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The Hydrogenation of Cyclopropane on Hydrogen-Covered Metal Powders II. Cyclopropane Hydrogenation and Alkane Hydrocracking on Iron, Ruthenium and Osmium

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The hydrogenation of cyclopropane was investigated on iron, ruthenium and osmium. Apparent activation energies were 29.0 ± .8, 11.0 ± .3 and 12.0 ± 1 kcal/mole, respectively. Cyclopropane adsorption was shown to take place by ring cleavage and 1,3-diadsorption. Hydrocracking to form methane and ethane was observed on all metals, but was only slight for osmium. It was more pronounced on ruthenium and severe on iron. Comparative studies of the hydrocracking of ethane and propane on iron and ruthenium were also carried out but in less detail. A mechanism is proposed to explain the experimental results.

INTRODUCTION

A gas chromatographic study of the hydrogenation of cyclopropane on rhenium was presented in Part I of this series (*1*). Part II continues the study by examining the reaction over iron, ruthenium, and osmium powders. Previous investigations have been reported on iron (*2*, *3*) but no comparative study has been carried out on ruthenium or osmium.

Anderson and Avery (*3*) noted that in addition to propane formation, significant quantities of methane and ethane were also observed when cyclopropane was reacted with deuterium over an iron film. At 165°C the relative molar proportions of methane, ethane, and propane were 1:0.42:0.58.

To determine if the cracking products could result from re-adsorption and subsequent cracking of the propane and ethane formed, it was decided to study hydrocracking of these alkanes on ruthenium and iron as a part of this investigation.

EXPERIMENTAL

The apparatus, procedure and method of analysing the data have been described in a previous article (*1*). The ruthenium and osmium catalysts were Johnson–Mathey sponge, the former at least 99.998% pure, the latter 99.999% or better. The iron powder, supplied by A. D. MacKay Inc. was 99.9% pure. Prior to use, the catalysts were reduced *in situ* in a hydrogen flow for 2 hr. Reduction temperatures were 200° for ruthenium, 300° for osmium and 500° for iron.

With the exception of cyclopropane which was Canadian Liquid Air medical grade gas, all gases were C. P. grade supplied by Matheson of Canada Ltd. They were further purified as described in Part I of this series (*1*).

In addition to the hydrogenation of cyclopropane, which was investigated on all three metals, the hydrocracking of propane and ethane was briefly examined on iron and ruthenium. A few experiments on the hydrogenation of propylene were also carried out on these two metals.

RESULTS

Osmium

Plots of propane peak height versus the partial pressure of cyclopropane injected were made in the manner described in Part I (*1*). Such a plot for osmium is shown in Fig. 1. Table 1 shows the conversions of

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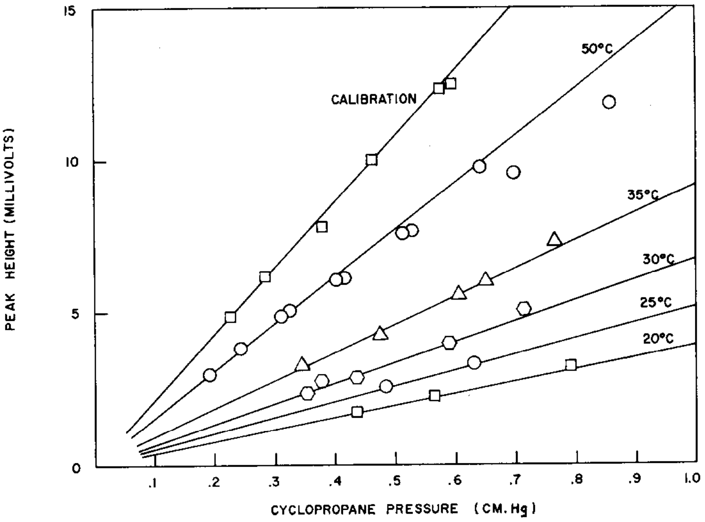


FIG. 1. Plot of propane peak height versus cyclopropane pressure for osmium.

cyclopropane to methane, ethane and propane as a function of temperature.

