JOURNAL OF CATALYSIS **47**, 159–165 (1977)

Calorimetric Studies of Hydrocarbon Adsorption on Metal Films

I. Cyclopropane on Platinum and Molybdenum

S. ČERNÝ, M. SMUTEK, F. BUZEK,[1] AND A. CUŘÍNOVÁ[2]

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 cyclopropane were measured at room temperature in an adsorption calorimeter on platinum and molybdenum films deposited in the 10^{-9} Torr region. An initial heat of 123.6 kcal/mole, mildly decreasing with increasing adsorbed amount, was obtained with molybdenum, while a coverage-independent heat of 47.1 kcal/mole resulted with platinum.

The experimental data for molybdenum are consistent with the concept that extensive fragmentation of the C_3 skeleton occurs at low surface coverage, giving rise to C_1 and C_2 species of the basic structure Mo=C=Mo and Mo=(CH)–(CH)=Mo. The proposed species are essentially the same as suggested for the adsorption of saturated hydrocarbons. The possible simultaneous operation of a nonfragmentation mechanism is not excluded. The mild fall of the heat with increasing surface coverage has not been satisfactorily explained.

I. INTRODUCTION

The behavior of cyclopropane in chemisorption and hydrogenation on metal surfaces makes this hydrocarbon attractive as a model compound for the study both of the activity and the selectivity of metal catalysts, and of the relation between chemisorption and catalysis. Therefore, much experimental and theoretical work has been devoted to cyclopropane–metal systems.

Data on the heat of adsorption of cyclopropane on metals are, however, scarce and open to questions. Benson and Kwan (*1*) measured the isotherms of cyclopropane on a silica–alumina supported nickel catalyst at 0 and 32°C and obtained isosteric heats from 7.0 to 8.8 kcal/mole. Other estimates of the heat have been inferred from kinetic measurements only: the adsorption coefficient resulting from a kinetic equation fitted to the rates of cyclopropane hydrogenation was substituted for the equilibrium constant K_a in the van't Hoff isochore $[\partial \ln K_a/\partial T]_P = \Delta H^0/RT$, from which ΔH^0 was obtained, and to this parameter the meaning of an approximate isosteric heat was ascribed. A few kilocalories per mole resulted for ΔH^0 on a number of metals (*2*). The complexity of the cyclopropane adsorption on metals, however, makes the validity of this approach questionable, and it is used only exceptionally at present (*3*). The relative strength of cyclopropane adsorption compared to hydrogen was often deduced from the reaction orders of cyclopropane hydrogenation (*3–13*). On this basis it was believed that hydrogen is more strongly adsorbed than cyclopropane, so that the catalyst surface in a hydrogenation reaction is occupied by relatively strongly adsorbed hydrogen, and the rate-determining step in-

---

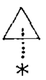
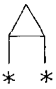
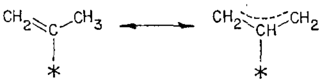
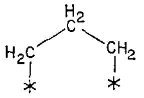
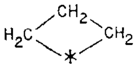
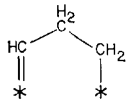
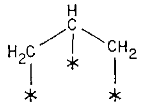
[1] Present address: Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 6.

[2] Present address: Geoindustria, Prague 7.

ISSN 0021-9517

TABLE 1

Proposed Forms of Chemisorbed Cyclopropane

Structure	Mechanism of formation	Refs.
	π-bond between the partially delocalized electrons of the ring and the vacant *d*-orbitals of the metal	(*2, 15, 16, 20–22*)
	Dissociation of one hydrogen atom	(*5, 8, 15, 16, 20*)
	Dissociation of two hydrogen atoms	(*25*)
	Ring opening	(*20, 26*)
	Ring opening	(*6, 14, 16, 18, 20, 23, 24, 26*)
	Ring opening	(*23*)
	Ring opening	(*25*)
	Ring opening	(*10, 26*)
$C_1 + C_2$ species	Dissociation of two C–C bonds	(*14, 15, 24, 25*)

volves weakly chemisorbed (*2*), physisorbed (*6*), or even gaseous (*3, 5*) cyclopropane.

