methane, Ethane and Propane on Molybdenum

M. SMUTEK AND S. ČERNÝ

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Máchova 7, Prague 2, Czechoslovakia

Received January 17, 1976; revised October 26, 1976

Heats of adsorption of methane, ethane and propane were measured at room temperature on molybdenum films in a calorimeter at 10^{-9} Torr. Initial heats of 65.3, 100.3, and 133.5 kcal/mole were obtained for methane, ethane and propane, respectively. The heats decrease with increasing surface coverage. The rate of the heat liberation falls in the sequence propane $>$ ethane $\gg$ methane. Methane differs from the other two alkanes by low extent of the surface occupation.

Methane is suggested to adsorb at low surface coverage as the species Mo=C=Mo with two of the dissociated hydrogen atoms localized on adjacent sites. When the coverage increases, species Mo≡CH with two hydrogen atoms localized in the close vicinity are gradually formed. Propane undergoes fragmentation into C_1 and C_2 species. The C_1 species is identical with that formed by methane, and its structure changes in the same way when the surface coverage increases. The C_2 species retains in the entire investigated range of coverage the structure Mo=(CH)–(CH)=Mo with four adjacent hydrogen atoms. Ethane is only partially cleaved into two C_1 species having the structure of adsorbed methane. About one half of the adsorbed ethane remains nonfragmented in the form of C_2 species identical with those formed from propane.

The low extent of the surface occupation and slow heat liberation observed with methane can be accounted for by the low energy of molecular orbitals in this molecule. The interpretation of ethane and propane chemisorption is similarly consistent with their molecular orbital description.

I. INTRODUCTION

The adsorption and catalytic behavior of low alkanes on metals and alloys have been studied by a variety of methods. The kinetics of hydrogenolysis and the exchange reactions with hydrogen isotopes have been investigated most frequently (*1–7*). As examples of other studies can serve the investigation of adsorption under static conditions at high temperature (*8*), thermal desorption experiments (*9–11*), work function measurements (*11, 12*), and field emission microscopy (*11, 13*). A comprehensive review of work up to 1970 was given by Anderson and Baker (*14*). In general, there is little agreement on the nature of the surface species formed, i.e., on the fission of the C–H and C–C bonds in the adsorption process, and on the sequence in which the bonds react with a surface.

The energetic aspect of chemisorption of alkanes has been treated but marginally as yet. Some ideas have been outlined about the effect of the strength of adsorption on the velocity of adsorption (*15*), on the rate of catalytic reaction (*16*), and on the reaction mechanism (*17, 18*). Energetic considerations for the CH_4/W system are delineated in Refs. (*8, 14*). It was also

ISSN 0021-9517

forecast that the heat of adsorption of the saturated hydrocarbons should fall sharply as the surface is covered (*19*). However, no direct enthalpic measurements have been accomplished.

The present paper reports the calorimetric heats of adsorption of the three lowest alkanes on molybdenum, which is representative of metals efficient in the cleavage of C–C bonds and was therefore selected also for preceding studies (*20, 21*). The observed initial heats, the heat-coverage dependence, the rate of the heat liberation, and the adsorbed amount of the particular alkanes are used to speculate on the surface species formed. First, thermochemical cycles are constructed for various modes of adsorption. Those modes for which the heat balance of the cycle differs grossly from the experimental heat of adsorption are rejected. In the remaining cases, fitting is attempted by assuming an energetically favorable localization of the dissociated hydrogen atoms in the vicinity of the adsorbed carbon atom, as in Part II (*21*). As auxiliary criteria are used the energies of the molecular orbitals in the particular alkanes, and the ratio of the adsorbed amounts of hydrogen and the alkane in question.

II. EXPERIMENTAL METHODS

The same apparatus and experimental procedures were employed as in Parts I and II (*20, 21*). All experiments were performed at approximately 295°K.

CP Grade gases from Matheson Co., East Rutherford, N.J., were filled into a reservoir on the apparatus. Ethane and propane were subjected immediately before each experiment to repeated freeze–evaporation cycles between liquid nitrogen and room temperatures, with pumping off the first and last portions of the vapor phase on evaporation. Methane was filled into the reservoir cooled by liquid nitrogen until it was liquefied. Before each experiment, it was newly liquefied by cooling the reservoir, and the gas phase above the condensate was pumped off for several minutes.

III. RESULTS

The characteristics of the prepared films are given in Table 1. The primary data were plotted in the form of integral curves and fitted by polynomials $\Sigma\Delta Q = b_0 + b_1 n + b_2 n^2 + b_3 n^3$ ($\Sigma\Delta Q$ stands for the heat evolved by the adsorption of gas amount n), according to the procedure outlined previously (*22*). Coefficients of the fitted polynomials are given in Table 2. Differentiation of these expressions gave the curves of differential heat vs adsorbed amount shown in Fig. 1. Obviously, the values of b_1 equal the initial heats of adsorption.

