the concentrations of the Zn(II)·PVI complex or of the Zn(II)·(PVI)$_4$ complexes were estimated to be 10^{-8} M, too low to be of measureable effect. It is not possible to add more Zn(II) to the PVI solution to obtain a higher concentration of the complex without effecting cross linking of the polymer and subsequent precipita-tion. Further studies on this and similar systems employing similar but stronger complexes are under way.

Catalytic Activity of Platinum Black. III. Adsorption and Decomposition of Butanes

D. W. McKee

The adsorption and catalytic decomposition of n- and isobutane on sintered platinum black has been studied in the temperature range 0–180°. Below 50° physical adsorption of both butanes occurred with coverages exceeding a monolayer, but increasing amounts of irreversible chemisorption took place at higher tempera-tures. Above 80°, methane, small amounts of ethane, and propane were desorbed, and a carbonaceous residue was deposited on the metal surface. The extent of decomposition was greater for n-butane than for iso-butane between 100 and 180°, and both cracked more readily than propane under the same conditions. The distribution of products was quite different from that observed in hydrocracking in the presence of excess hydrogen, and no isomerization was detected. The mechanism of butane decomposition is discussed, and it is suggested that the kinetics may be controlled by the rate of hydrogenation of adsorbed hydrocarbon residues.

Introduction

Considerable interest has recently arisen in the use of platinum black as an electrocatalyst in hydrocarbon fuel cells. In this application both dissociative ad-sorption of the hydrocarbon and electrochemical oxi-dation of adsorbed species occur at the metal surface.[1] However, although the rate of the catalytic decomposi-tion of the hydrocarbon plays an important role in determining the over-all performance of the fuel cell anode, the detailed mechanism of this process is not well understood. In particular, little information is available on the extent of adsorption of hydrocarbons on finely divided metals such as platinum black at temperatures where the rate of decomposition is small.

Previous work in this series[2,3] was concerned with the changes that occurred in the cracking patterns of simple hydrocarbons over platinum black during the pro-gressive sintering of the catalyst. In the case of the decomposition of propane and cyclopropane, the specific activity of the metal, or activity per square centimeter, decreased very rapidly during sintering,

suggesting that the latter process involved elimination of the active sites responsible for the hydrocarbon decomposition. The results also indicated that ad-sorption of the hydrocarbon preceded decomposition in every case.

The present paper describes a study of the adsorption and decomposition of normal and isobutanes in the temperature range in which the rate of cracking of the hydrocarbons was slow. It was hoped to compare the results of this work with those obtained previously on the kinetics of cracking of propane and cyclopropane[2,3] on an identical catalyst and with the reported results of hydrocracking of butanes on evaporated platinum films.[4]

Experimental

Materials. The platinum black used in this work was obtained from Fisher Co. and had a chloride content less than 60 p.p.m.; it was part of the same batch used in previous investigations.[2,3] The unreduced black as received had a B.E.T. nitrogen surface area of 19.5 m.^{2}/g., but, in order to eliminate sintering during the catalytic experiments, the metal was initially subjected to a standard reduction–evacuation procedure. About 0.8–0.9 g. of the black was sealed into the vacuum system, and evacuation was carried out at 150° over-night to a pressure below 10^{-6} mm. Dry nitrogen (10 cm.) was admitted to the sample after the latter had been cooled to room temperature, and pure hydrogen was allowed to flow slowly into the catalyst chamber through a palladium membrane. The pres-ence of nitrogen tended to decrease the initial sintering of the catalyst. Following reduction in flowing hy-drogen at room temperature for 1 hr., the temperature of the sample was slowly raised to 150° over a period of 30 min., the flow of hydrogen continuing during this time. Finally, the catalyst was evacuated at 150° for several hours to a pressure below 10^{-6} mm. This procedure was found to reduce the surface area of the black to 7–8 m.^{2}/g., and no further changes in surface area occurred during the subsequent catalytic runs.

