Calorimetric Studies of Hydrocarbon Adsorption on Metal Films

V. Hydrocarbons on Platinum

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Heats of adsorption of methane, ethane, propane, ethylene, propylene, acetylene, methylacetylene, allene, and cyclopropane were measured at room temperature in an adsorption calorimeter on platinum films deposited in the 10^{-9} Torr region. Adsorption of methane produced a relatively low heat at a very low rate, and only a very limited adsorbed amount was achieved. The heat fell strongly as the surface coverage increased. Dehydrogenation of the methane molecule to CH_2 and CH_3 surface species was proposed to explain this behavior. Initial heats of adsorption of ethane and propane were relatively high, pointing to both cracking and partial dehydrogenation of these alkanes. A strong decrease of the heats with increasing coverage and a rather low extent of adsorption suggested that some specific surface sites were required. Acetylene and methylacetylene gave virtually the same heat which was initially lower than that of ethane and propane, but higher than that of alkenes. The heat did not exhibit any clear-cut dependence on the coverage in the major part of the investigated range. Adsorption of alkynes took place on a higher proportion of the surface compared to alkanes and alkenes. Nondissociative adsorption with the formation of perpendicularly attached surface species CCH_2 and $CCHCH_3$, respectively, appears to be compatible with the experimental results. Heats of adsorption of monoalkenes were lower than the heats of alkanes and also of alkynes, and mildly decreased with the increasing surface coverage. Partial dehydrogenation of the hydrocarbons and adsorption of the mobile split-off hydrogen atoms on the energetically most favorable sites were suggested to account for the observed behavior. Adsorption of allene produced an essentially coverage-independent heat which was higher than the heat of monoalkenes. A tentative interpretation involves formation of the same adsorbed structure as in the case of the isomeric methylacetylene. The initial heat of adsorption of cyclopropane was higher than that of alkenes, but slightly lower than that of propane. Partial dehydrogenation and limited, if any, fragmentation of the molecule are likely.

INTRODUCTION

It is well known that transition metals differ from each other in their capability to activate molecules of hydrocarbons and to dissociate carbon–hydrogen and carbon–carbon bonds in these molecules. For example, energy spectra of the molecular orbitals of acetylene suggest that an increase in carbon–carbon distance and departure from linearity of the hydrocarbon takes place on $4d$ and $5d$ transition metals, but

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not on $3d$ metals (*1*). On the other hand, Mo was found to be a clear-cut representative of metals that both dehydrogenate and crack cyclopropane at room temperature and low pressure into one- and two-carbon units, while Pt in those conditions was active in cyclopropane dehydrogenation only, not in its cracking (*2, 3*). One can expect that the different number and type of dissociated and formed bonds will be reflected in the respective heats of adsorption.

The foregoing papers of the present series (*4–7*) reported on the calorimetric measurement of nine low molecular weight hydrocarbons on Mo films at room temperature. The results were interpreted in terms of a self-consistent pattern of the sur-

face species formed (*4–6*) and of the reactivity of the particular bonds in the hydrocarbon molecules toward the polycrystalline Mo surface (*7*). Photoemission spectra of ethylene, propylene, and cyclopropane on Mo(110) surface at 300 K (*8*) led to an interpretation fully confirming the suggestions inferred from the calorimetric measurements on Mo films.

The present study deals with heats of adsorption of the same nine hydrocarbons on Pt films at room temperature. The lower adsorption capacity of the prepared Pt films compared with Mo films in the foregoing experiments, and the lower molar heats of adsorption, made the calorimetric measurements more difficult: the amount of gas in the admitted doses had to be low (typically, $3-8 \times 10^{-2}$ μmole), and this diminished precision in the determination of the adsorbed amount, and thereby limited the precision and reproducibility of the final results.

EXPERIMENTAL METHODS

The calorimeter and adsorption apparatus were of the type described earlier (*9*). The section with the calorimeter vessel and ion gauge was protected after the bake-out from mercury vapor by four traps cooled by solid CO_2 in ethanol. The calorimeter wall was cooled during film deposition by streaming water (about 283 K). No subsequent sintering of the film was performed. The experiments were carried out at approximately 295 K. Specification of the gases used was given in Refs. (*4–6*) and that of the platinum wire in Ref. (*9*).

The heat produced by adsorption of a gas dose was evaluated from the deflection-time trace on the recorder chart in the following manner (*10*). The base line was fixed by hand and the deflections read in 10-s steps. The values were fed into a calculator which found the best cooling constant from the single-exponential falling branch of the trace by the least-square method. The calculator further used this cooling constant

for construction of the adiabatic curve by means of trapezoidal integration.