Methane differs from ethane and propane and from the hydrocarbons dealt with in Parts I and II (*20, 21*) by showing slow heat evolution and low extent of adsorption. In Expt 54, the liberation of heat in the first dose was completed only in 50 sec, instead of the usual 10–20 sec. This time gradually increased up to about 250 sec in the sixteenth dose which was the last one consumed without an equi-

TABLE 1

Characteristics of the Molybdenum Films[a]

Absorbate	1	2	3	4	5	6	7	8	9
Propane	45	10.7	75	4	—[b]	178	317	7.1	
	47	25.5	50	2	—[b]	218	701	8.3	7.5 ± 0.4
	49	14.4	59	4	1	118	413	7.0	
Ethane	48	24.6	67	7	—[b]	128	434	9.4	9.45
	50	23.7	83	6	3	120	483	9.5	
Methane	54	21.2	65	4	2	124	545	8.6	
	55	12.0	80	6	1	112			

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

[b] Calorimeter with the deposited film was separated from the ion gauge and remainder of the apparatus up to the inlet of the first dose by a magnetically operated ground ball valve.

TABLE 2

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

Adsorbate	Film	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
Propane	45	−0.79	0.58	130.86	133.5	2.56	0	0	−38.51	4.44	0.77	1	9	106.8
	47	−3.44	1.26	132.31	±2.1	1.72	0	0	−5.08	0.33	2.03	1	25	107.6
	49	−0.60	0.44	137.33		1.60	0	0	−30.51	1.89	0.57	1	12	105.4
Ethane	48	0.84	0.20	99.37	100.3	0.28	0	0	−2.58	0.05	0.32	1	19	85.8
	50	0.66	0.52	101.25	±1.0	0.74	0	0	−3.45	0.15	0.98	1	27	82.5
Methane	54	0.40	0.10	65.34		0.33	−18.90	0.22	0	0	0.13	0.85	17	33.0

[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 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^*.

librium pressure detectable by the McLeod manometer. From the seventeenth dose onwards, an equilibrium pressure higher than 2×10^{-5} Torr remained over the film, even after several tens of minutes after the dose inlet. The amount of gas adsorbed up to this point is denoted as in the foregoing papers (*20, 21*) by n^*. This quantity referred to 100 mg of film is denoted by N^*. When n^* was reached, further dosing of methane gave merely a very slight heat effect. Unfortunately, analysis of the equilibrium gas was not available. The heat of methane adsorption fell linearly from the lowest surface coverage.

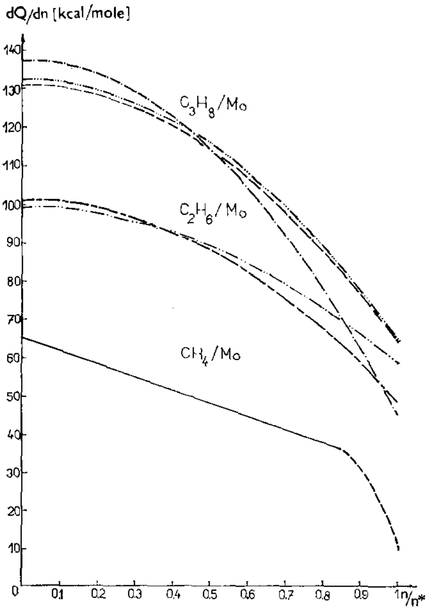


FIG. 1. Differential heat vs adsorbed amount curves obtained by differentiation of the best fit in the integral curves. Propane: (– –) Expt 45; (–···) Expt 47; (–·) Expt 49; Ethane: (–··) Expt 48; (– – –) Expt 50; Methane: (—) Expt. 54.

Experiment 55 confirmed all the essential features of Expt 54: the initial heat amounted approximately to 65 kcal/mole, it was evolved slowly, the heat and the rate of its liberation markedly diminished as the surface coverage increased, and the extent of adsorption was lower than with the other hydrocarbons. However, the heat liberation already after four doses became too slow for a reliable determination of the heat amount. Therefore, this experiment is not included in Table 2 and Fig. 1. The tenth dose was adsorbed still to an equilibrium pressure lower than 2×10^{-5} Torr, but it took 60 min. The total uptake reached 6.0 μmoles of methane/100 mg of film by this dose. The subsequent dose was again very slowly adsorbed.

Ethane was adsorbed up to $n/n^* \approx 0.8$ in 10–20 sec after the dose admission. From this coverage onwards, the heat evolution decelerated until at n^* it was completed only in 170 sec after the dose inlet. Adsorption of doses when n^* was exceeded proceeded with an increasingly retarding rate of heat evolution. When the equilibrium gas was pumped off and subsequently new ethane dosed, retardation of heat evolution continued.

Propane behaved in an analogous manner to ethane, but the deceleration in the heat liberation set in at $n/n^* \approx 0.9$ only, and at n^* the heat was evolved in approximately 60 sec after the dose inlet.