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(2) D. W. McKee, *J. Phys. Chem.*, 67, 841 (1963).
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(4) J. R. Anderson and B. G. Baker, *Proc. Roy. Soc.* (London), A271, 402 (1963).
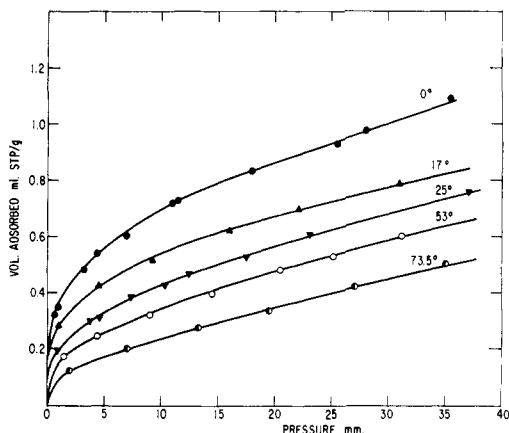
Figure 1. Adsorption isotherms of n-butane on platinum black. Surface area = 7.6 m.^{2}/g.

Figure 2. Adsorption isotherms of isobutane on platinum black. Surface area = 8.0 m.^{2}/g.

The n- and isobutanes were Phillips research grade materials and had purities of 99.90 and 99.98 mole %, respectively, the major impurities being the isomeric butanes. These gases were condensed, degassed, and distilled into the apparatus from a liquid nitrogen trap.

Apparatus and Procedure. The apparatus and experimental techniques were essentially those described previously.[2] Following sintering and reduction of the catalyst, in the case of adsorption measurements at low temperatures, increments of butane were added to the thermostated sample and either pressure was followed as a function of time or constant pressure measurements were made after equilibration at the isotherm temperature. Temperature control was generally made to within 0.5°, and pressure measurements to ±0.01 mm. At higher temperatures, where decomposition was appreciable, samples of the gas phase were condensed, after suitable time intervals, in cooled demountable traps attached to the apparatus and the contents were analyzed in an F & M temperature-programmed gas chromatograph Model 300, using an 8-ft. silica gel column. The residual noncondensable gas after cooling to −195° was always found to be methane, no gas phase hydrogen being detected in any of the cracking experiments. The initial dose of butane admitted to the samples in these runs was adjusted to 3.0 ± 0.2 × 10^{19} molecules, and analysis of the gas phase was usually carried out after a 60-min. contact period. It was found, however, that at the higher temperatures where the initial pressure decrease owing to adsorption was negligible the rate of pressure rise was an accurate measure of the rate of formation of methane in the gas phase.

As in previous studies, it was found that cracking of hydrocarbons led to the deposition of carbonaceous material on the metal surface which could only be slowly and often incompletely removed by hydrogen reduction at elevated temperatures. In fact, as discussed below, poisoning of the catalyst by carbonaceous residues appeared to be more pronounced with butane than with lower molecular weight hydrocarbons. For this reason a new sample of platinum black was generally used after each high temperature cracking experiment. Following adsorption measurements at temperatures below 80°, adsorbed hydrocarbons could
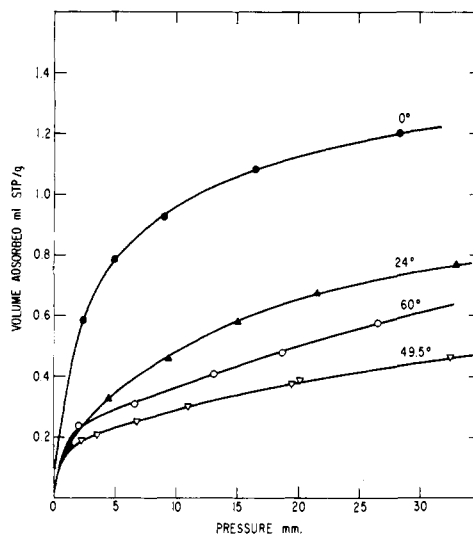
be completely removed by evacuation and reduction of the metal at 150°, and, hence, the same sample could be used for a series of adsorption experiments.

Results

Adsorption of Butanes on Platinum below 60°. Adsorption of n- and isobutanes was found to occur readily on the sintered platinum black samples at temperatures in the range 0 to 60°. With each increment of adsorbate, the gas pressure fell to an equilibrium value in 10 to 20 min., and in this way the typical isotherms shown in Figures 1 and 2 were measured. The isotherms were entirely reproducible after reduction with hydrogen for a few minutes at 100° followed by evacuation at this temperature; however, it was not generally found possible to desorb the hydrocarbon completely by evacuation at the isotherm temperature, and this irreversibility became increasingly marked with increase in the adsorption temperature. The volumes of butane adsorbed at constant pressure decreased with increasing temperature.

