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# The Reaction of Deuterium with Cyclopropane and Methylcyclopropane over Evaporated Metal Films

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The reactions between cyclopropane or methylcyclopropane and deuterium have been studied over evaporated films of platinum, palladium, nickel, rhodium, tungsten, and iron. Deuterocycloalkanes were formed only over tungsten, and this exchange proceeded very largely in the absence of multiple exchange. In addition to this exchange, deuteroalkanes from ring opening were also formed. Over platinum and palladium, only deuteroalkanes from ring opening were found, but over nickel and iron, this was accompanied by lower deuteroalkanes from more extensive fragmentation. On all metals, no deuteroalkane from ring opening was produced with less than two deuterium atoms per molecule. In the exchange of methylcyclopropane over tungsten, the hydrogens of the methyl group remained inert even at high conversions, and the methyl group had but little effect on the exchange reactivity. However, the deuteroalkanes formed by ring opening over tungsten were produced by extensive multiple exchange that included the methyl group.

It is concluded that in all cases cycloalkane adsorption occurred to give a $\pi$-bonded precursor, that ring opening occurred from this to give a $\sigma$-bonded 1,3-diadsorbed species, and that from the latter were formed the deuteroalkanes. In the case of tungsten, the $\pi$-bonded precursor could alternatively form a $\sigma$-bonded monoadsorbed cycloalkyl residue which was responsible for the formation of deuterocycloalkanes.

Over palladium and rhodium the distribution of deuteroalkanes from ring opening closely resembled the distribution produced by the exchange of the corresponding alkane. On the other hand, over tungsten and nickel the deuteroalkane from ring opening had a much higher mean deuterium number than the corresponding product from alkane exchange. An explanation is offered for this behavior in terms of the differing surface deuterium concentrations in the two reactions resulting from the relatively stronger cycloalkane adsorption. An explanation is offered for the formation of deuteroalkanes from the reaction on iron, despite the known absence of alkane exchange on this catalyst.

## INTRODUCTION

While the hydrogenation of cyclopropane has been the subject of considerable work (*1–7*) the corresponding reaction with deuterium has received much less attention and has only been studied in any detail by Bond and co-workers (*8*, *9*). By comparing the reactions of propane and cyclopropane with deuterium, Addy and Bond (*9*) suggested that both reactions involved similar surface intermediates. More recently, Bond and Newham (*3*) have compared the kinetics of hydrogenation of methylcyclopropane and cyclopropane and found that methylcyclopropane was more strongly adsorbed than cyclopropane during reaction. These authors interpreted this finding in terms of the cyclopropane ring utilizing its inherent olefinic character (*10*, *11*) to form a intermediate $\pi$-bonded to the surface. It has also been reported that the reaction of cyclopropane with deuterium over platinum group metals leads to the formation of

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deuterocyclopropanes in small but varying quantities (*9*, *12*). Recent work has shown that nickel also initiates hydrogenolysis to yield methane and ethane (*4*, *6*). Earlier studies failed to detect this secondary reaction (*1*, *2*). Cobalt (*6*) and platinum black (*5*) are also active towards hydrogenolysis.

The present study was undertaken to reinvestigate these reactions using metal films, since their catalytic properties are more reproducible and are more clearly defined: it has been shown that the kinetics of the reaction over supported catalysts depend, in an uncontrollable way, on the nature of the support (*7*) and on the particular batch of catalyst (*3*). Furthermore, since ring opening yields surface species that are related to those formed by the adsorption of alkanes on metal surfaces, the present results are of value in understanding the reactions of the alkanes themselves.

## EXPERIMENTAL

The apparatus and method of preparing the films have previously been described (*13*). The only modification was the introduction of a glass capillary sampling leak from the reaction vessel to the analyzer tube of an A.E.I. Model M.S. 10 mass spectrometer. Ionizing electrons at 20 eV (nominal) were used.

The cyclopropane was anesthetic grade and was purified on the vacuum line by trap-to-trap distillation. Methylcyclopropane was prepared by the method described by Shortridge (*14*) and later used by Bond and Newham, (*3*) except that it was found that the olefin absorbent used by the latter authors failed to remove the last 1% or so of isobutene impurity. Since for deuterolysis experiments it was important to remove this impurity, the final purification was effected by preparative gas-phase chromatography. With both hydrocarbons, analysis by gas-phase chromatography failed to detect any impurity. Deuterium was prepared by electrolysis of 99.5% heavy water and was purified by diffusion through a heated palladium thimble: no non-"hydrogen" impurity could be detected by mass spectrometry.

It was found that the background peaks in the mass spectrometer were eliminated almost as soon as the reaction mixture began to flush through the analyzer tube, so that no analytical difficulties were encountered if the reaction mixture was admitted to the film at the desired reaction temperature.

A standard reaction mixture was chosen so that the reaction temperature the partial pressures of cyclopropane (or methylcyclopropane) and deuterium were 10 torr and 100 torr, respectively. The tenfold excess of deuterium was desirable to limit its dilution with hydrogen during reaction. In the reaction volume of 570 ml, 1 torr at $T$ °K represents $5.5 \times 10^{21} \times T^{-1}$ molecules. Reaction temperatures in the range 0° to −64°C were obtained using appropriate molten slurries.

Reaction could possibly occur with cyclopropane to give a mixture containing deuterocyclopropanes and deuteropropanes, while from methylcyclopropane the reaction mixture could possibly contain deuteromethylcyclopropanes, deutero-*n*-butanes and deuteroisobutanes. Because of the possible complexity of the products, analysis was done by a combination of gas-phase chromatography and mass spectrometry.

The initial rates of reaction for "alkane"* formation were determined by gas chromatographic analysis of 10-ml samples taken at appropriate intervals during the reaction in the manner previously described (*13*). Better accuracy could be obtained by estimating the products rather than by observing the fractionally smaller decrease in the parent. Analyses showed complete mass balance.