Preliminary experiments were performed with admission of hydrogen onto the adsorbed hydrocarbon layer, after n^* was reached and the equilibrium gas phase pumped off. The admitted hydrogen was readily adsorbed without any detectable equilibrium pressure, and gave 14, 20, and 30 kcal/mole on preadsorbed propane, ethane, and methane, respectively.

IV. DISCUSSION

A. Propane and Methane

It is of advantage to discuss the behavior of methane and propane jointly, because the findings are complementary.

1. The Initial Heat of Adsorption of Propane

The initial heat of adsorption of propane is much higher than that of propylene and of other unsaturated hydrocarbons (*21*). It therefore seems likely that propane undergoes on the bare surface of molybdenum at room temperature dissociation both of the C–H and C–C bonds. This suits the expectations based on the electronic structure of propane, whose molecular orbitals localized on the C–C and C–H bonds have energies close to each other (*23*, *24*) and this indicates that both kinds of bonds can be dissociated with comparable ease.

The suggested adsorption behavior of propane can be examined by means of thermochemical cycles. Let us first assume that propane is adsorbed similarly to propylene, i.e., that it forms species Mo=(CH)–(C–CH$_3$)=Mo and four adsorbed hydrogen atoms. This can be formally expressed by the cycle

$$\begin{array}{llll}
C_3H_{8(g)} \rightarrow C_3H_{6(g)} & + H_{2(g)} & & -29.7\ \text{kcal/mole} \\
C_3H_{6(g)} \rightarrow C_3H_{4(ads)} & + 2H_{(ads)} & & +78.4\ \text{kcal/mole} \\
H_{2(g)} \rightarrow 2H_{(ads)} & & & +30.0\ \text{kcal/mole} \\
\hline
C_3H_{8(g)} \rightarrow C_3H_{4(ads)} & + 4H_{(ads)} & & +78.7\ \text{kcal/mole.}
\end{array}$$

The heat of the first formal step follows from the heats of formation of propane, propylene and methane (*25*), and the heats of the second and third step are taken from Refs. (*21*, *26*), respectively. The heat effect of the cycle is much lower than the initial heat of propane adsorption, amounting to 133.5 kcal/mole. Even if some additional heat were gained by coordination of the dissociated hydrogen atoms around the carbonaceous residue (see below), the heat effect of the cycle still would remain too low. Hence this nonfragmentation mode of the propane adsorption cannot be the only one at low surface coverage, if it becomes operative at all.

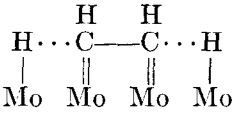
A thermochemical cycle for the adsorption by the two terminal carbon atoms does not fit the experimental initial heat of adsorption either.

Another alternative at low surface coverage is the cleavage of the C–C bond of propane. This suggestion is supported by localization of the frontier molecular orbitals of propane on the C–C bond which, therefore, probably dissociates with least activation energy in an adsorption process. The nature of the fragments is of course not known. By analogy with cyclopropane (*20*) and in view of the product distribution from the hydrogenolysis reactions, we assume as most likely the splitting of one C–C bond with the formation of a C$_1$ and a C$_2$ fragment. Taking the stable species with well-established heats of formation and adsorption, we can write:

$$\begin{array}{lllr}
C_3H_{8(g)} \rightarrow C_2H_{4(g)} & + CH_{4(g)} & & -\ 19.3\ \text{kcal/mole} \\
C_2H_{4(g)} \rightarrow C_2H_{2(ads)} & + 2H_{(ads)} & & +\ 69.5\ \text{kcal/mole} \\
CH_{4(g)} \rightarrow CH_{4(ads)} & & & +\ 65.3\ \text{kcal/mole} \\
\hline
C_3H_{8(g)} \rightarrow C_2H_{2(ads)} & + 2H_{(ads)} & + CH_{4(ads)} & +\ 115.5\ \text{kcal/mole.}
\end{array}$$

The heat effect of the first formal step follows from the heats of formation of propane, ethylene, and methane (*25*). The heat of adsorption of ethylene is taken from Part II (*21*). The nature of the species denoted provisionally as $C_2H_{2(ads)}$ and $CH_{4(ads)}$ is not known.

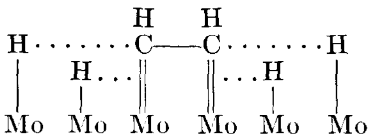
The heat balance of the cycle is 18 kcal/mole lower than the observed initial heat of adsorption of propane. The same difference was found with alkenes (*21*), and tentatively explained by assuming that the two hydrogen atoms dissociated from, e.g., an ethylene molecule, are localized in the vicinity of the carbonaceous residue so that one of them sits near to one Mo=CH– bond, and thereby an extra heat of approximately 18 kcal/mole of hydrogen is gained. Through this suggested interaction in the adsorbed layer, coincidence of the heat effect of the corresponding thermochemical cycle with the observed initial heat of ethylene adsorption was achieved, and the structure



$$\begin{array}{cccc} & \mathrm{H} & \mathrm{H} & \\ \mathrm{H}\cdots & \mathrm{C} & \!\!-\!\!-\mathrm{C} & \cdots\mathrm{H} \\ | & \| & \| & | \\ \mathrm{Mo} & \mathrm{Mo} & \mathrm{Mo} & \mathrm{Mo} \end{array}$$

was suggested for the surface species arising from ethylene.