Average values for the isosteric heat of adsorption of n-butane dropped from around 9.5 kcal./mole at low coverages to values of about 6.5 kcal./mole around the B.E.T. monolayer capacity, whereas the mean value for isobutane was 11.2 kcal./mole. The heat of adsorption was thus significantly greater than the heat of liquefaction which is around 5 kcal./mole for both adsorbates. The isotherms showed no tendency to approach limiting values, suggesting that at least at 0°, adsorption proceeded beyond the monolayer with both hydrocarbons. The values of the heats of adsorption and the general nature of the isotherms indicated that in this temperature range the adsorption was predominately physical in nature. However, the slow rate of desorption found at the higher temperatures suggested that some chemisorption was taking place, the chemisorbed species being removed by hydrogen reduction but not by evacuation.

Adsorption and Decomposition of Butanes above 80°. On admitting a sample of either butane to platinum black above 80°, the gas pressure over the metal at first decreased, reached a minimum value, and then

Table I. Cracking of Butanes on Platinum Black[a]

Hydro-carbon	Temp., °C.	$(d\Delta P/dt)$, mm./min.	ΔP, mm.	% CH_4	% C_2H_6	% C_3H_8	Reactant decompd.[b]
n-Butane	148	0.1	5.75	96.1	3.7	0.2	0.45
	131	0.049	1.82	88.7	6.4	4.9	0.34
	125.5	0.02	0.90	85.1	6.4	8.5	0.16
	110	0.02	0.71	73.7	15.8	10.5	0.10
	94.5	...	...	76.9	15.4	7.7	...
Isobutane	180	0.12	4.83	95.9	4.1	...	0.42
	150	0.056	2.45	88.9	6.0	4.9	0.40
	105	0.025	0.97	64.5	3.2	32.3	0.20
	91	0.020	0.77	55.1	4.1	40.8	0.10

[a] Catalyst weight = 0.8–0.9 g.; surface area = 7–8 m.^{2}/g.; initial pressure of butane, 12 ± 1 mm. ≡ 1.2 ml. at STP. [b] After 60 min.; in ml. at STP.

increased slowly with time. Subsequent analysis of the gas phase indicated the presence of decomposition products, mostly methane, with small quantities of ethane and propane. The rate of cracking of the hydrocarbon increased rapidly with increasing temperature. The onset of cracking is illustrated in Figures
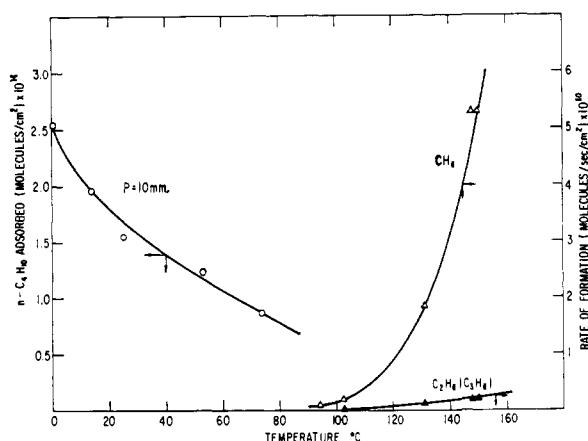

Figure 3. Adsorption and decomposition of n-butane on Pt (0.8–0.9 g., 7–8 m.^{2}/g.). n-Butane admitted = 3 × 10^{19} molecules.
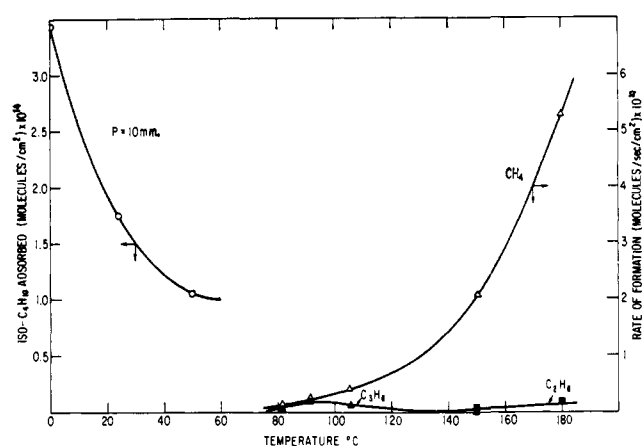

Figure 4. Adsorption and decomposition of isobutane on Pt (0.8–0.9 g., 7–8 m.^{2}/g.). Isobutane admitted = 3 × 10^{19} molecules.