The degree of cracking on this metal is very slight, with essentially equimolar quantities of methane and ethane being produced. A plot of $\log[T/273 \ln(1/1 - x)]$ versus $1000/T$ is shown in Fig. 2, where x is the total conversion of cyclopropane to propane. An apparent activation energy of 12 ± 1 kcal/mole was calculated from the slope of this line.

Ruthenium

The hydrogenation of cyclopropane on ruthenium was examined several times to check for reproducibility and accuracy of the experimental technique. Figure 3 depicts in a different manner, the results of plots of the type shown in Fig. 1. The number of moles of product resulting per mole of cyclopropane injected is plotted versus catalyst temperature. At lower temperatures the methane to ethane ratio is slightly greater than unity and increases markedly at higher temperatures. The output of propane reaches a maximum at about 160°C and diminishes rapidly if the temperature is raised further. Methane production increases extensively at temperatures above 170°C whereas ethane formation begins to level off in the same range.

The results for the hydrocracking of propane and ethane on ruthenium are given in Fig. 4. Ethane cracking did not occur below 180°C and at 201°C only 2% of the ethane introduced decomposed to methane. Propane hydrocracking commences at about 150°C with substantially more methane being produced than ethane.

TABLE 1
CONVERSION OF CYCLOPROPANE TO METHANE, ETHANE AND PROPANE ON OSMIUM POWDER

Temperature °C	Percent molar conversion of cyclopropane to		
	methane	ethane	propane
50.0	6.22	5.98	71.86
34.7	2.81	2.72	42.51
29.8	2.01	1.89	31.26
25.0	trace	trace	24.19
19.8	trace	trace	18.14

Iron

The cracking of propane on iron was observed at temperatures above 280°C. This reaction proved of great interest as methane was the only product observed. Mass balances of less than unity and a drop in activity indicated the probability that some of the products were being strongly adsorbed to the surface. An activation energy of 32.3 kcal/mole was calculated (Fig. 5),

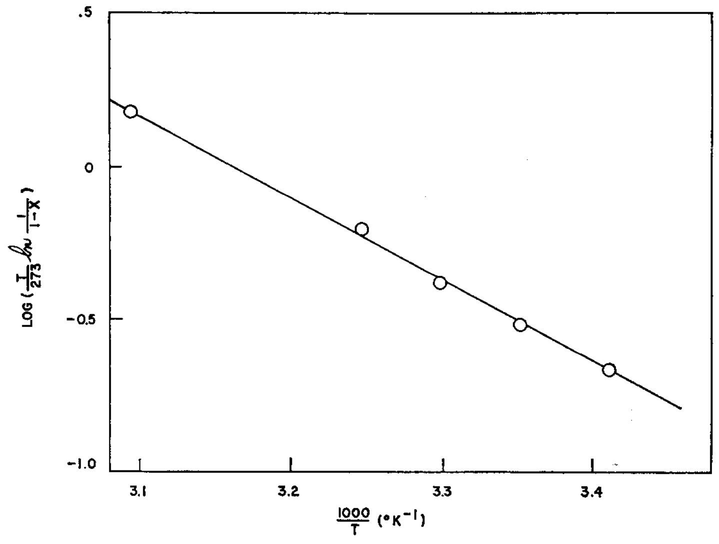


Fig. 2. Arrhenius plot for osmium.

Although no value is reported in the literature for this reaction on iron, the results compare favourably with the value of 34 kcal-mole reported for nickel (*4*). The cracking of ethane occurred at temperatures above 300°C. An approximate activation energy of 27.5 kcal/mole was calculated (see Fig. 5) which compares with 25.6 kcal/mole reported by Cimino, Boudart, and Taylor (*5*).

In the case of cyclopropane hydrogenation, methane was the principal product with lesser quantities of ethane and propane being formed. It is readily apparent that the results may be explained by three reactions which have the following overall stoichiometry.

$$C_3H_6 + H_2 \longrightarrow C_3H_8 \qquad (1)$$

$$C_3H_6 + 2H_2 \longrightarrow C_2H_6 + CH_4 \qquad (2)$$

$$C_3H_6 + 3H_2 \longrightarrow 3CH_4 \qquad (3)$$

Table 2 shows the degree to which these three reactions proceed at different temper-