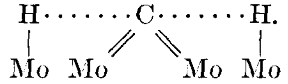
Applying this concept, let us ascribe the difference of 18 kcal/mole between the observed initial heat of propane and the heat balance of the cycle to the coordination of other two hydrogen atoms around the C_2 fragment, thus postulating that one carbon–molybdenum bond is able to localize in its vicinity *two* hydrogen atoms, provided they are available. Hence, the suggested structure of the C_2 species formed from propane is



$$\begin{array}{cccccc} & & \mathrm{H} & \mathrm{H} & & \\ \mathrm{H}\cdots\cdots & & \mathrm{C} & \!\!-\!\!-\mathrm{C} & & \cdots\cdots\mathrm{H} \\ | & \mathrm{H}\cdots & \| & \| & \cdots\mathrm{H} & | \\ | & | & \| & \| & | & | \\ \mathrm{Mo} & \mathrm{Mo} & \mathrm{Mo} & \mathrm{Mo} & \mathrm{Mo} & \mathrm{Mo} \end{array}$$

(hereon referred to as species I), i.e., the structure of adsorbed ethylene plus two extra hydrogen atoms coordinated on the adjacent sites. It should be emphasized that the number of molybdenum atoms representing the metal surface is of course formal, because the available evidence does not permit us to distinguish between, e.g., Mo=(CH)–(CH)=Mo and Mo_2=(CH)–(CH)=Mo_2.

The nature of the C_1 fragment can be proposed only after discussion of the adsorption of methane. It is shown below to be



2. The Initial Heat of Adsorption of Methane

The high initial heat of adsorption of methane points to its dissociative chemisorption under the given conditions. Provided the concept of the adsorption of propane suggesting formation of species I and a C_1 species is valid, *the C_1 species arising from propane and methane must be identical:* if they were different, the initial heat of propane adsorption would not coincide with the heat effect of the abovementioned thermochemical cycle involving formation of Structure I. The decrease of the evolved heat with increasing adsorbed amount (see below) invalidates the possible objection that the extra 18 kcal/mole in the heat of adsorption of propane is in fact due to mutual interaction of the vicinal C_1 species.

When seeking for the mode of adsorption of methane, it is useful to take into consideration the carbon–molybdenum bond strengths of the assumed species. The observed initial heat $\Delta Q = 65.3$ kcal/mole may be taken as the difference between the sum of the energies of the bonds dissociated and formed in the adsorption process:

$$\Delta Q = -\Sigma E_{\text{bonds diss.}} + \Sigma E_{\text{bonds formed}}.$$

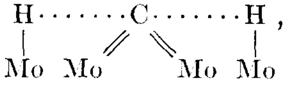
(The dissociation energy and dissociation heat of a bond are rather close and, therefore, are not distinguished from each other in the present considerations.) The stepwise bond dissociation energies in methane required for insertion into the above relation have been published (*27*). We have, however, preferred to estimate the carbon–molybdenum bond energies of the assumed adsorbed species CH_x as their hypothetical heats of adsorption from the gaseous state, obtained from a cycle:

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

The values of Q_1 referring to the particular species CH_x result from the heats of formation of methane (−17.9 kcal/mole) and of the gaseous CH_x species, amounting to (*28*) 31.9, 95, and 171.3 kcal/mole for CH_3, CH_2, and the monoatomic gas C, respectively. The heat of formation of CH, not available in the tables, was estimated by cubic interpolation between CH_3 and $C_{(g)}$ to be 141.5 kcal/mole. This value implies in CH the bond energy of 81.9 kcal/mole, in very good agreement with the 81 kcal/mole established in the stepwise dissociation of methane (*27*). The resulting values of Q_1 are then 49.8, 112.9, 159.4, and 189.2 kcal/mole for CH_3, CH_2, CH, and C, respectively.

If the heat effect of the cycle is equated with the observed initial heat of adsorption of methane (65.3 kcal/mole), the hypothetical initial heats of adsorption Q_2 of CH_3, CH_2, CH, and $C_{(g)}$ are 100.1, 148.2, 179.7, and 194.5 kcal/mole, respectively, provided the independent adsorption of the dissociated hydrogen atoms with the initial heat of 30 kcal/mole (*26*) is considered. It appears, however, logical to assume that by analogy with the C_2 species, two of the dissociated hydrogen atoms can be coordinated by each C_1 species with an additional effective heat of interaction of 18 kcal/mole. Hence we obtain 91, 130, 162, and 176 kcal/mole for the initial heat of adsorption Q_2 of CH_3, CH_2, CH, and $C_{(g)}$, respectively. As mentioned, these heats are taken as equal to the required carbon–molybdenum bond energies.