3 and 4, which also show the adsorption isobar for the two adsorbates at an equilibrium pressure of 10 mm. n-Butane cracked more easily than isobutane at temper-

atures above 120°, but the distribution of products was similar in both cases. Below 120°, a greater proportion of propane and a smaller proportion of ethane was formed from isobutane than n-butane.

Typical pressure vs. time curves for n-butane are shown in Figure 5 at a series of temperatures. Below 80° the pressure fell monotonically with time as a result of adsorption of the hydrocarbon on the metal surface. Above this temperature the curves were
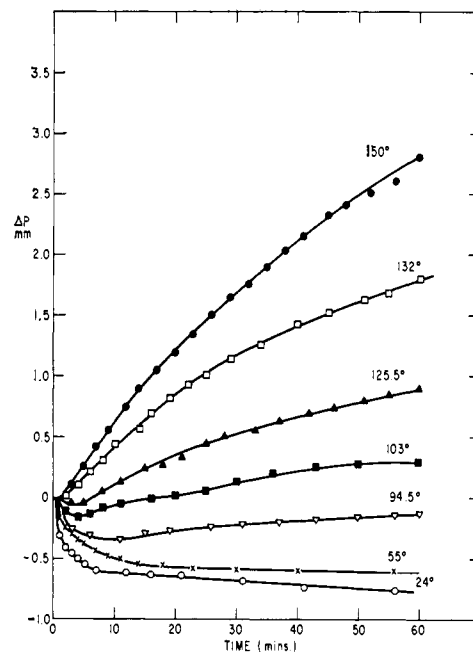

Figure 5. Adsorption and decomposition of n-butane; pressure vs. time. n-Butane admitted = 3 × 10^{19} molecules.

composites of the pressure decrease owing to adsorption and pressure increase owing to the liberation of gaseous decomposition products. At temperatures above 130° where the adsorption effects are negligible, the total increase in pressure over a 60-min. time interval was approximately equal to the pressure of methane found by analysis of the gas phase, the amounts of ethane and propane formed being small at the higher temperatures. The rate of pressure rise was not in general linear throughout this period owing to the poisoning of the metal and retardation of the cracking reaction by carbonaceous residues which progressively built up on the catalyst surface.
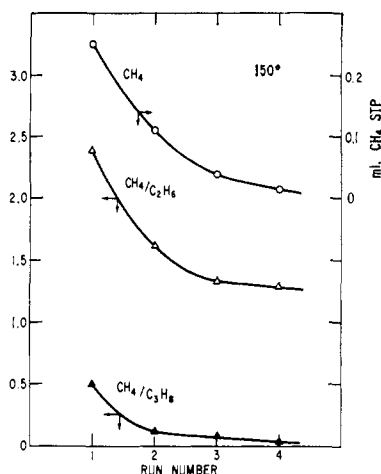
Figure 6. Poisoning of Pt by carbonaceous residues. Successive cracking runs with *n*-butane at 150°.

A summary of results for several different samples of platinum black is shown in Table I. Column 2 gives the temperature of the run; columns 3 and 4, the initial rate of pressure increase and the total pressure change after 60 min. The remaining columns give the percentage composition of the gaseous products at the end of this period and the approximate volume of reactant decomposed after 60 min.

At the lower temperatures, isobutane gave a higher percentage of propane and a lower percentage of ethane than did *n*-butane.

Three different methods were used to estimate the activation energy of the cracking reaction. The rate of formation of methane was obtained from the initial rate of pressure rise over the metal, $(\Delta P/dt)_0$, from the total increase in gas pressure after a 60-min. time interval, ΔP, and from the total volume of methane formed during this period, V, as obtained by analysis. The first method was subject to errors at the lower temperatures owing to initial adsorption of the hydrocarbon, and the other two methods were rendered uncertain at high temperatures by the deposition of carbonaceous residues on the metal. A summary of the results obtained by the three methods is given in Table II.

Table II. Activation Energies for Methane Formation (kcal./mole)

React-ant	Log $(\Delta P/dt)_0$	Log ΔP	Log V
n-C₄H₁₀	17.0	16.2	18.0
			Mean value = 17.1
i-C₄H₁₀	9.7	9.0	11.3
			Mean value = 10.0

n-Butane showed a significantly higher activation energy than isobutane. The corresponding mean frequency factors were 4.2×10^{19} and 3.2×10^{15} molecules of CH₄ formed/(sec. cm.²) for the *n*- and isoparaffin, respectively.