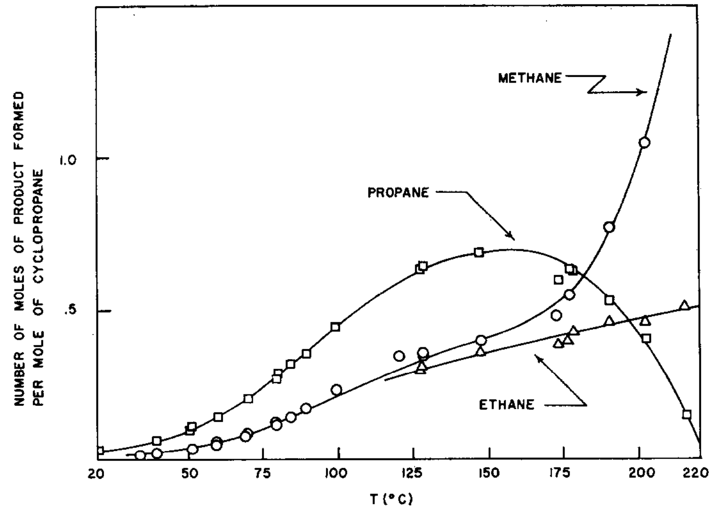


Fig. 3. Plot of moles of product versus temperature for the reactions of cyclopropane on ruthenium.

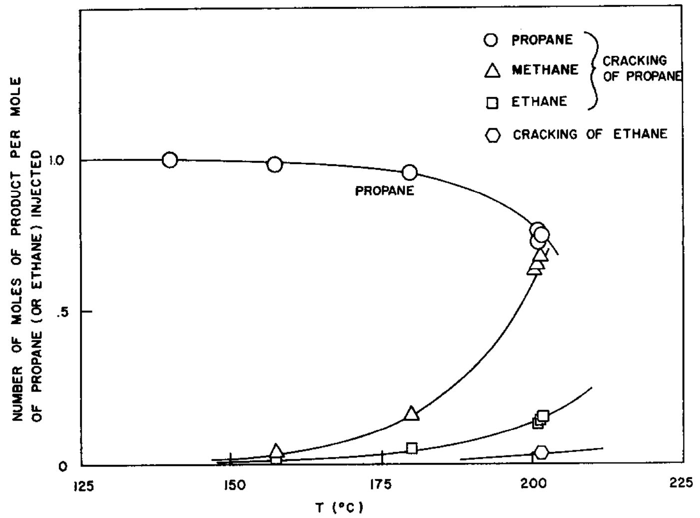


FIG. 4. Plot of moles of product versus temperature for the cracking of propane and ethane on ruthenium.

atures, where x_1, x_2 and x_3 indicate the fraction of cyclopropane converted via reactions (1), (2), and (3), respectively. x_1 was calculated from the amount of propane produced and was corrected for subsequent re-adsorption and cracking of the product propane using the experimental data obtained for the cracking of propane. x_2 was calculated from the ethane production, since ethane cracking occurred to an extent less than 2% at 320°C, the effect of ethane re-adsorption and cracking was ignored. x_3 was calculated from the total methane formed, less the amounts formed in reaction (2) and in the re-adsorption and cracking of propane.

The Hydrogenation of Propylene

Propylene was hydrogenated on ruthenium and iron and gave no products other than propane, even at high temperatures. The reaction proceeded so quickly as to

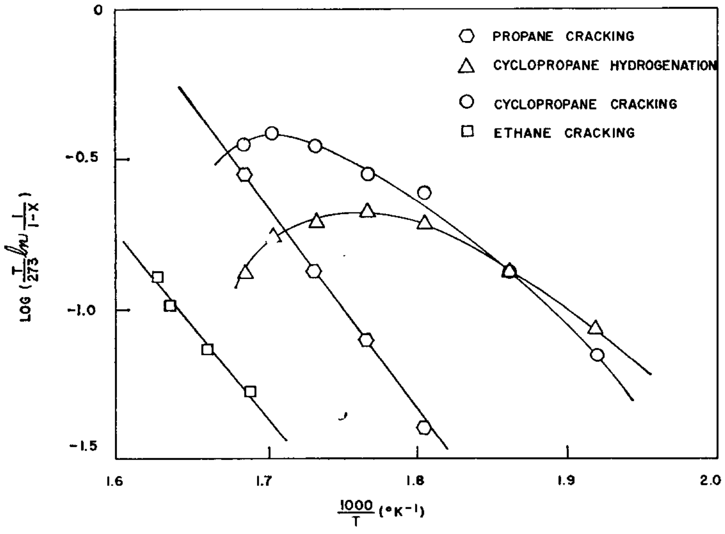


FIG. 5. Arrhenius plots for the hydrocracking of ethane and propane on iron, and for propane and ethane production on iron.