Further investigation of cyclopropane adsorption and hydrogenation on metals has revealed that dissociation both of the C–H and C–C bond can occur, that the latter may involve not only the ring opening but also cracking (fragmentation) of the three-carbon skeleton, and that the extent of these processes depends on the nature of the metal and on the experimental conditions (*11, 14, 15*). The disclosed complexity of the adsorbed layer also prompted suggestion of the strong adsorption of cyclopropane, generally accepted nowadays (*16–19*). However, no direct thermochemical data have been available.

A number of modes of cyclopropane adsorption have been proposed from a variety of experiments (Table 1). Besides the adsorption, also collision and interaction of gaseous cyclopropane with the adsorbed hydrogen atoms dissociated from another cyclopropane molecule should be considered (*5, 23*).

Further complications arise by the likely conversion of the adsorbed species into other structures, and by their reactions with surface hydrogen (*5, 7, 12, 14–16, 18, 20, 23*). Likelihood of the occurrence of the particular species was discussed, e.g., by Merta and Ponec (*20*). The experimental (*7, 16, 20, 27, 28*) and theoretical (*29*) studies of the cyclopropane–iron system give a further insight into the complexity of processes which may take place.

Extensive splitting and formation of bonds in the suggested schemes makes cyclopropane chemisorption attractive for a calorimetric investigation. Molybdenum is very active in the cracking of the C_3 skeleton of cyclopropane into C_1 and C_2 fragments, while platinum does not fragment it at all at room temperature (*20, 25, 28, 30*). Therefore, we have selected these two metals for the present study.

II. EXPERIMENTAL METHODS

The calorimeter and adsorption apparatus have been described in detail elsewhere (*31*). The system was fitted with a mercury diffusion pump and mercury float valves. The section with the calorimeter and ion gauge was protected from mercury vapor after the bake-out by two traps cooled by solid CO_2 in ethanol.

Cyclopropane B. P. (ICI Ltd., Wilmslow, England) was taken from a cylinder. Immediately before each experiment the gas was subjected to repeated freeze–evaporation cycles between liquid nitrogen and room temperatures, the first and last portions of the vapor phase being pumped away. Mass-spectrometric analysis of the gas dosed to the film showed 0.06% of C_4 species as admixtures.

Hydrogen, prepared by electrolysis, was purified by diffusion through a hot palladium thimble.

The platinum and molybdenum wires for the preparation of films were the same as in Refs. (*31*) and (*32*), respectively. The films were deposited at about 285°K. The area of the calorimeter wall covered by film was always about 100 cm^2.

III. RESULTS

Three films of platinum and three films of molybdenum were prepared for the calorimetric experiments (Table 2). Column 6 gives the time spent in putting the calorimetric system into operation (evacuation of the jackets, wiring into the measuring circuit, thermal stabilization). All experiments were carried out at approximately 295°K.

As is well known, cyclopropane dosed to the bare film at room temperature is at the

TABLE 2

Characteristics of the Platinum and Molybdenum Films[a]

No.	1	2	3	4	5	6	7	8	9	10
Pt films										
23	34.0	187	4	—[b]	4	283	352	5	0.80	0.85 ±0.04
30	18.0	37	7	—	—[c]	313	436	5	0.93	
61	43.1	285	9	—	—[c]	114	226	10	0.82	
Mo films										
38	12.6	30	7	—	—[c]	180	429	17	11.0	10.4 ±0.3
51	12.3	30	5	—	3	124	324	15	10.2	
52	18.3	78	5	—	2	150	509	24	10.1	

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

[b] Heated for 30 min at 80°C.

[c] Calorimeter with the film separated from the remainder of the apparatus up to the inlet of the first dose by a magnetically operated ground ball valve.