Carbonaceous Residues. The chemisorption of the butanes and their decomposition above 80° was always accompanied by the buildup of strongly ad-

sorbed residues on the metal surface. This material had an over-all C/H ratio between 0.8 and 1.2. After contact with butane at 100°, the metal could be completely reactivated by treatment with hydrogen for a few minutes at 100°; however, more lengthy reduction was required after cracking runs at higher temperatures, and, following butane decomposition at 150° and above, it became impossible to restore the metal to its original activity. The progressive poisoning of a platinum black sample on successive cracking runs with *n*-butane at 150° is illustrated in Figure 6, the metal being reduced with hydrogen for several hours at 150° and then evacuated to 10⁻⁶ mm. after each run. The activity of the catalyst decreased rapidly in spite of this treatment, and the proportion of ethane and propane in the products increased steadily.

Discussion

The behavior of butane at the surface of platinum black can be divided into three temperature regions.

(1) Below about 50°, adsorption is mostly reversible, rapid, and probably physical in nature. The heats of adsorption are somewhat greater than expected for pure physical adsorption, and as desorption becomes progressively slower on raising the temperature it is likely that even at these temperatures there is some contribution from chemisorption. The monolayer capacities as calculated by application of the B.E.T. equation to the low temperature isotherms are shown in column 3 of Table III, and the corresponding cross-

Table III. Properties of Physically Adsorbed Butane Monolayers

Adsor-bate	Temp., °C.	V_m, ml./g.ᵃ	A_m, Å.²	A_l, Å.²	P_0, mm.
n-C₄H₁₀	0	1.0	27.7	32.1	774
	17	0.87	31.9		1417
i-C₄H₁₀	0	1.27	21.8	32.9	1174

ᵃ At STP.

sectional areas of the adsorbate molecules in the monolayer are given in column 4. These latter values are slightly smaller than the values calculated from the liquid density, assuming 12 nearest neighbors (column 5), suggesting that at 0° the adsorbate molecules are more tightly packed than in a condensed liquid. Column 6 gives the approximate saturation vapor pressures of the adsorbates at the isotherm temperatures. In each case the monolayer is complete at a relative pressure around 0.05.

(2) Between 50 and 80° the adsorption is still appreciable but irreversible. Although no gaseous decomposition products are detected in this range, chemisorption is certainly taking place, probably with some dissociation of C–H bonds in the surface layer. At these temperatures the metal is mostly covered with chemisorbed fragments. Thus, an adsorption of 0.26 ml. at STP/g. on a surface of 7 m.²/g. amounts to 1.0×10^{14} molecules/cm.² Assuming that there are approximately 1.2×10^{15} Pt sites/cm.², 1 adsorbed butane would occupy 12 metal sites.

(3) Above 80° decomposition takes place with the formation of methane, small amounts of ethane, and propane and the deposition of a carbonaceous residue

on the metal surface. No hydrogen could be detected in the gas phase although the analytical method was rather insensitive to small amounts of hydrogen; chemisorbed hydrogen atoms were certainly present in the surface. No isomeric butanes were found in the products. The carbonaceous material on the catalyst could only be partially removed by hydrogenation, and the fraction remaining irreversibly adsorbed increased with the temperature of decomposition.

The results indicate that the metal surface is substantially covered with a layer of chemisorbed material before decomposition of the hydrocarbon becomes appreciable. A similar conclusion was reached in the case of propane cracking on nickel.[5] The extent of decomposition was greater for n-butane than isobutane between 110 and 180° although the activation energy for methane formation was somewhat lower in the case of isobutane. This difference may be related to the configuration of the hydrocarbon molecule, the branched chain conferring additional stability. Thus, the free energy of formation of isobutane is less than that of n-butane below about 170°.[6] However, the thermodynamic stability of the molecules may not be related to the ease of dissociation of C–H bonds. Thus, Galwey and Kemball[7] report that dissociative chemisorption takes place more readily with 2-methylbutane than with n-pentane over supported nickel, and results of exchange experiments of isobutane with deuterium have indicated that on some metals exchange of the tertiary hydrogen atom occurs much more rapidly than the primary hydrogens.[8] It is possible that the higher isosteric heat of adsorption observed with isobutane than with n-butane is traceable to the lower energy of dissociation of the tertiary hydrogen in the former case.