TABLE 2
The Reactions of Cyclopropane on Iron

Temperature °C	x_1	x_2	x_3	x_t
320	.059	.148	.767	.974
314	.078	.165	.708	.921
304	.088	.152	.605	.845
293	.096	.127	.462	.685
281	.091	.092	.305	.508
264	.067	.066	.125	.258
248	.044	.036	.052	.132

$x_t = x_1 + x_2 + x_3$

result in complete conversion at room temperature and below.

Discussion

The results for the hydrogenation of cyclopropane on ruthenium, as shown in Fig. 3, were corrected for the subsequent readsorption and cracking of propane using the data on propane cracking presented in Fig. 4. Such a corrected plot is shown in Fig. 6. It is therefore readily apparent that the presence of methane and ethane in the products cannot be explained as resulting from cracking of the product propane. Complete fragmentization during the hydrogenation of cyclopropane has previously been demonstrated on silica-supported ruthenium and osmium (*6*). From the corrected conversions of Fig. 6, the values of $\log[T/273 \ \ln(1/1 - x)]$ were calculated over the temperature range of 50–160°C. The values of this function calculated from the fractional conversions for the individual hydrogenation and cracking reactions, and for the total conversion are plotted versus $1000/T$ in Fig. 7. As in the case for rhenium (*1*), the Arrhenius plots for the individual reactions of cracking and hydrogenation are curved, whereas the plot for the total reaction yields a straight line. The apparent activation energy for the total reaction is 11.0 ± .3 kcal/mole.

A similar pattern also emerges for iron. Figure 5 shows similar plots for reactions (1) and (2) as well as the Arrhenius plots for ethane and propane hydrocracking. A marked curvature is apparent. Figure 8 shows the Arrhenius plots for reaction (3) and the total reaction. The total reaction has an activation energy of 29.0 ± .8 kcal/mole.

It has been shown (*1*) that, for several parallel first order reactions preceded by a common rate determining step, a plot of $\log[T/273 \ \ln(1/1 - x_t)]$ versus $1/T$ will be a straight line, if x_t is the total conversion of reactant to all products. As with rhenium, the rate determining step for the reaction of cyclopropane on iron and ruthenium is the cleavage of the cyclopropane ring fol-

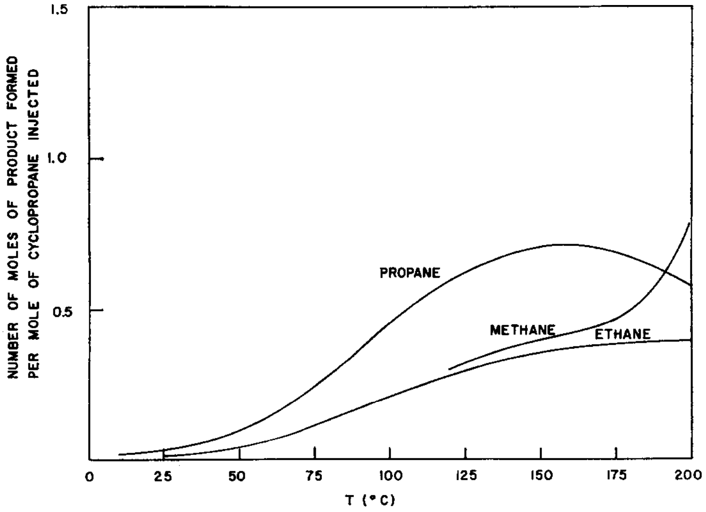


Fig. 6. Plot of moles of products versus temperature for the hydrogenation of cyclopropane, corrected for the cracking of product propane and ethane.