The integral plot of the individual heat values ΔQ vs the adsorbed amount values Δn was 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 produced by the adsorption of the gas amount $\Sigma \Delta n = n$) according to the procedure outlined earlier (*9*). Differentiation of these expressions gave the curves of differential heat vs adsorbed amount. As criteria for the selection of the best fit, the lowest standard deviations both of the overall fit and of the individual coefficients in the polynomial, and the lowest number of these coefficients, i.e., the simplest possible expression, were taken. We consider this procedure superior to the fitting of the plotted $\Delta Q/\Delta n$ quotients, since the error in the individual quotients may be sizeable. The imposed criterion of the simplest possible expression involves a risk of disregarding the local departures from the smooth curve. In some studies, even slight departures were regarded to contain important information (*11–15*), but in the present case we are inclined to consider most fluctuations not to be established firmly enough. In many of our experiments, however, an intercept $b_0 < 0$ was obtained on the abscissa axis when the integral curve was extrapolated from the experimentally covered range to lower coverages, indicating a non-zero uptake with zero heat. This is doubtlessly related to the extraordinarily low heat values obtained for the initial doses in these cases. A similar phenomenon was reported for the systems $O_2/Co,Ni,W$ (*16*); H_2/Ti (*17, 18*); H_2/Ni (*19*); H_2/Pt (*9*). On the other hand, this behavior was not found in the H_2/Fe system (*14*), and was but slight or entirely absent in our experiments with hydrocarbons on Mo (*4–6*). Missing experimental points in the low-coverage region of the presented heat-coverage curves in other published work do not permit one to judge whether this phenomenon occurs or not.

Its origin is not clear: it might be due to some deep physical cause (*20*), but it might

merely be an artifact resulting from partial adsorption of the first admitted doses in cold traps (20) and/or on the outgassed tubing of the apparatus (17–19), or it might be explicable in terms of displacement of some impurities from the film by the initial doses. In the present case we shall disregard the initial too low heat values and consider them to be an artifact.

The time which elapsed between the dose admission and the moment when the deflection-time curve assumed the form of the established single-exponential cooling, served as an approximate measure of the rate of the heat-producing process.

RESULTS

Characteristics of the films prepared in the 19 reported experiments, and the initial heats of adsorption are given in Table 1. Each experiment provided the following information: (i) initial heat of adsorption, i.e., the heat resulting from the best fit to the measured data extrapolated to zero coverage; (ii) dependence of the heat on the adsorbed amount; (iii) an approximate estimate of the rate of the heat production; (iv) the maximum extent of chemisorption, i.e., the total amount of gas adsorbed with an appreciable and relatively rapidly produced heat effect. For the sake of comparison of the particular experiments, the adsorbed amounts were referred to 100 mg of the film. However, determination of the film weight was subject to an appreciable error, and thus the values of the adsorbed amount per 100 mg of the metal are of an approximate nature only.

A. Alkynes

The initial heat of adsorption of acetylene amounted approximately to 45 kcal/mole (188 kJ/mole). This was lower than the heat of the studied alkanes, but higher than that of the studied alkenes. No clear-cut dependence of the heat on the adsorbed amount

TABLE 1

Characteristics of the Experiments on Pt Films and Heats of Adsorption Extrapolated to Zero Coverage

Expt No.	1	2	3	4	5	6	7
Acetylene							
I	42.8	254	1	0.5–1	140	521	45.5(190.2)
II	33.2	251	4	2–20	107	247	44.9(187.7)
III	35.8	170	1	6–8	168	594	46.0(192.3)
IV	32.3	175	1	4–8	99	271	42.5(177.6)
Methylacetylene							
V	32.6	225	3	5–30	169	266	45.1(188.5)
VI	17.4	300	2	8–9	146	370	44.1(184.3)
Ethylene							
VII	26.3	145	3	3–13	95	155	35.0(146.3)
VIII	39.7	232	0.5	0.8–1	146	312	34.9(145.9)
IX	34.0	191	0.5	2–3	121	303	36.5(152.6)
Propylene							
X	43.9	325	2	2–6	154	455	41.9(175.1)
XI	36.4	130	2	25–30	221	318	42.7(178.5)
Allene							
XII	35.3	250	2	3–10	163	254	47.0(196.5)
Cyclopropane							
XIII	34.0	187	1	3–5	283	98	53.7(224.5)
XIV	18.0	37	5	6–8	253	205	50.5(211.1)
Methane							
XV	39.3	320	3	2–5	189	76	36.1(150.9)
Ethane							
XVI	52.9	242	1	1–4	79	155	52.5(219.4)
XVII	41.2	290	1	6–12	105	182	52.1(217.8)
Propane							
XVIII	24.2	137			238	127	67.9(283.8)
XIX	36.0	370	2	5–8	164	230	59.3(247.9)

Note. Columns: (1) film weight (mg); (2) time of the film deposition (min); (3) background pressure before the film deposition (Torr $\times$ 10^{-9}), 1 Torr = 133 Nm^{-2}; (4) pressure during the film deposition (Torr $\times$ 10^{-9}); (5) time from the end of deposition to the first dose (min); (6) time from the first to the last dose inlet (min); (7) heat of adsorption extrapolated to zero coverage (kcal/mole), the values in parentheses in kJ/mole.

was obtained in the major part of the measured coverage range. The extent of rapid chemisorption with the above mentioned heat (i.e., the adsorbed amount up to the abrupt fall in the heat-coverage dependence) was high compared to alkenes and particularly to alkanes (Fig. 1).