The reaction rates and product distributions in this work are quite different from those observed in the case of hydrocracking by Anderson and Baker[4] on platinum films in the presence of a large excess of hydrogen. Although the reactions were carried out at considerably higher temperatures in the latter case, there was no evidence of catalyst poisoning, and it is likely that the excess hydrogen tends to keep the metal surface free of carbonaceous residues. The rate-determining step of the over-all reaction is probably different for hydrocracking, and the proportion of higher molecular weight products tends to be greater. Thus, for the hydrocracking of n-butane over platinum at 287°, the distribution of products was 21% CH$_4$, 23% C$_2$H$_6$, 40% C$_3$H$_8$, and 16% i-C$_4$H$_{10}$, whereas with isobutane at 285° the product composition was 15% CH$_4$, 8% C$_2$H$_6$, 19% C$_3$H$_8$, and 58% n-C$_4$H$_{10}$. These compositions represent analyses after 60-min. contact; no attempt was made to study changes in product distribution as a function of time, and the influence of carbonaceous residues on the results was not known. No isomerization products were found in the present work, and molecular rearrangements appear to require the presence of hydrogen. The high proportions of C$_2$ and C$_3$ products found during hydro-

cracking probably arise as a result of hydrogenation of surface residues which remain on the catalyst in the absence of excess hydrogen. The product distributions found in hydrocracking led Anderson and Baker to conclude that the slow step in this process involves C–C bond rupture rather than product desorption. In the present case, it seems likely that the kinetics of cracking of butanes are controlled by the rate of hydrogenation of the surface residues.

According to Robertson, the decomposition of n-butane on an incandescent platinum filament gives rise mainly to ethyl radicals.[9] Thus at 1050° the products are ethane, ethylene, and only a trace of methane. In this case selective fission occurs at the central C–C bond. This distribution of products is also quite different from that found in the present work. The rates of formation of methane from n-C$_4$H$_{10}$, i-C$_4$H$_{10}$, and C$_3$H$_8$ over sintered platinum black at 150° are 5.3 × 10^{10}, 2.1 × 10^{10}, and 0.8 × 10^{10} molecules/ (sec. cm.^{2}), respectively. Thus, if appreciable amounts of ethane and propane were formed, they would tend to accumulate in the gas phase. If C–C bond fission occurred with equal probability at the 1,2- and 2,3-positions in n-butane and if CH$_4$ and C$_3$H$_8$ are both produced in the former case, but only C$_2$H$_6$ in the latter, the expected product distribution would be 33% CH$_4$, 33% C$_2$H$_6$, and 33% C$_3$H$_8$. The fact that only very small amounts of C$_2$ and C$_3$ species are found with n-butane indicates that fission occurs almost entirely at the terminal C–C bond at the higher temperatures. C$_3$ species which are formed simultaneously remain on the metal surface and contribute to the carbonaceous residue. In isobutane where only terminal C–C bond fission is possible, the theoretical product distribution would be 50% CH$_4$ and 50% C$_3$H$_8$. This ratio is approximately correct below 100°, but the proportion of C$_3$H$_8$ in the products decreases rapidly with increasing temperature. In the case of the cracking of propane,[2] a higher proportion of ethane was found in the products and probably arose from the slow hydrogenation of C$_2$H$_x$ surface species by chemisorbed hydrogen atoms. The mechanism of propane cracking was formulated as[5]
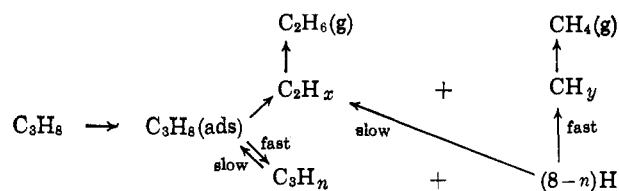
The surface residue is made up of (C$_2$H$_x$ + C$_3$H$_n$) fragments, the C$_2$ species being slowly removed at higher temperatures so that the C/H ratio of the surface phase increases with increasing temperature as a result of increasing coverage by C$_3$ fragments. A similar shift in the composition of surface species has been observed in the case of the decomposition of ethylene on nickel.[10] In the case of butane a similar scheme can be formulated

As the hydrogenation of monocarbon fragments and desorption as methane is probably rapid and C$_2$ fragments are not formed to an appreciable extent,