Individual "alkane" and "cycloalkane" components were collected as they were eluted from the gas-phase chromatography column (*13*) and each was analyzed mass spectrometrically for the distribution of deuterocomponents. In those cases where gas-phase chromatography showed that there was no deuterocyclopropane formed, continuous analysis from the reaction vessel via the capillary leak for deuteropropane products was possible without loss of accuracy. On the other hand, even in those cases where no deuteromethylcyclopropane

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* The terms "alkane" and "cycloalkane," etc., designate these species irrespective of isotopic content.

was formed in the reaction of methylcyclopropane, both deutero-*n*-butane and deuteroisobutane were formed simultaneously, so that accurate analysis for the distribution of all deuterobutane components required the prior separation of "*n*-butane" and "isobutane" by gas-phase chromatography. The purity of these separated components was checked by re-injecting them onto the gas-phase chromatography column. This showed that the separated "*n*-butane" contained about 5% of "isobutane," this contamination arising from the tail of the relatively large "isobutane" component in the original separation. The contribution from this "isobutane" impurity to the mass spectrum of the "*n*-butane" component was subtracted out. The observed mass spectra were corrected for naturally occurring $C^{13}$ and D.

Mass spectral fragmentation corrections were obtained in the following way. The "propyl" ion peak heights from $C_3H_8$ and from $C_3D_8$ were measured to be 96% and 60%, respectively, of the corresponding parent peaks. Values for intermediate species were interpolated as follows. It was assumed that the ratio of *total* "propyl" to "parent" from $C_3D_xH_y$ could be linearly interpolated by

$$\tfrac{1}{8}(0.96y + 0.60x)$$

Now, it is known that the ratio of the probabilities of individual C–H bond ruptures in $CHD_3$ and $CH_4$ is 1.8 [Field and Franklin (*15*)]. We assume that the corresponding ratio for $C_3HD_7$ and $C_3H_8$ under the present conditions is also 1.8. The species $C_3D_xH_y$ were assigned corresponding relative probabilities ($T$) for the loss of a hydrogen by linear interpolation

$$T = 1.8 - [0.8(y - 1)/7]$$

Thus the ratio of "propyl" to "parent" for the loss of a hydrogen from $C_3D_xH_y$ is

$$(\tfrac{1}{8}y \times 0.96 \times T)$$

The ratio of "propyl" to "parent" for the loss of a deuterium from $C_3D_xH_y$ is thus

$$\tfrac{1}{8}(0.96y + 0.60x) - (\tfrac{1}{8}y \times 0.96 \times T)$$

The "propylene" ion peaks from $C_3H_8$ and $C_3D_8$ were 13% and 8%, respectively, of the corresponding parent peaks. Thus, in each case the "propylene" peak was about 13% of the corresponding "propyl" peak, and this was assumed to be true for the intermediate deuteropropanes. Fragmentation corrections for "*n*-butane" and "isobutane" were computed in an analogous manner. Calculations of this type assume an equal probability for fragmentation by the loss of a primary, secondary, or tertiary "hydrogen." While this assumption may not be valid with high accuracy, there is no reasonable alternative available when the deuteroalkanes have deuterium atoms not confined to one particular type. The accuracy of the fragmentation correction is considered later.

Fragmentation corrections for the deuterocyclopropanes and deuteromethylcyclopropanes were applied using the measured fragmentation patterns of the parent hydrocarbons and statistical weighting factors according to the isotopic content. This procedure was adopted because of the difficulty of preparing the pure perdeutero compound as a mass spectral reference material and also because, in the reaction where deuterocycloalkane was a substantial reaction product (tungsten catalyst), the monodeutero compound was the most abundant component, and highly accurate fragmentation corrections were not needed. Relative to the parent, the peaks for the loss of one, two, and three hydrogen atoms from cyclopropane were 0.74, 0.19, and 0.17, respectively, while from methylcyclopropane the corresponding figures were 0.195, 0.026, and 0.035.

Since it proved necessary accurately to compare the specific rates of reaction of cyclopropane and methylcyclopropane, the areas of individual films were determined after each experiment by the BET method using xenon adsorption at 90°K (*16*).

It has previously been reported that palladium film which had reacted at 250°C physically broke down when the hydrogen, absorbed during catalysis, was pumped away prior to xenon adsorption (*13*). This effect was also observed with the present palladium films which had been reacted at less than 0°C except that the effect was now much slower. Nevertheless, by the time all the deuterium could be pumped from the film, visible evidence for a breakdown of the film could be observed since the film lost its metallic luster and started to flake from the vessel. Thus the areas of the Pd films were estimated from film weight, using an area vs. weight relation obtained from unreacted films. Reproducible results were obtained provided the average rate of deposition was in excess of about 1 mg min$^{-1}$.

Some high-temperature reactions with methylcyclopropane were carried out with platinum wire catalysts. For this, a length of 0.1-mm diameter platinum wire (Johnson and Matthey Spectrographically Standardized) was strung about a light silica frame which was suspended in the reaction vessel. The length of wire was in the range 10–60 cm, the shorter lengths being used at higher reaction temperatures. The wire was outgassed in vacuum at 1200°C in 50 torr of hydrogen for 1 hour before use as a catalyst.

## RESULTS

### *Reactions over Pt, Pd, Ni, Rh, and Fe*

**a. Cyclopropane.** The reaction of cyclopropane with deuterium was studied over films of platinum, palladium, nickel, rhodium, and iron in the temperature ranges given in Table 1. The analytical technique was estimated to be capable of detecting down to about 0.3 mole % deuterocyclopropane in the hydrocarbon fraction of the reaction mixture, but in no case was any deuterocyclopropane detected. On platinum, palladium, and rhodium "propane" was the only reaction product. Over nickel, "methane" and "ethane" were also formed in equimolar proportions, the reaction product containing "methane," "ethane," and "propane" in the relative molar proportions of 1:1:3.5. These proportions showed no significant variation with temperature in the range 0° to 46°C or with a partial pressure ratio of deuterium to cyclopropane in the range 2.5 to 40. Over iron, on the other hand, "methane," "ethane," and "propane" were formed in the relative molar proportions of 1:0.42:0.58 at about the middle of the temperature range (165°C).

Product concentration vs. time plots were sufficiently linear over the initial stages of the reaction (< about 20 mole % conversion) directly to determine the initial rate of reaction. Typical data are plotted in Fig. 1. The effect of temperature on reaction rate is provided by the Arrhenius plots in Fig. 2 for the overall disappearance of cyclopropane. The corresponding activation energies and frequency factors are listed in Table 1.