Methylacetylene exhibited much the same behavior except a somewhat lower extent of rapid chemisorption with constant heat.

B. Alkenes

Adsorption of ethylene produced an initial heat of approximately 35–36 kcal/mole (146–150 kJ/mole) (Fig. 2). The heat fell
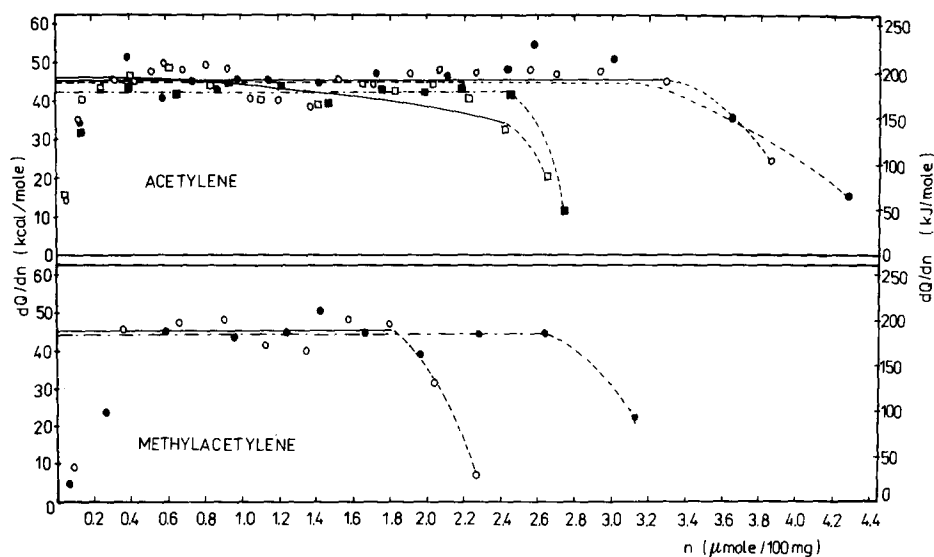
FIG. 1. Differential heat vs adsorbed amount for acetylene and methylacetylene. Points represent the quotients $\Delta Q/\Delta n$ (ΔQ is the heat produced by the adsorbed amount Δn) referred to 100 mg of the film. The smooth curves were obtained by differentiation of the best fit to the integral curves, except the terminal parts of the curves (marked by a different type of line) which were drawn by hand. Acetylene: (○) Expt I; (●) Expt II; (□) Expt III; (■) Expt IV. Methylacetylene: (○) Expt V; (●) Expt VI.

moderately but steadily as the coverage increased. The maximum adsorbed amount attained was only some $\frac{2}{3}$ of the value for alkynes. Production of the heat was rapid up to high adsorbed amounts.

The heat of adsorption of propylene extrapolated to zero coverage amounted to about 42 kcal/mole (176 kJ/mole) (Fig. 2). It was distinctly higher than the heat of ethylene, but did not reach the value for alkynes. The decrease in the heat of propylene with increasing coverage was similar to that of ethylene, as was the adsorbed amount attained.

The initial heat of adsorption of allene was clearly higher than the heat of propylene (Fig. 3). No convincing evidence was obtained for a dependence of the heat on coverage. The extent of adsorption of allene was rather close to that found with monoalkenes. However, the rate of the heat production after admission of allene doses was somewhat lower compared to mono-
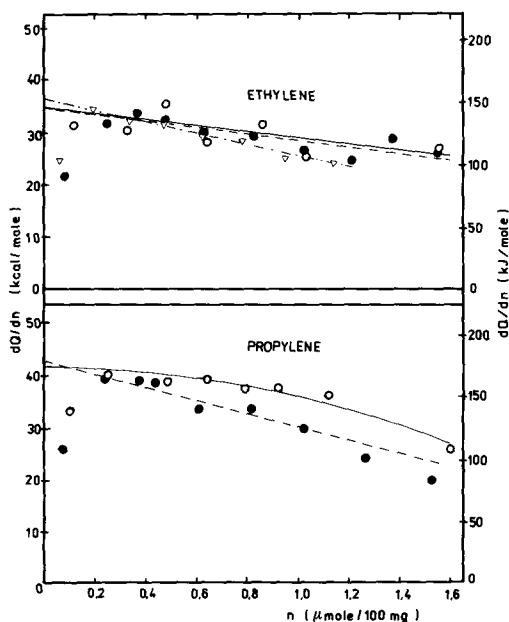