TABLE 3

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

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
Pt films													
23	−0.13	0.24	46.13	47.1 ±1.0	1.50	—	—	—	—	0.23	1	5	45.2
30	−0.20	0.08	46.15		0.75	—	—	—	—	0.08	1	5	44.6
61	0.30	0.09	49.06		0.42	—	—	—	—	0.14	1	10	49.5
Mo films													
38	−1.17	0.40	118.88	123.6 ±2.6	1.27	−9.51	0.86	—	—	0.52	1	17	105.0
51	−0.27	0.29	127.79		1.84	—	—	−3.30	0.65	0.48	0.93	15	120.1
52	0.07	0.17	124.09		0.39	—	—	−2.01	0.16	0.42	0.90	24	116.0

[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 average 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^*.

beginning rapidly adsorbed to a very low residual pressure. After an uptake of n^* micromoles, the equilibrium pressure reaches the value of 2×10^{-5} Torr (1 Torr = 133 Nm^{-2}) detectable by the McLeod manometer. It increases progressively when further increments of cyclopropane are added.

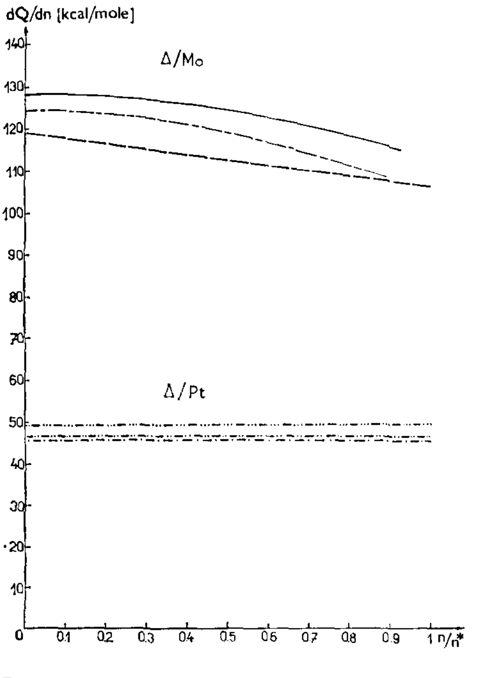


FIG. 1. Differential heat-coverage curves of cyclopropane adsorption on molybdenum and platinum obtained by differentiation of the best fit to the integral curves. Molybdenum films: 38 (– –), 51 (——), 52 (—–); platinum films: 23 (·–), 30 (··–), 61 (···–).

Heat evolved by further dosing after n^* had been attained can be determined only approximately due to the lack of knowledge of the equilibrium gas composition, and due to the increasingly appreciable heat transport between the calorimeter and cold traps via the gas phase.

The primary experimental data up to n^* were plotted in the form of integral curves $\Sigma\Delta Q$ vs $\Sigma\Delta n$ (ΔQ stands for the heat evolved by the adsorption of Δn micromoles) and fitted by a computed analytical expression, the differentiation of which gave the required differential heat vs adsorbed amount curve. A more detailed outline of this method is given in Ref. (*31*). Parameters of the best fitting polynomials $\Sigma\Delta Q = b_0 + b_1 n + b_2 n^2 + b_3 n^3$ are given in Table 3. The resulting curves are shown in Fig. 1. In the experiments 51 and 52, the fit broke down before n^* was reached, and the heat fell to approximately 80 kcal/mole. The values of b_1 obviously equal the initial heats of adsorption, viz, 46.1, 46.1, and 49.1 kcal/mole in the particular experiments with platinum, and 118.9, 127.8, and 124.1 kcal/mole with molybdenum. As criteria for the selection of the best fit were taken 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. The intercept $b_0 < 0$ on the abscissa axis, obtained by extrapolation of the integral curve from the experimentally covered range to lower coverages, indicates a nonzero uptake with zero heat, which is likely to be due to partial adsorption of the first dose in the cold traps (*31*).