The pressure dependences of the reaction rates were determined by using reaction mixtures in which one component had been reduced by a factor of 4 compared to a mixture of standard composition. The results are collected in Table 1. The estimated uncertainties in the pressure dependence exponents, the activation energies, and the logarithms of the frequency factors are ±0.1, ±0.5 kcal mole$^{-1}$, and ±0.3 (frequency factor in molec sec$^{-1}$ cm$^{-2}$), respectively.

TABLE 1

ARRHENIUS PARAMETERS AND PRESSURE DEPENDENCE EXPONENTS FOR THE REACTION OF CYCLOPROPANE AND DEUTERIUM

| Metal | Temperature range (°C) | Activation energy (kcal mole$^{-1}$) | log$_{10}$ (frequency factor) (molec sec$^{-1}$ cm$^{-2}$) | Rate $\propto p^{x}_{C_3H_6} \times p^{y}_{D_2}$ | |
|---|---|---|---|---|---|
| | | | | $x$ | $y$ |
| Pt | −78° to −23° | 11.0 | 24.6 | 0.2 | −0.2 |
| Pd | −46° to −8° | 14.5 | 25.3 | 0.1 | −0.9 |
| Ni | −46° to 0° | 7.5 | 19.3 | 0.6 | −0.1 |
| Fe | 148° to 171° | 23.0 | 24.7 | ~1.0 | — |
| Rh | −78° | rate = 8.0 × 10$^{13}$ molec sec$^{-1}$ cm$^{-2}$ | | — | — |

The initial distributions of deuteropropanes formed over each metal under a variety of temperature conditions are given

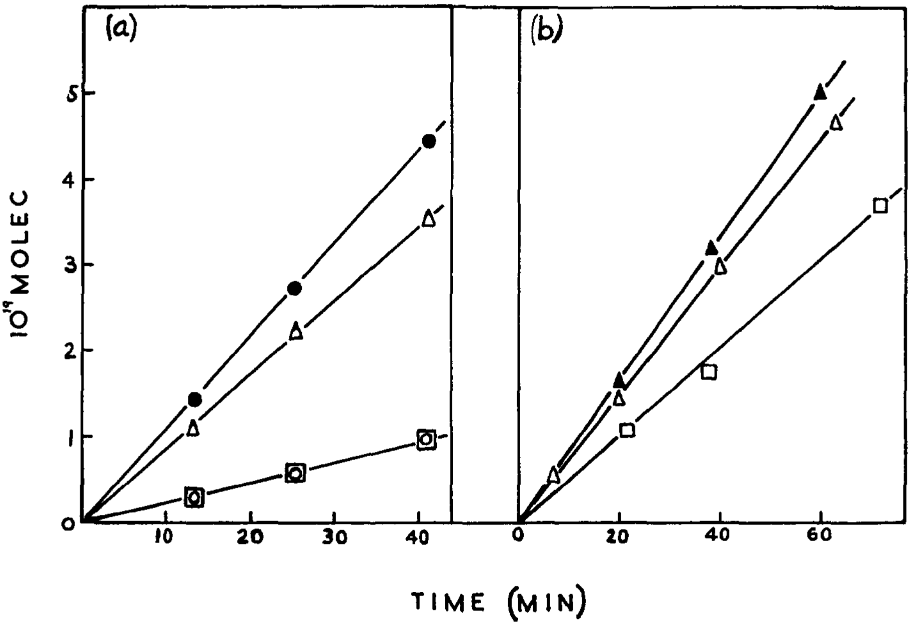

FIG. 1. Reaction of cyclopropane and deuterium over metal films. (a) "$CH_4$," □; "$C_2H_6$," ○; "$C_3H_8$," △; total "alkane" in $C_3$ equivalents, ●; over 26.2 mg of nickel at −23°C: area 3900 cm². (b) Total "alkane" in $C_3$ equivalents formed over △, 8.9 mg platinum at −64°C, area 1000 cm²; ▲, 13.0 mg palladium at −23°C, area 2600 cm²; □, 1.2 mg rhodium at −78°C; area 105 cm².

in Table 2. The average number of deuterium atoms per "propane" molecule ($M$) is given by

$$M = \sum_{i=1}^{i=8} ix_i$$

where $x_i$ is the fraction of "propane" molecules carrying $i$ deuterium atoms. In no case was a significant amount of $C_3H_7D$ found, the product species with the lowest deuterium content always being $C_3H_6D_2$. After applying fragmentation corrections, the mass spectral residue at mass 45 at < about 20% reaction never exceeded about 5% of the mass 46 peak. Furthermore, the residues at masses 43 and 44 also never exceeded about 5% of the mass 46 peak, and this is taken as an index of the adequacy of the general fragmentation correction scheme.

The effect of added propane on the overall reaction rate and on the deuteropropane distribution was studied by (i) the addition of 2.3 torr of propane to a standard reaction mixture over a palladium film at −23°C, and (ii) the addition of 7.0 torr of propane to a

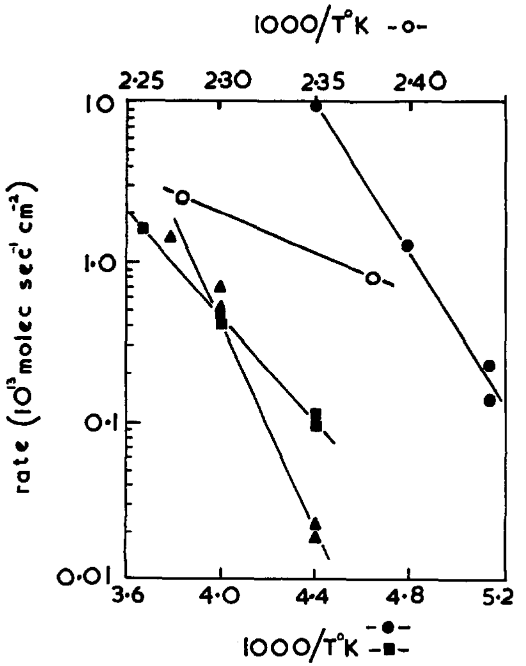

FIG. 2. Effect of temperature on the rate of reaction of cyclopropane and deuterium over films of platinum, ●; palladium, ▲; nickel, ■; iron, ○.