FIG. 2. Differential heat vs adsorbed amount for ethylene and propylene. Points and smooth curves were obtained as in Fig. 1. Ethylene: (○) Expt VII; (●) Expt VIII; (▽) Expt IX. Propylene: (○) Expt X; (●) Expt XI.
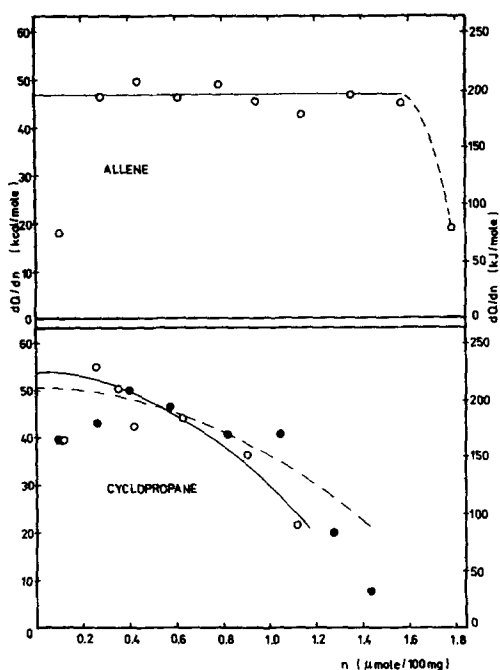
FIG. 3. Differential heat vs adsorbed amount for allene and cyclopropane. Points and smooth curves obtained as in Fig. 1. Allene: (O) Expt XII. Cyclopropane: (O) Expt XIII; (●) Expt XIV.

FIG. 4. Differential heat vs adsorbed amount for methane, ethane, and propane. Points and smooth lines obtained as in Fig. 1. Methane: (◆) Expt XV. Ethane: (O) Expt XVI; (●) Expt XVII. Propane: (O) Expt XVIII; (●) Expt XIX.

alkenes and alkynes, particularly at low adsorbed amounts.

C. Cyclopropane

The initial heat of adsorption of cyclopropane was higher than that of alkenes and alkynes, but somewhat lower than the heat of propane. No clear dependence of the heat on the coverage could be obtained from the measured data at low adsorbed amount. With the increasing coverage, however, the heat falls (Fig. 3). The heat production was rapid up to high adsorbed amounts.

D. Alkanes

Adsorption of methane, ethane, and propane gave heats strongly falling with increasing adsorbed amount (Fig. 4). The initial heat value, as well as the maximum amount of gas adsorbed wit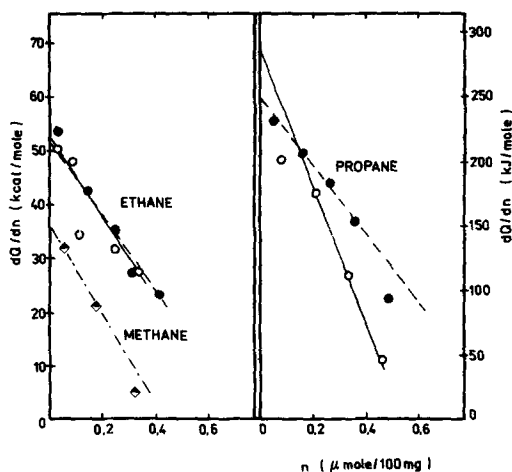h an appreciable and measurably fast heat production in-creased in the order methane < ethane < propane. The rate of the heat production increased in the order methane ≪ propane < ethane. The heat of adsorption of methane was evolved at a strikingly low rate from the first dose already, while adsorption of ethane and propane led to a decelerating heat production at higher adsorbed amounts only. The extent of chemisorption of alkanes was by far the lowest of all the hydrocarbons studied.

When the chemisorption of ethane in Expt XVI came to an end and further dosing of ethane gave only an extremely low and slowly produced heat, admission of ethylene resulted in a rapidly evolved heat of the same magnitude as on the bare platinum film. Subsequently dosed ethane was again practically not adsorbed.

DISCUSSION

Interpretation of adsorption measurements on polycrystalline materials in terms of the structure of the surface species formed is generally difficult and debatable.

Nevertheless, many of the results of the present study can be explained consistently with the current ideas on the structure of the surface species formed in the adsorp-

tion of hydrocarbons on platinum. Our arguments are based mainly on the measured heat effects. The data obtained for the extent of adsorption per 100 mg of the film are of limited precision and are therefore used as secondary evidence only.

A. Alkynes

1. Acetylene. The approximately constant heat of acetylene adsorption can be accounted for by immobility of the chemisorption products. In addition, several other factors may operate, such as a single type of adsorption product in the coverage range in question, a constant distribution of species in a mixture formed on the surface, or formation of a varying mixture of surface species which, however, give rise to much the same heat effect. The relatively low heat value indicates that the number of Pt–C and Pt–H bonds (if the latter are formed at all) resulting in the adsorption of acetylene is not too high, though multiple bonding of the adsorbed species to the surface is not excluded. The extensive adsorption of acetylene compares well with the adsorption of hydrogen on Pt films (9), suggesting that approximately two adsorption sites are involved in the adsorption of one molecule of acetylene, in accordance with the literature data (1).