The energy of the formally double bond Mo=C of the C_2 species Mo=(CH)–(CH)=Mo was estimated to be approximately 80 kcal/mole (*21*). The energy of the formally triple bond Mo≡CH might then amount to 120–130 kcal/mole. When comparing these values with the carbon–molybdenum bond energies estimated for the particular CH_x species in the preceding paragraph, we are inclined to conclude that methane on a sparsely covered molybdenum surface forms probably the species Mo=C=Mo, with the total energy of bonding of 176 kcal/mole, whence 88 kcal/mole results for the energy of one Mo=C bond. Two of the dissociated hydrogen atoms are adsorbed independently, and two are localized in the vicinity of the carbon–molybdenum bond, so that the complete adsorbed complex is



referred to later as species II. The indicated number of molybdenum atoms involved in the bonding should be taken as formal only, as mentioned with species I.

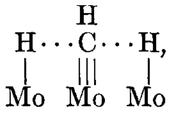
The outlined concept is in accord with the foregoing qualitative considerations, and moreover is corroborated by the heat of formation of solid dimolybdenum carbide which is −11.0 kcal/mole (*28*). By adding the heat of formation of the monoatomic carbon gas (*28*), we obtain 182.3 kcal/mole, in reasonable agreement with the above calculated value of 176 kcal/mole.

3. The Fall of the Differential Heat of Adsorption of Methane with Coverage

The steep decrease in the heat of adsorption of methane might be caused by (i) the falling heat of adsorption of the hydrogen atoms that have remained mobile on the heterogeneous surface, (ii) by the gradually lessening dehydrogenation of the methane molecules at higher coverages, or (iii) by interaction of the adsorbed species with the newly dosed methane at higher coverages.

The first factor is likely to be of minor importance, since the heat of hydrogen on bare molybdenum falls less steeply than the heat of methane (*26*). The operation of the second factor implying coexistence of adsorbed species dehydrogenated to a different extent is questionable, since the low heat of 9 kcal/mole observed immediately before attaining n^* is hardly compatible with an undetectably low equilibrium pressure.

The possible operation of the last mechanism can be analyzed if it is postulated that the species II formed at low surface coverage interacts with an arriving new molecule of methane with formation of two similar adsorbed species CH_x. The observed heat of 9 kcal/mole at n^* is then composed of the bond energies E of the two species of the surface, decreased by the initial heat of adsorption of methane: $9 = 2E - 65.3$ (kcal/mole). Hence, the energy of bonding of the species CH_x to the surface is 37 kcal/mole. The species best compatible with this bond energy term can be found by a thermochemical cycle for the overall process $CH_{4(g)} \rightarrow CH_{x(ads)} + (4 - x)H_{(ads)}$. Let us assume that the energies of bonding between the surface and the species $Mo{\equiv}CH$, $Mo{=}CH_2$, $Mo{-}CH_3$, amount to 130, 80, and 50 kcal/mole, respectively, and that each of the carbon–molybdenum bond can coordinate two hydrogen atoms with an additional heat of 18 kcal/mole, as in the cases discussed above. Then, the heat effect of the cycle amounts to 15, 15, and 36.4 kcal/mole for the species $Mo{-}CH_3$, $Mo{=}CH_2$, and $Mo{\equiv}CH$, respectively. The last value almost coincides with the energy of 37 kcal/mole estimated for bonding of the unknown species CH_x to the surface. Therefore, the species



$$\begin{array}{ccccc} & & H & & \\ H & \cdots & C & \cdots & H, \\ | & & ||| & & | \\ Mo & & Mo & & Mo \end{array}$$

referred to below as species III, appears to be the most probable of the particular alternative. This species is thus assumed to arise on the increasingly covered surface.

The linear character of the heat decrease can be accounted for by the very low energy of the highest occupied molecular orbital of methane, permitting only the most active surface sites to be utilized for chemisorption (*23*). Even the partially occupied active sites are preferentially used by the newly arriving molecules, and thus a lack of suitable sites emerges, despite the fact that plenty of free sites of lower adsorption capability are available. Therefore, the less site-demanding species III arises in spite of being less energetically favorable than species II, and the observed heat of adsorption falls from the lowest surface coverage.