The heat liberation in each dose up to n^* was completed within 10–20 sec. No subsequent heat evolution was observed. The uptake of cyclopropane dosed after n^* was reached proceeded with gradually decreasing rate and increasing equilibrium pressure. The heat liberated by the first doses after n^* was both on platinum and on molybdenum of the same order of magnitude as before n^* was reached.

When a molybdenum or platinum film consumed an amount of cyclopropane exceeding n^*, the equilibrium gas phase was pumped off, and a dose of hydrogen admitted; rapid evolution of approximately 10 kcal/mole on platinum and of approximately 20 kcal/mole on molybdenum took place. When the equilibrium gas phase was pumped off and a new dose of hydrogen was admitted, it was again rapidly adsorbed with the same heat and equilibrium pressure as the preceding dose. A number of subsequent hydrogen doses were adsorbed with a decreasing heat and increasing equilibrium pressure.

IV. DISCUSSION

The heats of adsorption of cyclopropane on platinum and on molybdenum differ markedly from each other. This points to different adsorption mechanisms. Merta and Ponec (*20*, *25*) concluded from mass spectrometric experiments that on platinum at room temperature, only opening of the cyclopropane ring occurs, leading eventually to self-hydrogenation of the C_3 species into propane. Over molybdenum, however, in addition to propane also methane and ethane appear in the self-hydrogenation products, indicating fragmentation of the C_3 skeleton into C_1 and C_2 species. It was not possible, however, to deduce from this evidence the nature of the surface species. We will now examine how the calorimetric data could contribute to the specification of the adsorbed species.

A. Platinum

The comparatively low heat of adsorption points to a nonfragmentation mechanism of adsorption. The constant heat up to n^* suggests that no change in the mechanism of adsorption occurs in this range of adsorbed amount.

The data obtained, however, are not sufficient for a proposal to be made of the nature of the species formed. The heat of adsorption of propylene would be required for a thermochemical analysis. Measurement of this heat is under way and it seems useful to postpone further discussion until it is available.

B. Molybdenum

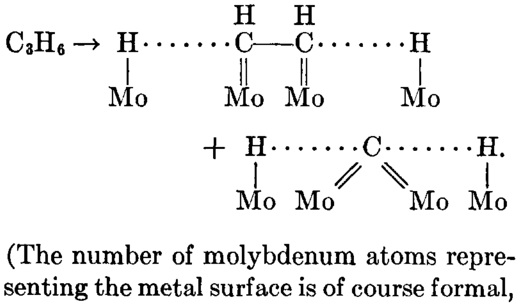
1. *Initial Heat*

The high initial heat of adsorption indicates that fragmentation of the C_3 skeleton of cyclopropane occurs, in accordance with Merta and Ponec (*20*, *25*). Let us assume a complete fragmentation into C_1 and C_2 species on the sparsely covered surface, and write a formal thermochemical cycle:

$$\begin{array}{llll}
C_3H_{6(g)} \rightarrow CH_{4(g)} & + C_2H_{2(g)} & & + Q_1 \\
CH_{4(g)} \rightarrow CH_{4(ads)} & & & + Q_2 \\
C_2H_{2(g)} \rightarrow C_2H_{2(ads)} & & & + Q_3 \\
\hline
C_3H_{6(g)} \rightarrow CH_{4(ads)} & + C_2H_{2(ads)} & + Q_1 + Q_2 & + Q_3.
\end{array}$$

Q_1 is the formal "heat of dissociation," calculated from the respective heats of formation (*34*) to be -23.6 kcal/mole. Q_2 and Q_3 are the observed initial heats of adsorption, i.e., 65.3 kcal/mole (*35*) and