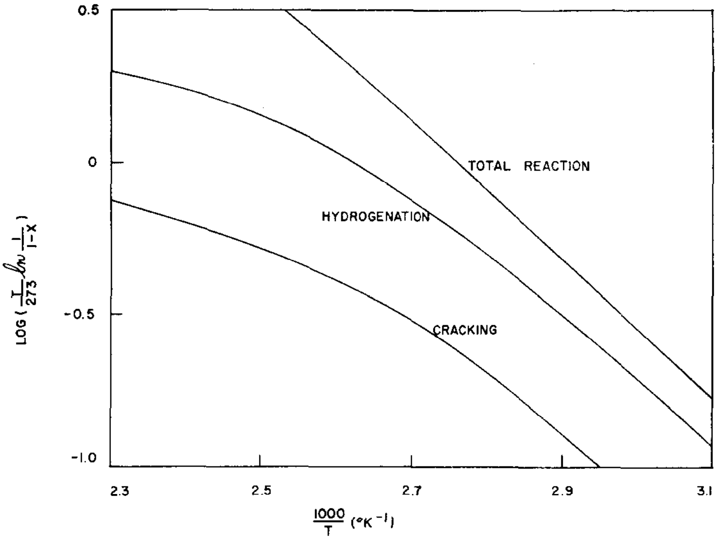
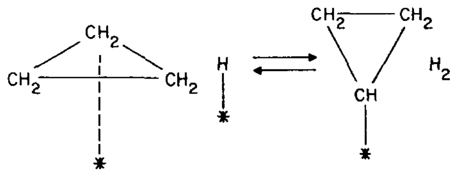


FIG. 7. Arrhenius plots for ruthenium derived from Fig. 6.

lowed by more rapid hydrogenation and cracking reactions. Osmium, which showed relatively little cracking gave a straight line for the Arrhenius plot calculated from the conversion of cyclopropane to propane.

Cyclopropane Chemisorption

The nature of the chemisorption of cyclopropane has been the subject of considerable discussion. It is highly probable that the cyclopropane is initially weakly bonded to the metal by sharing the delocalized electrons of the ring with a vacant *d* orbital of the metal (*3*). The failure to observe any deuterated cyclopropane, when deuterium and cyclopropane are reacted, indicates that the reaction



(4)

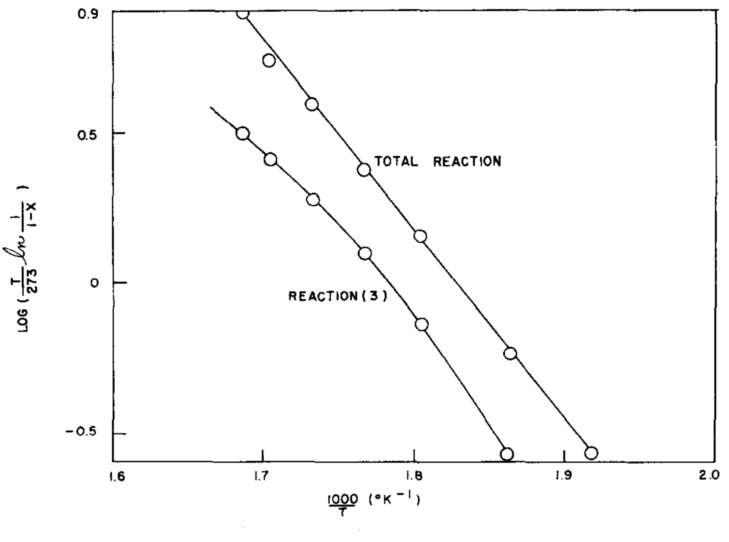
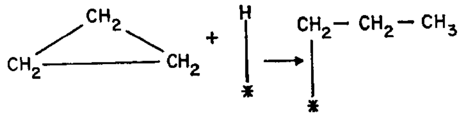
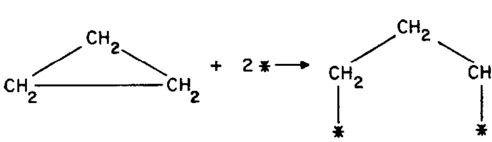


FIG. 8. Arrhenius plots for the hydrogenation of cyclopropane on iron.