A number of configurations have been proposed for acetylene adsorbed on platinum, both with the carbon–carbon bond axis parallel to the plane of the surface (21–32) and in essentially perpendicular orientation to the surface (25, 27, 33–41). The latter structures were suggested mainly for the Pt(111) surface. It has been established that the acetylene molecule adsorbs on Pt surfaces with only a negligible and reversible dissociation of hydrogen (1, 40). Below room temperature it is oriented parallel to the surface, forming two σ-bonds, and on the surface with triangular symmetry possibly an additional π-bond to a third Pt atom forms (27, 31, 35, 41). This surface species, however, is only metastable and at room temperature begins to convert to a

stable configuration (38). According to the current generally accepted view, this conversion is likely to be associated with migration of one hydrogen atom to form a CCH_2 species (34, 35). The tendency of the adsorbed acetylene to shift one hydrogen atom to the other carbon atom may be caused by the resulting energy gain due to a lesser distortion of the species adsorbed in this mode, or due to formation of the maximum number of carbon–Pt bonds (35). Two structures have been proposed for the CCH_2 species, namely a vinylidene structure $=C=CH_2$ bonded perpendicularly to the surface (27, 40, 41), and a 2-ethyl-1-ylidine structure $\equiv C—CH_2—$ (35). Provided a hydrogen atom is available, the ethylidyne species $\equiv C—CH_3$ was suggested to form on Pt(111) surface at room and higher temperatures (33, 34, 36, 40). The observed heat of adsorption appears to be better compatible with two than with three or four surface bonds formed.

2. Methylacetylene. The virtual identity of the observed heats of adsorption of methylacetylene and acetylene points to the same type of bonding of the two hydrocarbons to the surface. In full accordance with this, LEED measurements showed similar behavior of acetylene and methylacetylene on Pt(111) surfaces (42). Recently, the LEED patterns and the intensity vs voltage spectra were found to be nearly identical for room temperature phases of acetylene, methylacetylene, ethylene, and propylene on Pt(111) surface (41). Hence, a species $=C=CH—CH_3$ fully analogous to the proposed acetylene-induced species $=C=CH_2$, appears to be formed in our system.

Moreover, the equal heats of methylacetylene and acetylene adsorption suggest a perpendicular and not a parallel attachment of the adsorbed species to the surface from the following reasoning. Parallel orientation of the methylacetylene species would make the distance of the rotating CH_3 group low enough for van der Waals interaction with the surface, so that a higher heat of methyl-

acetylene compared to ethylene would result. This was actually found with Mo films (5), while the present experiments gave clearly almost the same heat for both gases.

As an additional evidence of a perpendicular orientation of the adsorbed species one could take the similar extent of adsorption of acetylene and methylacetylene per 100 mg of the platinum film, obtained in Expts. III, IV, and VI. On the other hand, Expts. V and/or I and II show a relatively lower adsorbed amount for methylacetylene compared to acetylene. This might be interpreted in terms of a partial blockage of the vacant sites by the rotating CH_3 group of methylacetylene adspecies in parallel orientation to the surface, similarly as on Mo films (5). However, we have already mentioned that the arguments based on the estimated film weight should be taken with reservation.

B. Alkenes

1. Ethylene. An explanation of the fall in the heat of adsorption of ethylene with increasing adsorbed amount can be sought in the varying proportion of the particular modes of adsorption. Indeed, a decreasing degree of ethylene dehydrogenation with increasing surface coverage has been suggested (43, 44). According to another proposal (36, 45), ethylene is bonded on a sparsely populated platinum surface in a mode with its C–C axis parallel to the plane of the surface, while as the coverage increases, species in perpendicular orientation with only one carbon atom attached to the surface gradually prevail. Furthermore, increasing surface coverage may necessitate an increasing energy amount consumed to displace surface species that partly block the domains required for adsorption of ethylene (cf. Refs. (43, 46)). The changing pattern of adsorption with coverage can be accounted for by surface heterogeneity (44), either of the primary nature (limited number of suitable sites), or of the induced na-

ture (electronic perturbation or geometrical blocking of the adsorption sites). Explanation of the observed fall of the heat of ethylene adsorption in terms of surface heterogeneity, however, implies the debatable assumption of an appreciable mobility of the adsorbed species. Moreover, it is not clear why a similar decrease in the heat would not be then observed with alkynes.

A more likely explanation of the heat fall can be based on the dissociation of hydrogen from the adsorbing ethylene molecule. Recently it has been established that ethylene adsorbs on platinum in the form of associatively di-σ-bonded species only well below room temperature (27, 35, 40, 41, 45). At 300 K and above, a hydrogen atom is split off and the remaining C_2H_3 species blocks two adsorption sites. Our heat data are consistent with this picture, provided the dissociated hydrogen does not desorb appreciably from the platinum surface under our experimental conditions (room temperature, total equilibrium pressure 10^{-5} Torr at most). Namely, atoms of hydrogen are mobile on Pt surface at room temperature and thus they can seek the most favorable sites that have remained still unoccupied on the heterogeneous surface. Then the total heat of adsorption gradually falls, similarly as when hydrogen alone is adsorbed on Pt films (9). An alternative cause of the observed heat decrease might lie in slight displacement of hydrogen atoms from the surface by each new dose of the alkene. The extent of this desorption should grow with the increasing coverage.