4. The Fall of the Differential Heat of Adsorption of Propane with Coverage

The decrease of the heat of adsorption of propane can be explained similarly to that of methane. Let us assume that the nature of the C_2 fragment formed from propane, i.e., species I, remains unchanged in the whole range of the surface coverage, while the C_1 fragment is identical with the adsorbed methane: it is species II at low surface coverage which transforms into species III as the coverage increases. Then, the low-coverage species II contributes to the initial heat of adsorption of propane with $65.3 + 18 = 83.3$ kcal/mole. The high-coverage species III, for which the heat of adsorption of 37 kcal/mole was inferred in the preceding section, has only one hydrogen atom available for the energetically favorable localization on an adjacent site, so that it contributes to the initial heat of adsorption of propane with $37 + 9 = 46$ kcal/mole. This is 37.3 kcal/mole less than in the former case. Provided each molecule of propane newly adsorbed at high surface coverage leads to the transformation of one species II into species III, the heat of adsorption of propane at n^* should be $133.5 - (2 \times 37.3) = 58.9$ kcal/mole. The observed values in three experiments were approximately 63, 66, and 46 kcal/mole. The mean heat of adsorption would amount to $133.5 - 37.3 = 96.2$ kcal/mole. The observed heat is about 106 kcal/mole.

Another explanation might be the gradually diminishing dissociation of the C–C bonds on the increasingly occupied surface, until at high coverages propane is adsorbed without dissociation of the C–C bond.

Still another mechanism might become operative at higher coverages. Suppose that the chemisorption of propane has a lower activation energy in the close vicinity of previously adsorbed C_1 species due to the simultaneous occurrence of two processes, viz, formation of a C–C bond between the C_1 species and the adsorbed C atom of propane, and rupture of the neighboring C–C bond in propane. In this way, two C_2 species can be formed. To write the heat balance, we start with the equation $2C_3H_{8(g)} \rightarrow 3C_2H_{4(g)} + 2H_{2(g)} - 87.0$ kcal/mole, which gives for the initial heat of adsorption $3 \times 69.5 + 2(30 + 18) - 133.5 - 87 \approx 84$ kcal/mole, decreasing to 70–74 kcal/mole at high coverages.

5. *The Extent of the Surface Occupation by Methane*

The conclusions resulting from an analysis of N^* measured for acetylene and hydrogen have been reasonable, despite a debatable implication that the two gases occupy the same number of surface sites at the equilibrium pressure of 2×10^{-5} Torr (*21*). Hydrogen and methane can probably use the same adsorption sites (*4*). Provided we assume tentatively that also the adsorption of methane and hydrogen yields the same surface coverage at N^*, the ratio $N_{H_2}^*/N_{CH_4}^* = 33.0/8.6 = 3.84$ shows that one methane molecule should occupy $3.84 \times 2 = 7.7$ sites. [$N_{H_2}^* = 33.0$ μmoles is the mean of 32.6 and 33.3 μmoles required to reach the equilibrium pressure of 2×10^{-5} Torr (*26*).] Even with a 10% allowance for the possible experimental error and unaccessible sites, this requirement can hardly be met by a reasonable surface species formed by methane. If each methane molecule at n^* is disintegrated into a Mo≡CH species and three hydrogen atoms, only 57% of sites covered by hydrogen at n^* are covered by methane at n^*.

This suggestion is in line with the great difference between the energies of the frontier orbitals in methane (*23*, *24*) and the Fermi level of molybdenum (*29*), making only the most active sites able to overcome the activation barrier for chemisorption of this compound.

A further corroboration follows from the rapid liberation of 30 and 17 kcal/mole under no equilibrium gas, when two small doses of hydrogen (1.4 and 4.4% of n^*) were admitted to a film precovered by methane and subsequently submitted to pumping off the gas phase. This suggests that some free sites were available.

Finally, incomplete occupation of the metal surfaces by methane has been reported by a number of other authors (*4*, *14*), in qualitative agreement with our conclusions.

6. *The Site Requirement of Propane*

The interpretation of N^* for acetylene in Part II (*21*) leads to a conclusion agreeing with the outcome of the independent thermochemical analysis. As an implication, the same surface coverage by the hydrocarbon and by hydrogen at N^* was involved. Although it is not clear how to rationalize such an assumption, let us apply it tentatively with propane. We obtain from the ratio $N_{H_2}{}^*/N_{C_3H_8} = 33.0/7.47 = 4.42$, that $2 \times 4.4 = 8.8$ sites are needed by a propane molecule at N^*. Accounting for a 9% deficiency observed with acetylene, we arrive at 8 sites.

It is noteworthy that similarly as in the case of unsaturated hydrocarbons the result agrees, despite the debatable assumption involved, with the thermochemically deduced suggestion, i.e., that close to N^*, propane is fragmented into species I and III, requiring in total 8 sites.

7. *The Deceleration of the Heat Liberation*

The slow rate of the heat liberation and its progressive retardation observed in the adsorption of methane can be again explained by the low energy of its highest occupied orbital (*23*). The activation energy for transition from the physisorbed into the chemisorbed state can be overcome on the most active portions of the surface only, and these become gradually blocked as the surface coverage increases.

With propane, the gradual fall in the rate of heat evolution starts only at $n/n^* \approx 0.9$. Energies of the frontier molecular orbitals of propane lie between the energies of the frontier orbitals in the unsaturated hydrocarbons and in methane (*23*, *24*). The former compounds do not exhibit any deceleration of the heat evolution (*21*), while with methane it is conspicuous. Hence, it is in line with the expectation that retardation in the heat evolution of propane was found only close to N^*. Furthermore, this concept is supported by the behavior of ethane.