62.5 kcal/mole (*33*). We must, however, still take into account the interaction between the particular species in the adsorbed layer. In Parts II (*33*) and III (*35*) arguments are given in favor of a hypothesis that each molybdenum-bonded carbon atom of a hydrocarbon species has in its vicinity two sites on which hydrogen atoms, if available, are adsorbed with a heat effectively increased by 18 kcal/mole. According to Part III (*35*), methane on a sparsely covered molybdenum surface undergoes complete dehydrogenation and forms the species Mo=C=Mo with two hydrogen atoms localized on adjacent sites. The remaining two hydrogen atoms which cannot be coordinated by the single adsorbed carbon atom, are freely mobile on the surface. In the case of cyclopropane, however, the two hydrogen atoms can be coordinated by the C_2 fragment. The heat effect of the cycle is thereby increased by 18 kcal/mole to $-23.6 + 65.3 + 62.5 + 18 = 122.2$ kcal/mole. This is very close to the observed average initial heat of cyclopropane adsorption, amounting to 123.6 kcal/mole. Hence it can be suggested that cyclopropane disintegrates at low surface coverage into two species, one of which is identical with the adsorbed methane, and the other one with the adsorbed acetylene having two extra hydrogen atoms localized on the adjacent sites. Referring to the structures discussed in Parts II and III (*33, 35*), we can therefore write:



(The number of molybdenum atoms representing the metal surface is of course formal, since the available evidence does not permit to distinguish between, e.g., Mo=C=Mo and Mo_2=C=Mo_2.)

The consistency of this proposal with the observed data does not exclude that another mechanism is operative. The extent of the fragmentation is not known, and thus in some of the cyclopropane molecules, only one C–C bond might be broken and a trimethylene biradical formed, as suggested by quantum chemical considerations (*29*). From the biradical, a 1,3-adsorbed species could eventually be formed. Thermochemical estimates indicate such a mechanism as compatible with the observed initial heat of adsorption of cyclopropane. The fragmentation and nonfragmentation mechanisms might operate simultaneously at low surface coverage.

2. Decrease of the Heat with the Increasing Coverage

Explanation of the observed fall in the heat with the increasing coverage is difficult. It is shown in Part III (*35*) that the falling heat of methane, ethane and propane can be satisfactorily accounted for by the gradual transformation of the low-coverage species Mo=C=Mo into the species Mo≡CH, while the structure of the C_2 species remains unchanged. If this mechanism is tentatively applied to cyclopropane, the coverage-independent C_2 species requires 4 sites, the high-coverage species Mo≡CH requires 1 site, and the hydrogen atom localized in its vicinity also 1 site, i.e., in total 6 sites. By definition, n^* represents the number of micromoles adsorbed up to the appearance of an equilibrium pressure of approximately 2×10^{-5} Torr, which is just detectable with McLeod manometer. This magnitude referred to 100 mg of the film is denoted by N^*. Experiments in Ref. (*32*) gave for N^* of hydrogen defined in this way 32.6 and 33.3, i.e., an average of 33.0 μmoles. N^* for cyclopropane is 10.4 ± 0.3 μmoles (Table 2). Provided we assume tentatively that the surface coverage by hydrogen and by cyclopropane is essentially the same at the equilibrium pressure of 2×10^{-5} Torr [cf. Refs. (*33*) and (*35*)], the effective number of sites required by one cyclopropane molecule at n^* is $(33.0 \times 2)/10.4 = 6.3$. This points to 6 sites involved in bonding.

It is worth noting that the site requirement deduced in this way coincides fairly well with the number of sites needed by the surface species suggested from the thermochemical analysis. On the other hand, the assumption of the same surface coverage by hydrogen and cyclopropane at the mentioned equilibrium pressure is certainly debatable, and thus the obtained coincidence might be but fortuitous. Furthermore, a mere qualitative look at the much milder fall of the heat of cyclopropane as compared to the mentioned alkanes, indicates that a common explanation based on the changing nature of the C_1 species is not likely to be entirely realistic. This is suggested also by thermochemical calculations along the same lines as in Part III (*35*). Gradually decreasing fragmentation and increasing operation of the biradical mechanism mentioned in the preceding paragraph might be connected with the observed heat fall.