Compatible with this approach is the lower extent of adsorption of ethylene compared to acetylene in that one extra adsorption site is required for the hydrogen atom split off from the adsorbing ethylene molecule, while alkynes are adsorbed without dissociation.

Ethylidyne $O{\equiv}C$—CH_3 (33, 34, 36, 37, 47), ethylidene $={=}CH$—CH_3 (35, 38, 47), and vinyl O—$CH{=}CH_2$ (27, 48) species were proposed for the Pt(111) surface. Evidence of vinyl species on the Pt(100) 5 × 20

surface at 330 K was also reported (46). Two layers of ethylene exhibiting a different behavior were observed in a work function study on Pt films at 298 K (49). The coexistence of different modes of ethylene adsorption was found in various systems. Vibration spectroscopic data on Pt(111) at room temperature are preferentially interpreted in terms of an ethylidyne species $\equiv C$—CH_3 bonded to three Pt atoms (33, 34, 36). Another assignment of the EELS data, however, led to a proposal of a CH–CH_2 species multiply bonded to Pt(111) surface by both carbon atoms (45). The C_2H_3 species readily exchanges its hydrogen atom with deuterium (40). On the other hand, it is very stable against further dehydrogenation to a C_2H_2 species: a temperature of approximately 450 K is necessary for this process, and rupture of the carbon–carbon bond appears to occur (40). Adsorbed acetylene, however, is reported to be easily hydrogenated to the same C_2H_3 species (33–35, 41). This would suggest a higher heat of adsorption for ethylene compared with acetylene, in contrast to our experimental finding.

Some arguments in favor of weaker adsorption of ethylene compared with acetylene can be found in the earlier literature (21, 29, 50), but they appear to be discarded in recent spectroscopic and other work. The main selectivity phenomena in the hydrogenation of acetylene are explicable in terms of the weaker adsorption of ethylene (21–23), but this evidence is only indirect. A clue might lie in different modes of adsorption on the particular crystal planes. Fischer and Kelemen (46) actually found a rather different adsorption behavior of ethylene on Pt(100) and Pt(111) surfaces, while acetylene behaved on the both planes in a similar way. In particular, adsorption of ethylene on Pt(100) surface gave rise to adsorbed acetylene besides the C_2H_3 species, in one case even at 200 K. Moreover, the kinetics of ethylene adsorption on Pt(100) surface was governed by a law indicating that four nearest neighboring sites

must be vacant if the molecule arriving at the central site is to be adsorbed. However, the inferred conclusions should be accepted with some caution, particularly the argument that ethylene is adsorbed on Pt(100) surface more weakly than acetylene.

2. Propylene. The heat of adsorption of alkenes was earlier claimed to decrease with increasing substitution (21). A heat of about 12 kcal/mole (50 kJ/mole) was reported for the propylene/Pt system (51). However, the present calorimetric experiments gave a higher heat of adsorption of propylene than of ethylene in the major part of the measured range. This points to a different mode of adsorption of the two gases on Pt films, while LEED results on Pt(111) surface provided evidence of similar, perpendicularly oriented surface structures of room temperature ethylene and propylene, as well as of acetylene and methylacetylene (41). One way to explain the observed heats may be the formation of multibonded species in parallel orientation to the surface, involving some interaction of the unadsorbed CH_3 group with the surface. A more likely interpretation may lie in a higher degree of dehydrogenation of propylene at room temperature compared to ethylene. Actually, the results of Salmerón and Somorjai (40) can be taken as evidence that dehydrogenation of adsorbed species increases from ethylene to butenes. Further work is desirable to elucidate this problem.

Leaving aside the heats, the observed similar extents of adsorption of ethylene and propylene are compatible with the concept that the room temperature propylene species assumes a propylidyne structure by analogy with the ethylene-induced species (41). One could also speculate that only a fraction of sites on platinum can activate the molecules of alkenes to a degree sufficient for their adsorption. However, quantitative comparison of the observed extents of adsorption is uncertain due to the reasons outlined.

3. Allene. On the strength of hydrogenation studies on Group VIII metals, allene

was claimed to be adsorbed more strongly than propylene (*29, 52*). The strength of adsorption was expected to decrease slightly in the sequence acetylene > methylacetylene > allene (*53*).