B. Ethane

1. *The Initial Heat of Adsorption of Ethane*

The initial heat of adsorption of ethane is much higher than that of ethylene and of acetylene (*21*). This points to an appreciable dissociation of the C–C bond. A thermochemical cycle considering fragmentation of ethane into two adsorbed methane species and two hydrogen atoms, has a heat effect of 116.1 kcal/mole: $C_2H_{6(g)} \rightarrow 2CH_{4(ads)} + 2H_{(ads)} + 116.1$ kcal/mole. This is approximately 16 kcal/mole *more* than the observed initial heat of 100.3 ± 1 kcal/mole. Consequently, only a portion of ethane is fragmented into C_1 species, which are assumed to have structure of adsorbed methane (species II). The other portion of ethane is adsorbed without cracking of the carbon skeleton. Assume that these C_2 species are the same as those formed in the adsorption of propane (species I). The heat effect of a thermochemical cycle for this nonfragmentation mode of ethane adsorption amounts to 85 kcal/mole [heats of formation of ethane and ethylene are taken from Ref. (*25*), and an additional heat of 18 kcal/mole accounts for the assumed coordination of two hydrogen atoms around each carbon–molybdenum bond]. Simple calculations show that the two adsorption mechanisms of ethane are operative to approximately the same extent, i.e., that about half of the ethane molecules are adsorbed as C_1 species, and the other half as the C_2 species.

This interpretation is supported by localization of the frontier molecular orbital of ethane both on the C–C and C–H bonds (*23*, *24*). Hence, the activation energies for rupture of the C–C and C–H bonds may be expected to be near to each other. This is a difference from propane, whose highest occupied molecular orbital is located on the C–C bond, making probable its preferential interaction with a surface (*23*). However, the suggested equal operation of the two adsorption mechanisms of ethane actually implies that the C–C bond has somewhat lower activation energy of dissociation than the C–H bond, since the statistical weights for the two processes are 1:6. Preferential configuration of the precursor state might play a role.

2. The Fall of the Differential Heat of Adsorption of Ethane with Coverage

The decrease of the heat to about 55–60 kcal/mole at n^* can be ascribed similarly as in the case of propane to a gradually increasing abundance of the surface species III in the place of the low-coverage species II. Uncertainty in the individual heats, however, does not allow us to discern whether the extent of fragmentation is constant or changes with the increasing coverage.

3. The Site Requirement of Ethane

Referring to Sect. A.6 of this Discussion, let us tentatively assess the number of sites required for the adsorption of ethane at N^* from the ratio $N_{H_2}^*/N_{C_2H_6}^* = 33.0/9.45 = 3.49$. Hence, the effective number of the required sites is $3.49 \times 2 = 7$. If a 9% allowance is made as with propane, we obtain 6.4. Furthermore, the highest occupied molecular orbital of ethane lies rather low, and it may be therefore expected that the least active portion of the surface remains unoccupied due to a too high activation energy of adsorption (*23*). Consequently, the actual number of sites involved in the bonding of an ethane molecule at N^* can be assessed as 6. It should be noted that both suggested modes of ethane adsorption meet this site requirement.

4. The Decelerating Heat Liberation at Higher Coverage

Gradual exhausting of the sufficiently active sites can also elucidate the retardation of the heat liberation which sets in at $n/n^* \approx 0.8$, i.e., sooner than with propane, but later than with methane. This corresponds to the sequence of the respective energy levels of the highest occupied molecular orbitals, which energy correlates with the capability of the particular molecules to be perturbed by a surface (*23*).

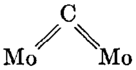
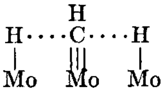
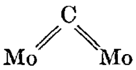
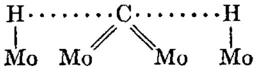
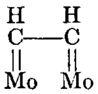
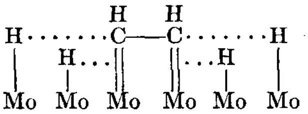
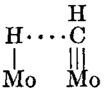
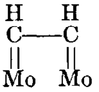
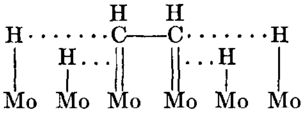
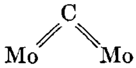
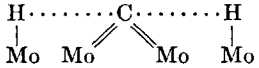
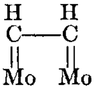
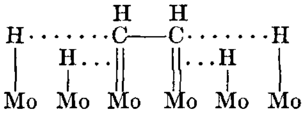
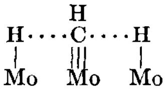
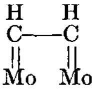
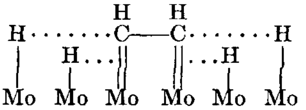
CONCLUSION

Summarizing, we suggest that the alkanes form on molybdenum under the given conditions essentially three kinds of surface species, sketched in Table 3. The dotted link between the hydrogen atoms coordinated to the adsorbed carbon atoms is of schematic significance only, and represents either a direct interaction or an indirect interaction via the metal phase, as pointed out in Part II (*21*). The number of molybdenum atoms involved in the bonding of the suggested species is only formal, since it is not known how many sites, i.e., how many suitable orbitals, one surface atom of the metal possesses.