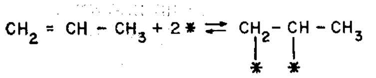
does not proceed, although Anderson and Avery (*3*) present evidence to support its existence on tungsten. Bond and Turkevich (*7*) have proposed the addition of an adsorbed hydrogen atom upon ring opening to give an adsorbed *n*-propyl radical as follows:


(5)

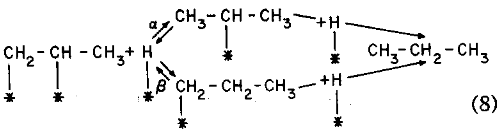
Addy and Bond (*8*) have also proposed 1,3-diadsorption requiring two vacant sites,


(6)

The hydrogenation of propylene on ruthenium provides support for the latter mechanism. Propylene hydrogenation takes place very rapidly, even at 0°C, and produces no product, other than propane at temperatures of 99°C or higher. It can be seen from Fig. 6, that at 99°C the hydrogenation of cyclopropane on the same metal results in considerable quantities of methane and ethane being produced. These products account for about a third of the propane being reacted. It is generally accepted that the hydrogenation of propylene proceeds via the half hydrogenated intermediates (*9*, *10*)


(7)

$$CH_2{=}CH-CH_3+2* \rightleftharpoons \underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH}}-CH_3$$


(8)

One of the half-hydrogenated states is the adsorbed *n*-propyl radical formed by route 3, which is the same intermediate as is postulated in reaction (5). If reaction (5) were, in fact, the mechanism for cyclopropane adsorption, it is difficult to imagine why it should result in cracking whereas the same species produced by another reaction at the same temperature should not.

Propane Cracking

The generally accepted mechanism for the hydrocracking of alkanes is the one proposed by Cimino, Boudart, and Taylor (*5*). Gaseous propane undergoes adsorption by dehydrogenation according to the following scheme:

$$C_3H_8 \rightleftharpoons (C_3H_x) + \left(\frac{8-x}{2}\right) H_2 \qquad (9)$$

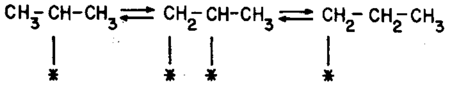
where σ represents bonding to the surface and x is an integer less than eight. In some cases a high degree of dehydrogenation occurs resulting in strongly bonded residues which poison the catalyst for further reaction (*4*, *11*). Such poisoning was observed on iron, but not on ruthenium. The adsorbed dehydrogenated residues undergo cleavage into fragments,

$$H_2 + (C_3H_x)_\sigma \longrightarrow (C_2H_x)_\sigma + (CH_z)_\sigma \qquad (10)$$

followed by more rapid hydrogenation of the fragments.

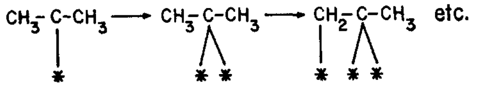
The carbon–hydrogen bond dissociation energies for propane are 99.5 kcal/mole for the end carbon atoms and 94 ± 2 kcal/mole for the central carbon atom (*12*). Therefore it would be expected that initial adsorption would be chiefly by breaking of the secondary carbon–hydrogen bond and attachment to the surface as the adsorbed *i*-propyl species.

The observation that deuterium exchange with alkanes proceeds at temperatures well below that at which hydrocracking commences, indicates that after adsorption an equilibrium of the following type exists,


(11)

$$\underset{*}{\underset{|}{CH_3}}-CH-CH_3 \rightleftharpoons \underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH}}-CH_3 \rightleftharpoons \underset{*}{\underset{|}{CH_2}}-CH_2-CH_3$$

To undergo cracking a species must possess multiple point adsorption where at least one of the carbon atoms is held to the surface by the loss of more than one hydrogen atom (*13*). The case of iron, however, where deuterium–hydrocarbon exchange does not occur at temperatures below those at which hydrocracking is observed initial adsorption must be followed by a very rapid irreversible dehydrogenation, for example



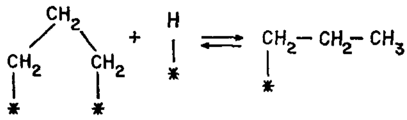
(12)

The end product of this dehydrogenation is a highly dehydrogenated residue which eventually breaks up into fragments which hydrogenate to form methane. Some of these fragments are so tenaciously held to the surface that they poison the surface for further reaction.