TABLE 2

INITIAL DISTRIBUTION OF DEUTEROPROPANES FROM THE REACTION OF CYCLOPROPANE AND DEUTERIUM

| Metal | Temp. (°C) | $p_{D_2}/p_{C_3H_6}$ | Deuteropropanes (%) | | | | | | | $M$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | |
| Platinum | −78° | 10 | 55 | 18 | 15 | 3 | 3 | 1 | 4 | 2.99 |
| | −64° | 10 | 49 | 20 | 17 | 5 | 3 | 1 | 4 | 3.07 |
| | −64° | 2.5 | 53 | 20 | 18 | 4 | 1 | 1 | 3 | 2.98 |
| Palladium | −46° | 10 | 21 | 2 | 4 | — | 17 | 12 | 43 | 6.02 |
| | −23° | 10 | 10 | 3 | 2 | — | 15 | 15 | 53 | 6.78 |
| | −8° | 10 | 8 | 4 | 1 | — | 14 | 18 | 56 | 6.89 |
| Nickel | −46° | 10 | 14 | 3 | 7 | 6 | 8 | 8 | 56 | 6.28 |
| | −23° | 10 | 10 | 5 | 8 | 5 | 9 | 10 | 53 | 6.41 |
| | −23° | 2.5 | 9 | 2 | 7 | 6 | 4 | 15 | 57 | 6.70 |
| Iron | 165°, 171° | 10 | — | — | — | <1 | 2 | 9 | 89 | 8.07 |
| Rhodium | −78° | 10 | 16 | 8 | 10 | 10 | 10 | 13 | 33 | 5.61 |

standard reaction mixture over a nickel film at −23°C. No effect on the overall reaction rate or on the product distribution was found.

**b. Methylcyclopropane.** Reaction between deuterium and methylcyclopropane yielded a mixture of "*n*-butane" and "isobutane" over palladium and platinum, while over nickel, "methane" and "propane" were also formed in equimolar proportions. In no case was any deuteromethylcyclopropane formed. The proportions of the various "alkanes" in the initial reaction products are given in Table 3. Overall reaction rates were only measured at a single selected temperature for each metal and the values are also given in Table 3, together with the ratio $R$ of rates at the same temperature,

$$R = \frac{\text{overall rate of methylcyclopropane reaction}}{\text{overall rate of cyclopropane reaction}}$$

The initial distributions of the deuterobutanes are given in Table 4. In no case was a significant amount of $C_4H_9D$ found, the product species with the lowest deuterium content always being $C_4H_8D_2$.

Since Bond and Newham (*3*) have reported data for the mode of ring opening in the hydrogenation of methylcyclopropane in the range 0–300°C over a supported

TABLE 3

REACTION OF METHYLCYCLOPROPANE OVER EVAPORATED METAL FILMS

| Metal | Temp. (°C) | Alkane product distribution (%) | | | | | Specific rate ($10^{13}$ molec $sec^{-1}$ $cm^{-2}$) | $R$ |
|---|---|---|---|---|---|---|---|---|
| | | "$CH_4$" | "$C_2H_6$" | "$C_3H_8$" | "iso-$C_4H_{10}$" | "$n$-$C_4H_{10}$" | | |
| Pd | −64° | — | — | — | 89 | 11 | — | — |
| | −23° | — | — | — | 85 | 15 | 2.35 | 5.6 |
| | 0° | — | — | — | 84 | 16 | — | — |
| Ni | −46° | 9.5 | — | 9.5 | 76.6 | 4.4 | 1.54 | 3.4 |
| | −23° | 8.5 | — | 8.5 | 77 | 6.0 | — | — |
| | 0° | 10 | — | 10 | 72 | 8.0 | — | — |
| Pt | −64° | — | — | — | 98.1 | 1.9 | 1.2 | 1.1 |
| | −23° | — | — | — | 97.5 | 2.5 | — | — |
| | 0° | — | — | — | 96.3 | 3.7 | — | — |

TABLE 4

INITIAL DISTRIBUTION OF DEUTEROBUTANES FROM THE REACTION OF METHYLCYCLOPROPANE AND DEUTERIUM

| Metal | Temp. (°C) | Isomer | Distribution (%) | | | | | | | | | M |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | $d_9$ | $d_{10}$ | |
| Ni | −23° | Isobutane | 4 | 8 | 6 | 6 | 4 | 4 | 7 | 18 | 43 | 8.30 |
| | | *n*-Butane | 11 | 11 | 12 | 10 | 9 | 8 | 7 | 11 | 21 | 6.28 |
| Pd | −23° | Isobutane | 8 | 2 | 2 | 2 | — | — | 13 | 26 | 47 | 8.48 |
| | | *n*-Butane | 3 | 4 | 5 | 5 | 6 | 7 | 10 | 23 | 37 | 8.05 |
| Pt | −64° | Isobutane | 55 | 33 | 6 | 1 | <1 | <1 | <1 | <1 | <1 | 2.64 |
| | | *n*-Butane | 42 | 23 | 12 | 4 | 2 | 2 | 2 | 2 | 5 | 3.63 |

platinum catalyst, comparative data were obtained for reaction over unsupported platinum. Reaction mixtures of standard composition were used. In the range −64° to 0°C evaporated platinum film catalysts were used, but at higher temperatures platinum wire catalysts were used in order to work with small catalyst surface areas, thus keeping the total reaction rate within reasonable bounds. While *n*-butane and isobutane were the major products, isobutene and *n*-1-butene were also produced at temperatures above 190°C. Thus, the relative importance of the two alternative modes of ring opening in methylcyclopropane is presented in Fig. 3 in terms of the ratio (total $n$-$C_4$)/(total iso-$C_4$).