ACKNOWLEDGMENTS

We are grateful to Drs. Z. Knor and S. Beran for many stimulating discussions. Our thanks are due to Dr. V. Kubelka for the mass-spectrometric analysis of cyclopropane.

REFERENCES

1. Benson, J. E., and Kwan, T., *J. Phys. Chem.* **60**, 1601 (1957).
2. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56**, 1501 (1960).
3. Antl, L., and Schneider, P., *Collect. Czech. Chem. Commun.* **38**, 2408 (1973).
4. Bond, G. C., and Sheridan, J., *Trans. Faraday Soc.* **48**, 713 (1952).
5. Bond, G. C., and Turkevich, J., *Trans. Faraday Soc.* **50**, 1335 (1954).
6. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 368 (1957).
7. Hayes, K. E., and Taylor, H. S., *Z. Phys. Chem. Neue Folge* **15**, 127 (1958).
8. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 383 (1957).
9. Bond, G. C., "Catalysis by Metals," Chap. 11.7. Academic Press, London, 1962.
10. Newham, J., *Chem. Rev.* **63**, 123 (1963).
11. Sinfelt, J. H., Yates, D. J. C., and Taylor, W. F., *J. Phys. Chem.* **69**, 1877 (1965).
12. Proudhomme, J. C., and Gault, F. G., *Bull. Soc. Chim. Fr.* **1966**, 827, 832.
13. Thomson, S. J., and Webb, G., "Heterogeneous Catalysis," Chap. 6.5. Oliver & Boyd, Edinburgh, 1968.
14. Knor, Z., Ponec, V., Herman, Z., Dolejšek, Z., and Černý, S., *J. Catal.* **2**, 299 (1963).
15. McKee, D. W., *J. Phys. Chem.* **67**, 1336 (1963).
16. Anderson, J. R., and Avery, N. R., *J. Catal.* **8**, 48 (1967).
17. Sridhar, T. S., and Ruthven, D. M., *J. Catal.* **16**, 363 (1970).
18. Wallace, H. F., and Hayes, K. E., *J. Catal.* **29**, 83 (1973).
19. Hegedus, L. L., and Petersen, E. E., *J. Catal.* **28**, 150 (1973).
20. Merta, R., and Ponec, V., *Proc. Int. Congr. Catal., 4th, 1968* **2**, 53 (1971).
21. Taylor, G. F., Thomson, S. J., and Webb, G., *J. Catal.* **12**, 150 (1968).
22. Dalla Betta, R. A., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **19**, 343 (1970).
23. Roth, J. A., *J. Amer. Chem. Soc.* **92**, 6658 (1970).
24. Merta, R., and Ponec, V., *J. Catal.* **17**, 79 (1970).
25. Merta, R., dissertation, Inst. Phys. Chem. Czech. Acad. Sci., Prague, 1968.
26. Beelen, J. M., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **28**, 376 (1973).
27. Merta, R., *Collect. Czech. Chem. Commun.* **36**, 1504 (1971).
28. Bastl, Z., unpublished data.
29. Beran, S., and Zahradník, R., *Collect. Czech. Chem. Commun.* **41**, 2303 (1976).
30. Kadlecová, H., Kadlec, V., and Knor, Z., *Collect. Czech. Chem. Commun.* **36**, 1205 (1971).
31. Černý, S., Smutek, M., and Buzek, F., *J. Catal.* **38**, 245 (1975).
32. Černý, S., *Surface Sci.* **50**, 253 (1975).
33. Černý, S., Smutek, M., and Buzek, F., *J. Catal.* **47**, 166 (1977).
34. Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., "The Chemical Thermodynamics of Chemical Compounds." Wiley, New York, 1969.
35. Smutek, M., and Černý, S., *J. Catal.* **47**, 178 (1977).