In the present study on platinum films, the sequence of the initial heats is propylene < methylacetylene < allene. Heats of formation and hydrogenation of allene are 1.6 kcal/mole (6.7 kJ/mole) higher than the respective heats of the isomeric methylacetylene (*54*), and this compares well with the difference of 2–3 kcal/mole (8.5–12.5 kJ/mole) found in the heats of adsorption. Both allene and methylacetylene exhibited essentially constant adsorption heat over a large range of coverage. All this points to the same mode of adsorption of allene and methylacetylene, viz. a $=C=CH-CH_3$ surface species. Compatible with this suggestion is the somewhat lower rate of heat production after admission of allene doses compared to monoalkenes and alkynes, particularly at low adsorbed amounts. Some activated process connected with the complex shift of hydrogen atoms might account for this. The maximum coverage of allene is lower than that of methylacetylene, and is close to that of monoalkenes. One can again speculate that the same sites are required for activation of monoalkenes and dialkenes, while alkynes can be adsorbed on a larger portion of the surface.
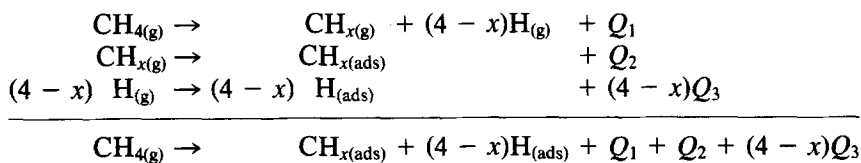
C. Cyclopropane

A number of modes of cyclopropane adsorption have been proposed from a variety of experiments (*4*). The observed lower heat of cyclopropane compared to propane suggests a lower number of bonds formed to the Pt surface. This is compatible with the results of mass spectrometric analysis of the gas phase over Pt films (*2, 3*) which did not reveal any fragmentation of the cyclopropane molecule into C_1 and C_2 fragments. Therefore the observed heat appears to be due to the ring opening and dehydrogenation, diminishing at higher adsorbed amounts. No recent spectroscopically based suggestions for the structure of the adspecies are available, and our heat data are not sufficient for detailed proposals.

D. Alkanes

1. Methane. Chemisorption of the methane molecule doubtlessly involves rupture of one or several of its C–H bonds. The low extent of methane adsorption shows that this rupture can be accomplished only on a limited number of sites. High activation energy is needed for this process, as indicated by the slow production of the heat (cf. Ref. (*55*)). This behavior is probably due to the large gap between the energy level of the highest occupied molecular orbital of methane and the Fermi level of Pt (*7*), resulting in a low reactivity of the molecule toward the platinum surface.

We may try to estimate the number of hydrogen atoms dissociated from the methane molecule by means of the thermochemical cycle

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

(Q_i stands for the heat effect accompanying the respective step). The energy Q_3 for $H_{(g)}$ $\rightarrow H_{(ads)}$ amounts approximately to -260 kJ/mole (*9*). The values of Q_1 were esti-

mated as $+208$, $+472$, $+666$ and $+791$ kJ/mole for CH_3, CH_2, CH and C, respectively (6). Equating the heat effect of the cycle, $Q_1 + Q_2 + (4 - x)Q_3$, to the observed initial heat of adsorption of methane (-151 kJ/mole), we obtain for Q_2 the values -99, -103, -37 and $+98$ kJ/mole corresponding to the adsorption of CH_3, CH_2, CH and C, respectively. The value obtained for the adsorption of C is obviously not acceptable, and also the value for CH is too low. Hence, CH_3 and CH_2 are left as the possible surface species. Additional evidence, given below, is in favor of the CH_2 species.

The steep fall of the heat-coverage curve of methane cannot be explained by the mobility of the dissociated hydrogen atoms, because they cover only a small fraction of the surface, on which only a slight decrease in the heat of adsorption of hydrogen gas alone would occur (9). Lateral repulsion cannot account for the observed heat fall either. Such a fall occurs when the adspecies are sufficiently mobile as to find the energetically most favorable sites. However, this is not the case here: there is no reason why most of the sites could not bind CH_3 or CH_2 species, once they were formed on the appropriate active sites. Since the extent of methane adsorption was very limited, one has to assume that there is an essentially immobile adsorption, without any appreciable distribution of the surface species by surface migration.

An explanation could be based on the assumption that activation energy and enthalpy of the methane adsorption vary in opposite direction, as the coverage increases. However, it is not likely that formation of one kind of species would lead to such a large variation of values as indicated by our results. Therefore, formation of two kinds of active species on different types of active sites appears as more probable: the species CH_2 would arise on the most active sites, while the species CH_3 would be formed on another type of sites, not permitting further dissociation to CH_2 species and

having a high energy barrier for adsorption. The low heats of adsorption at higher coverage may indicate that the formation of CH_3 species is reversible, its reversed course being prevented by dispersion of the dissociated hydrogen atoms over the surface. However, such a low heat of adsorption for the CH_3 species is very unlikely; about one-half the value for CH_2 species would seem to be plausible.

One might also assume that toward the end of adsorption the formation of CH_3 surface species from CH_4 is accompanied to some degree by the endothermic conversion of CH_2 into CH_3 species, provided that the dissociated hydrogen atoms prefer sites close to the CH_2 and CH_3 species (similarly as on Mo films—cf. Ref. (6)). However, the basic assumption of all these hypotheses, namely that the less exothermic reaction is accompanied by a high energy barrier (a sort of "compensation effect"), seems to be rather artificial in this case.