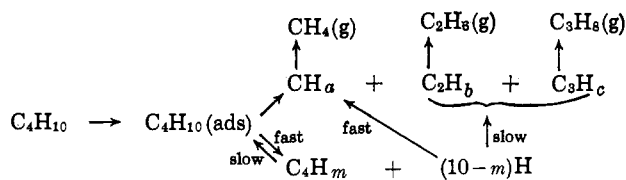(5) D. W. McKee, *J. Am. Chem. Soc.*, **84**, 4427 (1962).
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$$CH_4(g) \qquad C_2H_8(g) \qquad C_3H_8(g)$$
$$\uparrow \qquad \uparrow \qquad \uparrow$$
$$CH_a \;+\; C_2H_b \;+\; C_3H_c$$

$$C_4H_{10} \;\longrightarrow\; C_4H_{10}(ads) \quad \underset{slow}{\overset{fast}{\nearrow}} \quad \overset{fast}{\nwarrow} \qquad \uparrow slow$$
$$C_4H_m \;+\; (10-m)H$$

the kinetics of the cracking reaction may be controlled by the rate of hydrogenation of the C_3 species. The more rapid C–H bond rupture and the higher concentration of hydrogen on the surface accounts for the greater ease of cracking of butane than propane. The fact that the adsorbed hydrocarbon residue is more strongly held in the former case suggests that the relative rate of hydrogenation of surface species of this type increases with the molecular weight of the fragments. As the surface becomes progressively poisoned by residues, increasing proportions of C_2 and C_3 desorption products appear in the gas phase, as shown in Figure 6. From a study of the rate of forma-

tion of methane by the hydrogenation of hydrocarbon radicals from nickel, Galwey[11] concludes that the attack of surface species by hydrogen atoms controls the kinetics of the decomposition of unsaturated hydrocarbons. In addition, the rate of methane formation was generally first order in hydrogen pressure. Similar investigations of the rates of hydrogenation of radicals formed from the dissociative adsorption of an homologous series of saturated hydrocarbons and of the kinetics of hydrocracking as a function of hydrogen pressure would shed further light on the mechanism of these complex hydrocarbon decomposition reactions.

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Ion–Molecule Reactions between Rare Gas Ions and Methane[1]

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Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. Received July 22, 1964

The reactions of He^+, Ne^+, Ar^+, Kr^+, and Xe^+ with methane have been studied over an energy range of 2–200 e.v. The yields of the fragment ions of methane correspond well to the findings of other investigators working at both thermal and higher energies and are found to vary only slightly with the energy of the incident ions. The relative cross sections show some deviations from the predictions of the theory of ion–molecule reactions. Exothermic reactions show an initially decreasing cross section as the kinetic energy of the encounter increases. At higher energies the cross sections level off and tend to increase. $E^{-1/2}$ energy dependence is followed only in the He^+–CH_4 reactions at energies below 10 e.v. Endothermic reaction cross sections are very low and show slight increases with energy over the entire range studied.

Introduction

For almost 40 years, methane has been subjected to irradiation by just about everything from γ-rays to low velocity heavy particles.[3] Experiments have progressed from the original α-radiation study in which the pressure changes in a mixture of methane and radon were taken as evidence of reaction[4] to mass spectrometric analyses of the ionic fragments produced when methane was bombarded by various atomic and molecular ions.[5]

Mass spectrometric evidence has demonstrated that the polymerization observed in the radiolysis occurs to a large extent through ion–molecule reactions.[6,7] The irradiation of an argon–methane mixture by X-rays and 1.5 Mev. electrons yielded the same major products as the α-radiation.[8] Mass spectrometric analysis revealed that the major contribution of the argon ions produced by the irradiation was $Ar^+ + CH_4 = Ar + CH_3^+ + H$. Additional work[9] using krypton indicated two almost equally probable charge-exchange reactions

$$Kr^+ + CH_4 = Kr + CH_4^+$$
$$Kr^+ + CH_4 = Kr + CH_3^+ + H$$
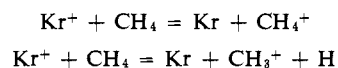
These same systems were studied in a "high" pressure mass spectrometer, and cross sections for the various reactions, including the production of CH_4^+ and CH_2^+ from the argon–methane mixture, were reported.[10]

Xenon–methane mixtures have also been studied in "high" pressure mass spectrometers[11,12] with interesting results. In addition to the usual CH_n^+ fragments, small amounts of ionic complexes, XeH^+ and $XeCH_n^+$

(1) This work was done under the auspices of the United States Atomic Energy Commission.
(2) Lever Brothers Foundation Fellow.
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