### *Reactions over W*

**a. Cyclopropane.** Reaction between deuterium and cyclopropane was studied over tungsten in the range −23° to 48°C. The reaction was characterized by the production of deuterocyclopropanes as the major product, but "propane," "ethane," and "methane" were also produced. Typical product vs. time curves are given in Fig. 4 for reaction of a mixture of standard composition. "Ethane" and "methane" were formed in equimolar proportions, and the

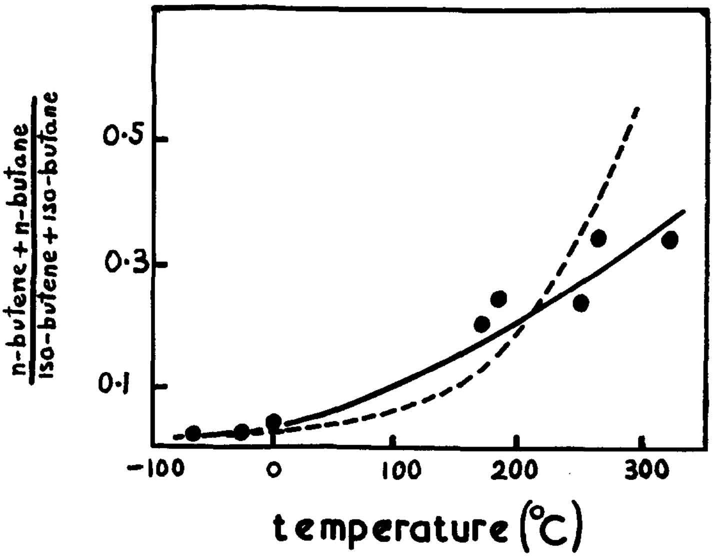

FIG. 3. The effect of temperature on the mode of ring opening of methylcyclopropane over platinum. The broken line gives the corresponding data from ref. (*3*).

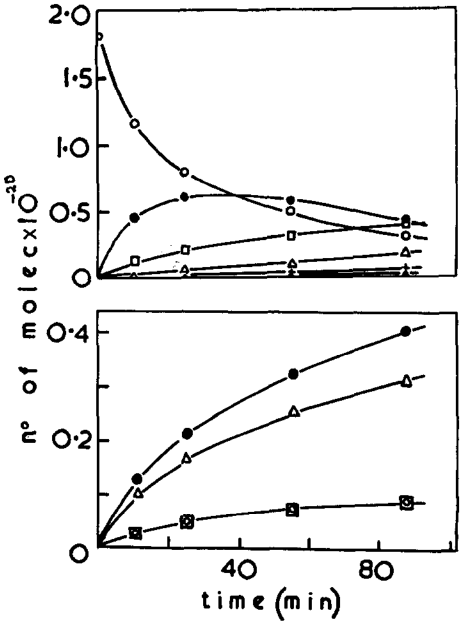

Fig. 4. Reaction of cyclopropane and deuterium over 8.2 mg tungsten film at 27°C. Top: formation of deuterocyclopropanes; $C_3H_6$, ○; $C_3H_5D$, ●; $C_3H_4D_2$, □; $C_3H_3D_3$, △; $C_3H_2D_4$, +; $C_3HD_5$, ▲. Bottom: formation of "alkanes"; "$C_3H_8$," △; "$C_2H_6$," ○; "$CH_4$," □; total "alkane" in $C_3$ equivalents, ●.

relative proportions of "alkanes" are given in Table 5 for various reaction conditions. Because of the curvature of the plots, initial rates of "alkane" formation could not be accurately obtained. However, it was found that the ratio

$$\frac{\text{total ``alkane'' (in cyclopropane equivalents)}}{\text{total exchanged ``cyclopropane''}}$$

varied linearly with time, and the value of this ratio extrapolated to zero time was 0.21 ± 0.03 and was independent of temperature and reactant partial pressure. This decreasing rate of "alkane" formation became more severe with reaction mixtures containing reduced proportions of deuterium and clearly points to a self-poisoning reaction. This was only observed on tungsten and it should be noted that even on tungsten the exchange reaction remained unpoisoned. The initial distribution of deuterocomponents in the "propane" is given in Table 6, where it will be seen that the distributions do not vary with reactant partial pressure, but the proportions of the less-deuterated "propanes" increase with increasing temperature.

TABLE 5

Initial Distribution of "Alkanes" from the Reaction of Cyclopropane and Deuterium over Tungsten

| Temp. (°C) | $p_{D_2}$ (torr) | $p_{C_3H_6}$ (torr) | Distribution (%)<br>"Methane" and "ethane" | "Propane" |
|---|---|---|---|---|
| 0° | 100 | 10 | 11 | 78 |
| 10° | 100 | 10 | 12 | 76 |
| 27° | 100 | 10 | 17 | 66 |
| 48° | 100 | 10 | 19 | 62 |
| 16° | 100 | 3.2 | 11 | 78 |
| −13° | 100 | 3.4 | 6.5 | 87 |
| −23° | 100 | 4.8 | 6 | 88 |
| 17° | 33 | 10 | 17 | 66 |

An examination of data at low exchange conversions gave a value of *M* (the mean

TABLE 6

Initial Distribution of Deuteropropanes from the Reaction of Cyclopropane and Deuterium over Tungsten

| Temp. (°C) | $p_{D_2}$ (torr) | $p_{C_3H_6}$ (torr) | Initial distribution (%)<br>$d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | *M* |
|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 100 | 10 | 25 | 21 | 14 | 12 | 10 | 7 | 11 | 4.26 |
| 27° | 100 | 10 | 21 | 20 | 16 | 11 | 10 | 8 | 14 | 4.49 |
| 48° | 100 | 10 | 16 | 16 | 15 | 13 | 12 | 10 | 18 | 4.81 |
| −23° | 100 | 4.6 | 36 | 36 | 18 | 17 | 9 | 6 | 8 | 3.81 |
| 5° | 100 | 4.0 | 29 | 18 | 13 | 11 | 8 | 8 | 12 | 4.16 |
| 16° | 100 | 3.2 | 22 | 18 | 15 | 11 | 9 | 9 | 15 | 4.50 |
| 17° | 33 | 10 | 22 | 17 | 15 | 11 | 11 | 10 | 14 | 4.58 |

number of deuterium atoms per exchange cyclopropane molecule) of 1.3.