Our interpretation of the experimental findings is consistent not only for the three alkanes, but fits also into the foregoing analyses of the adsorption behavior of unsaturated hydrocarbons (*21*) and of cyclopropane (*20*). It should be noted, however, that the concept of the energetically favorable localization of the dissociated hydrogen atoms on surface sites adjacent to the carbon atom of the hydrocarbon species, which has enabled us to formulate a common explanation of the experiments, is rather speculative in character. Further work, both experimental and theoretical, would be desirable for verification, refinement, or rejection of the proposed interpretation.

TABLE 3

Suggested Structure of the Surface Species

Gas	Degree of surface coverage	Basic hydrocarbon skeleton	Number of hydrogen atoms localized on adjacent sites	Complete surface complex	Number of free hydrogen atoms on the surface
Methane	Low		2		2
	High		2		1
Propane	Low		2		0
			4		0
	High		1[a]		0
			4		0
Ethane	Low		2		2
			4		0
	High		2		0
			4		0

---

[a] Due to the lack of available hydrogen atoms, one of the energetically favorable sites adjacent to the adsorbed carbon atom remains unoccupied.

ACKNOWLEDGMENT

We are grateful to Drs. S. Beran, I. Haslingerová and Z. Knor for many stimulating discussions and helpful comments.

REFERENCES

1. Sinfelt, J. H., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 23, p. 91. Academic Press, New York, 1973.
2. Sinfelt, J. H., *Catal. Rev.-Sci. Eng.* **9**, 147 (1974).
3. Kemball, C., *Catal. Rev.* **5**, 33 (1971).
4. Frennet, A., *Catal. Rev.-Sci. Eng.* **10**, 37 (1974).
5. Frennet, A., Degols, L., Lienard, G., and Crucq, A., *J. Catal.* **35**, 18 (1974).
6. Dowie, R. S., Whan, D. A., and Kemball, C., *J. Chem. Soc. Faraday I* **1972**, 2150.
7. Guczi, L., Sárkány, A., and Tétényi, P., *J. Chem. Soc. Faraday I* **1974**, 1971.
8. Winters, H. F., *J. Chem. Phys.* **62**, 2454 (1975).
9. Rye, R. R., and Hansen, R. S., *J. Chem. Phys.* **50**, 3585 (1969).
10. Stewart, C. N., and Ehrlich, G., *Chem. Phys. Lett.* **16**, 203 (1972).
11. Shigeishi, R. A., *Surface Sci.* **51**, 377 (1975).
12. Hopkins, B. J., and Shah, G. R., *Vacuum* **22**, 267 (1972).
13. Hellwig, S., and Block, J. H., *Surface Sci.* **29**, 523 (1972).
14. Anderson, J. R., and Baker, B. G., *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, Ed.), Vol. 2, p. 63. Academic Press, New York, 1971.
15. Trapnell, B. M. W., *Trans. Faraday Soc.* **52**, 1618 (1956).
16. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24**, 283 (1972).
17. Guczi, L., Gudkov, B. S., and Tétényi, P., *J. Catal.* **24**, 187 (1972).
18. Visser, C., Zuidwijk, J. G. F., and Ponec, V., *J. Catal.* **35**, 407 (1974).
19. Wright, P. G., Ashmore, P. G., and Kemball, C., *Trans. Faraday Soc.* **54**, 1692 (1958).
20. Černý, S., Smutek, M., Buzek, F., and Cuřínová, A., *J. Catal.* **47**, 159 (1977).
21. Černý, S., Smutek, M., and Buzek, F., *J. Catal.* **47**, 166 (1977).
22. Černý, S., Smutek, M., and Buzek, F., *J. Catal.* **38**, 245 (1975).
23. Beran, S., Černý, S., and Haslingerová, I., presented: First Czech-Italian Symposium on Catalysis, Prague, October 1976, in press.
24. Jorgensen, W. L., and Salem, L., "The Organic Chemist's Book of Orbitals." Academic Press, New York, 1973.
25. Stull D. R., Westrum, E. F., Jr., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." Wiley, New York, 1969.
26. Černý, S., *Surface Sci.* **50**, 253 (1975).
27. Kerr, J. A., *Chem. Rev.* **66**, 465 (1966).
28. Barin, I., and Knacke, O., "Thermochemical Properties of Inorganic Substances." Springer-Verlag, Berlin, und Verlag Stahleisen, Düsseldorf, 1973.
29. Berge, S., Gartland, P. O., and Slagsvold, B. J., *Surface Sci.* **43**, 275 (1974).