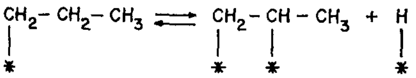
In the case of ruthenium, less dehydrogenation occurs resulting in a species less firmly bound to the surface. This accounts for the lack of surface poisoning and the fact that ethane can desorb before complete fragmentation occurs.

The Hydrogenation and Hydrocracking of Cyclopropane

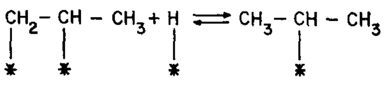
On the basis of the work done by Bond and Turkevich (*6*) on the deuteration of cyclopropane, the following mechanisms seem likely for the conversion of the adsorbed cyclopropane to propane:



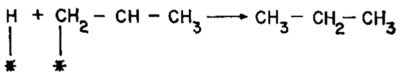
(13)



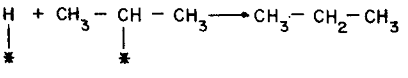
$$\underset{*}{\underset{|}{CH_2}}-CH_2-CH_3 \rightleftharpoons \underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH}}-CH_3 + \underset{*}{\underset{|}{H}} \quad (14)$$



$$\underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH}}-CH_3 + \underset{*}{\underset{|}{H}} \rightleftharpoons CH_3-\underset{*}{\underset{|}{CH}}-CH_3 \quad (15)$$



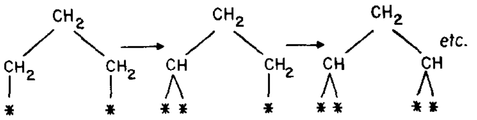
$$\underset{*}{\underset{|}{H}} + \underset{*}{\underset{|}{CH_2}}-CH-CH_3 \longrightarrow CH_3-CH_2-CH_3 \quad (16)$$



$$\underset{*}{\underset{|}{H}} + CH_3-\underset{*}{\underset{|}{CH}}-CH_3 \longrightarrow CH_3-CH_2-CH_3 \quad (17)$$

Where hydrocracking is evident, dehydrogenation reactions similar to those depicted by Eq. (9) must also take place. On osmium, the rate of such dehydrogenation reactions is slight but on ruthenium and iron the rates become progressively faster, such that cracking accounts for the majority of products on the latter metal.

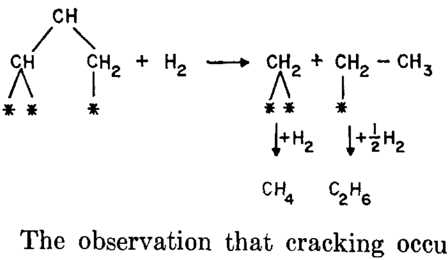
Two interesting differences were noted between the hydrogenation of cyclopropane and the hydrocracking of propane. It was observed that for the hydrogenation of cyclopropane on iron, ethane was present in the product, whereas for propane hydrocracking, methane was the only product even at similar temperatures. Also, as can be seen from Figs. 3 and 4, cracking products for the cyclopropane reaction are observed at temperatures below those at which the cracking of propane commences. It appears that the intermediates for these two reactions must therefore be different. The difference is that propane adsorption is initiated mainly via the central carbon atom, whereas cyclopropane is adsorbed via the two end carbon atoms. If dehydrogenation is rapid a reaction of the following type will compete with reaction (*13*)



(18)

In this equation the hydrogen atoms removed have been omitted for clarity.

It can be argued that for cyclopropane hydrogenation, more dehydrogenated intermediates exist where the central carbon atom is not held to the surface by two point attachment and rupture takes place to form ethane as well as methane as shown by the following example, although other similar intermediates can also produce the same products:



(19)

The observation that cracking occurs at lower temperatures in cyclopropane hydrogenation than in propane hydrocracking could be explained by the greater freedom of vibration of the central carbon atom of the 1,3-diadsorbed species. The C–C bond stretching vibrations of this species would be greater than would be the case if the central carbon atom were also firmly attached to the surface.

ACKNOWLEDGMENTS

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