Data for the exchange of cyclopropane may be plotted according to the equations

$$-\log_{10}(\phi_\infty - \phi) = (k_\phi t/2.303\phi_\infty) - \log(\phi_\infty - \phi_0) \quad (1)$$

$$-\log_{10}(\nu - \nu_\infty) = [k_\nu t/2.303(100 - \nu_\infty)] - \log_{10}(100 - \nu_\infty) \quad (2)$$

Here, $\phi$ is the number of deuterium atoms introduced into 100 cyclopropane molecules at time $t$, and thus

$$\phi = X_1 + 2X_2 + \ldots + 6X_6$$

where $X_m$ is the percentage of exchange product containing $m$ deuterium atoms, $\phi_\infty$ is the value of $\phi$ at exchange equilibrium, $\nu$ is the percentage* of $C_3H_6$ at time $t$, and $\nu_\infty$ is the value of $\nu$ at exchange equilibrium. The simultaneous reaction of cyclopropane to give "alkane" products makes it impossible to determine $\phi_\infty$ and $\nu_\infty$ experimentally, so the values of 460 and 1.2%, respectively, were used for these parameters, calculated statistically for exchange at equilibrium. The data of Fig. 4 are plotted according to Eqs. (1) and (2) in Fig. 5. It should be noted that in applying Eqs. (1) and (2), the reaction forming "alkane" has been included so that $k_\nu$ is the rate constant for the overall reaction of exchange plus deuteration, while $k_\phi$ will only be inaccurate to the extent that the fractions of the various deuterocyclopropanes may be diminished in unequal proportions by further reaction to "alkane," and the inaccuracy here should be negligible. Since only about 20 mole % of the initially reacting cyclopropane produced "alkane," $k_\nu$ and $k_\phi$ are not thus subject to gross uncertainty. The ratio $k_\phi/k_\nu$ for an exchange reaction equals $M$, the mean number of deuterium atoms entering each reacting cyclopropane molecule. The present data give a value for $M$ of 1.21, but this may be low to the extent of up to 20% because of the uncertainty in the exchange parameter $k_\nu$.

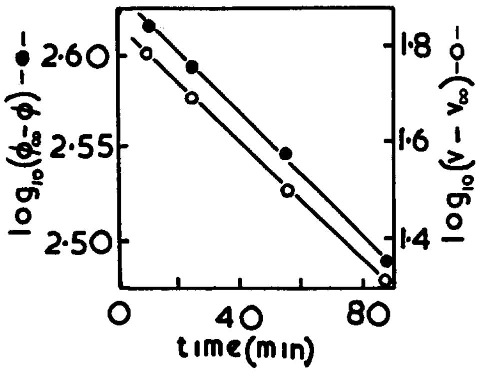

FIG. 5. Results of Fig. 4 plotted according to Eqs. (1) and (2).

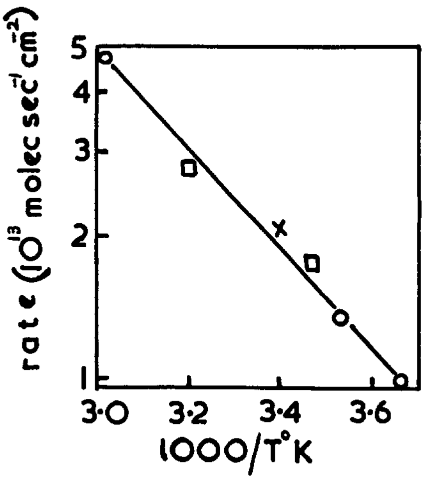

FIG. 6. Effect of temperature on the rate of reaction of cycloalkane and deuterium over tungsten films. Cyclopropane, ○; methylcyclopropane, □; cyclopropane plus propane, X.

The effect of temperature on the overall rate constant $k_\nu$ is given in Fig. 6, from which the activation energy and frequency factor were calculated to be 4.7 kcal mole$^{-1}$ and $5.8 \times 10^{16}$ molec sec$^{-1}$ cm$^{-2}$, respectively.

The pressure dependence exponents of the overall reaction were determined by the method of initial rates. In the expression

$$\text{rate} \propto p^x_{C_3H_6} \times p^y_{D_2}$$

the exponents were found to be

$$x = -1.0 \text{ at } -23°\text{C and } 5°\text{C}$$
$$y = 0.4 \text{ at } 17°\text{C}$$

The addition of 2 torr of propane to a standard reaction mixture was found to have no effect on the reaction rate at 21°C.

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* Calculated after expressing total "alkane" as cyclopropane equivalents.

**b. Methylcyclopropane.** Reaction between deuterium and methylcyclopropane was studied over tungsten at 15° and 40°C. Under no conditions, even at total conversions in excess of 50 mole %, was a more highly deuterated species than $C_4H_3D_5$ formed. Typical product vs. time curves are given in Fig. 7. The reaction was characterized by the production of deuteromethylcyclopropanes as the major product, but "methane," "ethane," "propane," "isobutane," and "n-butane" were also produced. "Methane" and "propane" were formed in equimolar proportions. The initial distribution of "alkanes" in the reaction product at 40°C is given in Table 7. The initial distribution deutero-components in the "butanes" is given in Table 8. It was found that the ratio

TABLE 7

INITIAL DISTRIBUTION (%) OF "ALKANES" FROM THE REACTION OF METHYLCYCLOPROPANE AND DEUTERIUM OVER TUNGSTEN AT 40°C

| "Methane" | "Ethane" | "Propane" | "Iso-butane" | "n-Butane" |
|---|---|---|---|---|
| 11.5 | 2.0 | 11.5 | 26 | 49 |

$$\frac{\text{total "alkane"} \quad \text{(in methylcyclopropane equivalents)}}{\text{total exchanged "methylcyclopropane"}}$$

extrapolated to zero time was 0.24 ± 0.04.

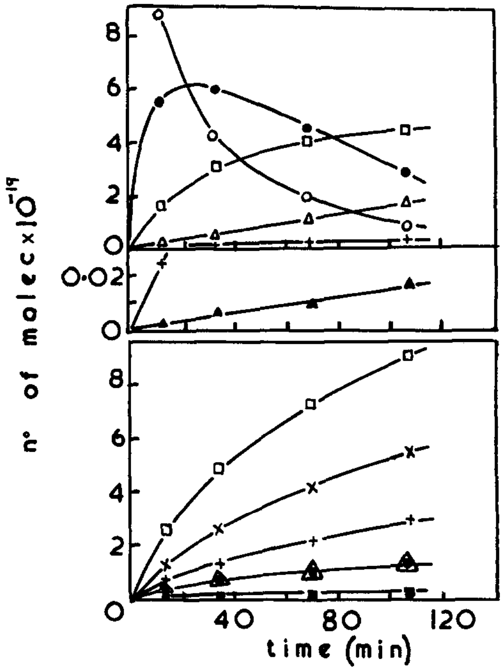


FIG. 7. Reaction of methylcyclopropane and deuterium over 12.2 mg tungsten film at 40°C. *Upper:* formation of deuteromethylcyclopropanes; $C_4H_8$, ○; $C_4H_7D$, ●; $C_4H_6D_2$, □; $C_4H_5D_3$, △; $C_4H_4D_4$, +; $C_4H_3D_5$, ▲. *Lower:* formation of "alkanes"; "n-$C_4H_{10}$," ×; "iso-$C_4H_{10}$," +; "$C_3H_8$," ●; "$C_2H_6$," ■; "$CH_4$," △; total "alkane" in $C_3$ equivalents, □.