Nevertheless, it is possible to formulate yet another model involving only one kind of active sites and varying environment, which appears as the most satisfactory. Kinks in steps, and perhaps other active surface sites, can dissociate the arriving methane molecules (either from the gas phase or by surface migration) into CH_2 species and two hydrogen atoms, provided there is enough room for this dissociation. The dissociated hydrogen adatoms sojourn preferentially near the CH_2 adspecies (cf. Ref. (6)) and preclude dissociation of two hydrogen atoms in the further arriving methane molecules, permitting dissociation of only one hydrogen atom. Thus the formation of CH_2 species is reduced while the formation of CH_3 species increases as the active sites are gradually filled. The arriving methane molecules are, however, able to react also with the CH_2 adspecies to CH_3 adspecies (disproportionation) with only a small net heat production. This reaction has a higher energy barrier and dominates in the last phase of the methane adsorption.

Further experimental material is required to prove or disprove the particular hypothetical models.

2. Ethane. The heats of adsorption of ethane and methane exhibit a parallel coverage dependence, the values for ethane lying some 16 kcal/mole (67 kJ/mole) higher. The chemisorbed amounts attained are similar. This indicates that the same type of sites on platinum surface are active in the chemisorption of both gases. However, the energy barrier for the interaction with unoccupied surface is lower with ethane than with methane, as revealed by the considerably higher rate of the heat production of ethane.

The energy of a surface Pt–H bond amounts to 57–67 kcal/mole (240–280 kJ/mole) (*9, 56–58*). The energy of a surface Pt–C bond is certainly higher; dissociation energy of the gas molecule PtC was determined as 145 kcal/mole (606 kJ/mole) (*59*). Hence, the rather high initial heat of ethane adsorption may in principle be due to an extensive dehydrogenation of the molecule with formation of several Pt–H bonds, or the major part of the heat may stem from cracking of the molecule and formation of two Pt–C bonds. In this case the CH_3 radicals would dissociate further to form CH_2 adspecies on the free surface. By analogy with the ethane/Mo system (*6*), and with reference to the work function study of the ethane/Pt system (*60*), we are inclined to interpret the measured heats in terms of both cracking and partial dehydrogenation of ethane on platinum. Provided that the above outlined model of methane adsorption involving dissociation of two hydrogen atoms is correct, the difference of 16 kcal/mole in the heats of adsorption of ethane and methane reflects the energy difference between a Pt_2–CH_2 and a C–C bond: the energy E of the Pt–C bond would be about $\frac{1}{2}E_{C-C}$ + 8 kcal/mole, i.e., approximately 51 kcal/mole (213 kJ/mole). Because ethylene and acetylene are adsorbed on Pt at room temperature without cracking, the rate-determining step in the ethane chemi-

sorption with the lowest activation energy is probably the dissociation of the C–C bond, followed by further dehydrogenation of the methyl moieties. The decrease of the heat of adsorption in the subsequent doses is due mainly to the blocking of the dehydrogenation of the CH_3 species, similarly as with methane, rather than to dehydrogenation of the ethane molecules. The same extent of adsorption as with methane points to a twofold number of occupied surface sites.

Cracking of the ethane molecule is likely to be conditioned by its suitable activation on some specific surface sites, e.g., at kinks of the surface steps (*61–63*). Chemisorption of ethane comes essentially to an end when the relatively scarce activation sites are used up. By contrast, chemisorption of ethylene occurs without cracking and thus it can be expected to be less site-demanding. Actually, when chemisorption of ethane in Expt XVI was practically terminated, admission of ethylene gave the same heat as on the bare film.

3. Propane. A gauge defect precluded monitoring of pressure during the film deposition in Expt XVIII. Therefore, more confidence should be given to Expt XIX which provided an initial heat only some 7 kcal/mole (29 kJ/mole) higher than the heat of ethane. The fall of the heat with increasing coverage is similar to that with methane and ethane. Essentially the same interpretation of the results as with ethane appears to be reasonable, consistent with the outcome of the work function measurements (*60*). The slightly higher initial heat may be due to a somewhat higher degree of dehydrogenation and/or cracking. The slightly slower heat production compared with ethane might result from a higher activation energy of the surface interaction required by the more bulky propane molecule.

Note added in proof. The same extent of adsorption of ethane and methane points to a twofold number of sites occupied by the C_1 species formed from ethane, but this does not necessarily indicate a doubling of the required *active* sites. Provided the sites active in dissociating the C–H bond in methane and the C–C bond in

ethane are on the surface, isolated or in a linear arrangement (e.g., on the edges of steps), the C_1 species formed can be accommodated without occupying any vicinal *active* site. The different chemisorption behavior of ethane and ethylene observed in Experiment XVI, and in general the different adsorption properties of alkanes and alkenes and the different surface sites for their adsorption, may have some relevance to the interpretation of the selectivity of the Fischer–Tropsch CO hydrogenation in terms of the adsorption–desorption properties of the primary reaction products [H. Schulz, S. Rösch, and H. Göckebay, *in* "Coal: Phoenix of the '80s, Proceedings, 64th CIC Coal Symposium" (A. M. Al Taweel, Ed.), p. 486, Canad. Soc. Chem. Eng., Ottawa, 1982].

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