The data of Fig. 7 are plotted according to the equivalent form of Eqs. (1) in Fig. 8. If all eight hydrogen atoms in methylcyclopropane were exchangeable, the statistically calculated value of $\phi_\infty$ would be 570, while if only five hydrogen atoms were exchangeable, $\phi_\infty$ would be 400. Plots with these two alternative values of $\phi_\infty$ are included in Fig. 8, and the plot with $\phi_\infty$ equal to 400 is clearly the more satisfactory. An examination of data at low exchange conversions gave a value of $M$ for the deuteromethylcyclopropanes of 1.3, indicating that, as with cyclopropane, deuterium exchange with the methylcyclopropane molecule occurs very largely without multiple exchange.

TABLE 8

INITIAL DISTRIBUTION OF DEUTEROBUTANES FROM THE REACTION OF METHYLCYCLOPROPANE AND DEUTERIUM OVER TUNGSTEN AT 40°C

| | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | $d_9$ | $d_{10}$ | $M$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Isobutane | 26 | 20 | 16 | 10 | 6 | 5 | 4 | 5 | 8 | 4.52 |
| n-Butane | 30 | 26 | 18 | 10 | 6 | 3 | 2 | 2 | 3 | 3.80 |

## DISCUSSION

### *The Main Modes of Adsorption*

Addy and Bond (*9*) have reported that deuterocyclopropanes were produced during the reaction of cyclopropane with deuterium over supported platinum, palladium, and iridium, but represented less than 2 mole % of the "cyclopropane." Similarly, Anderson and Kemball (*12*) reported the formation of deuterocyclopropanes over rhodium films at −100°C. The more accurate analytical procedure used in the present work shows that Anderson and Kemball's conclusion is certainly incorrect and an examination of the original experimental records shows that it arose from inadequate deuteropropane fragmentation corrections. Addy and Bond (*9*) estimated the deuterocyclopropanes by the difference in the mass spectra resulting from removal of all "cyclopropane" from the sample by absorption in sulfuric acid. The accuracy of such a procedure is not high, but the disparity with the present results probably represents a real difference in the behavior of supported and unsupported metal.

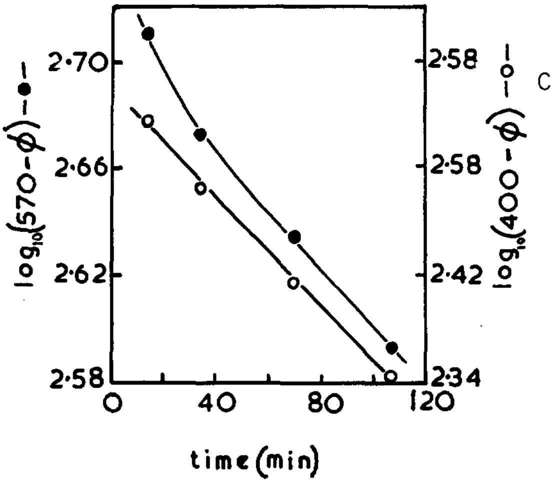
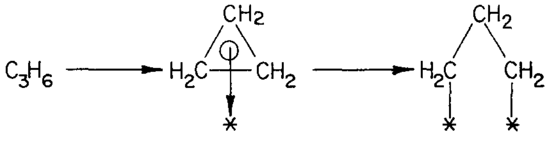


Fig. 8. Results of Fig. 7 plotted according to Eq. (1), with two alternative values of $\phi_\infty$, $\phi_\infty = 570$ and $\phi_\infty = 400$, corresponding to 8 and 5 exchangeable hydrogen atoms per molecule, respectively.

It is thus clear that in the present circumstance a surface intermediate based on an adsorbed cyclopropyl species may be rejected for reactions occurring over platinum, palladium, rhodium, nickel, and iron. With these metals, the adsorption path suggested by Addy and Bond is clearly reasonable, namely



(A) (B)

where the species (A) is $\pi$-bonded to the surface. It is possible to suggest a more explicit account of the process by which (A) is converted to (B). In cyclopropane each carbon atom may be considered to possess pseudo-$p_z$ orbitals which form delocalized $\pi$ orbitals. A pair of these $p_z$ orbitals may interact independently with a pair of metal orbitals to form a transition state for carbon–carbon bond rupture as in Fig. 9. As the strength of the carbon–metal $\sigma$ bonds increase, the electron density of the $\pi$ orbitals will be diminished, thereby removing the stabilization of the strained ring. Eventually the carbon–carbon bond breaks to give (B).

The question immediately arises whether an adsorbed cyclopropyl species $\sigma$-bonded to the surface is important for reactions on tungsten. In this regard we must note that the reaction of cyclopropane over tungsten produced an appreciable amount of deuteroalkane: about 20% of the reacted cyclopropane yielded this product. Furthermore, a value of $M$ of about 1.3 for the deuterocyclopropanes shows that exchange was almost exclusively a single-step process yielding monodeuterocyclopropane. Now there is no reason to suggest that the ring opening

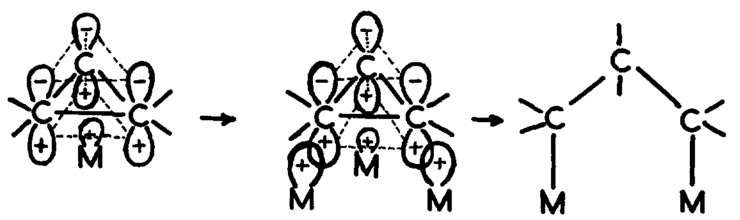
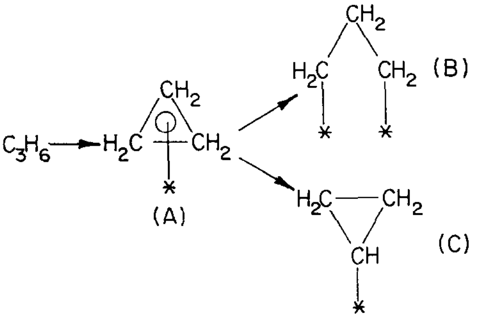


Fig. 9. Scheme for ring opening in cyclopropane.

on tungsten should occur by any process other than the one described above for the other metals, and it would follow that on tungsten there must be at least some adsorption as a π-bonded species (A). Further, it is clear that a mechanism could be formulated that would lead to exchange within a π-bonded species. However, if this were so, it would then be very difficult to understand why exchange should be limited almost entirely to the introduction of a single deuterium atom. Furthermore, it would be difficult to understand why on the other metals no deuterocyclopropanes at all were formed. In view of this, we suggest that the structure responsible for cyclopropane exchange on tungsten is a σ-bonded cyclopropyl residue, and that this is formed from a π-bonded species. Thus, a general scheme on tungsten may be written



The behavior of methylcyclopropane on all metals may be formulated in a generally analogous manner to that given above, but the behavior of the methyl group must be examined.

Exchange on tungsten proceeded to give deuteromethylcyclopropanes with the methyl group completely inert. Exchange within the ring gave a value of *M* of about 1.3, which is very similar to the behavior of cyclopropane. Furthermore, it will be seen from Fig. 6 that the overall reactivities of cyclopropane and methylcyclopropane are very similar on tungsten and it was also shown that the ratios of exchange to alkane formation were very similar for each molecule. We must therefore conclude that on this metal the methyl group exerts negligible steric influence on the exchange reaction and on the ring opening and fragmentation reactions. This conclusion is in agreement with the proposal that a π-bonded species is not the one directly responsible for exchange, since steric hinderance to π-bonding would then be difficult to avoid.

We conclude from the data for the pressure dependence of the reaction rates that relative to deuterium, cyclopropane was significantly more strongly adsorbed on tungsten than on the other metals.

Since the overall rate of the cyclopropane reaction was uninfluenced by the addition of propane to the reaction mixture, we conclude that cyclopropane was adsorbed much more strongly than propane. In confirmation of this we note that in the presence of propane no monodeuterpropane was observed although it is known (*17*) that on nickel and tungsten at these temperatures, this substance would be the main product from propane exchange. A comparison of corresponding pressure dependence data in Table 9 leads to the same conclusion.

### *The Alkane Formation Reaction*

On tungsten, it will be seen from Tables 6 and 8 that, in contrast to the predominantly single-step exchange, the products from ring opening were extensively exchanged, with *M* values in the range 3.8–4.8, and substantial amounts of perdeuteroalkane were formed. It is clear that once the ring opens the methyl group from methylcyclopropane is no longer inert, and this extensive deuterium content must have been produced by multiple exchange from an adsorbed species such as (B) or its methylcyclopropane analogue. Ring-opening products were also formed with high deuterium contents over the other catalysts, and in all cases higher temperatures tended to favor higher values of *M*. The metals fall into the following sequence of increasing ability to give highly deuterated ring-opening products:

$$\text{Pt} < \text{W} < \text{Rh} < \text{Ni, Pd} < \text{Fe}$$

It will be seen from the results that platinum and tungsten were, in fact, the only metals for which perdeuteroalkane was not the most abundant product.

On all metals, no deuteroalkane with less than two deuterium atoms was observed,

TABLE 9

COMPARISON OF KINETIC PARAMETERS FOR THE EXCHANGE REACTIONS OF PROPANE AND DEUTERIUM AND FOR THE REACTION OF CYCLOPROPANE AND DEUTERIUM

| System | Temperature range for reaction (°C) | Activation energy (kcal mole$^{-1}$) | Pressure dependence in rate $\propto p^x_{HC} \times p^y_{D_2}$ |  | M | Ref. |
|---|---|---|---|---|---|---|
|  |  |  | x | y |  |  |
| Ni |  |  |  |  |  |  |
| Cyclopropane | −46° to 0° | 7.5 | 0.6 | −0.1 | 6.2–6.4 |  |
| Propane | −47° to 0° | 10.4 | 1.0 | −0.6 | 1.0–1.1 | (*17*) |
| Pd |  |  |  |  |  |  |
| Cyclopropane | −46° to −8° | 14.5 | 0.1 | −0.9 | 6.0–6.9 |  |
| Propane | 146° to 185° | 23.7 | 0.9[a] | −0.8[a] | 7.5–7.8 | (*22*) |
| W |  |  |  |  |  |  |
| Cyclopropane | −23° to 48° | 4.7 | −1.0 | 0.4 | 3.8–4.8 |  |
| Propane | −82° to −24° | 9.0 | −0.4 | −0.4 | 1.2–2.0 | (*17*) |
| Rh |  |  |  |  |  |  |
| Cyclopropane | −78° | — | — | — | 5.6 |  |
| Propane | −25° to 20° | 13.3 | 0.5 | −0.8 | 5.7 | (*17*) |

[a] Estimated by comparison with ethane (*18*).

and this is clearly in agreement with the proposal that ring opening gives initially a diadsorbed species such as (B).

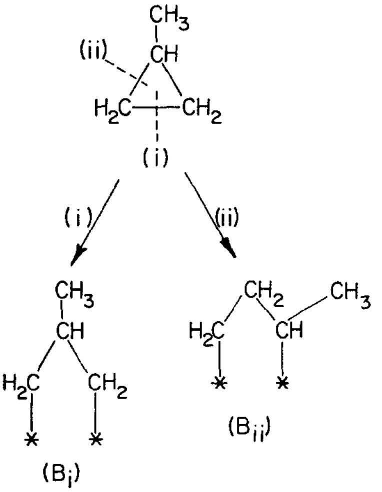
The question arises whether in metals other than tungsten the deuteriums were introduced into the product before or after opening of the ring. The evidence is that ring opening in a π-adsorbed species was very rapid and that most, if not all, of the deuterium was introduced into the residue after ring opening. Thus, if there were a significant amount of deuterium-containing π-adsorbed species on the surface it would be very unlikely that no deuterocycloalkane would be detected in the gas phase. We thus conclude that multiple exchange proceeds from (B) in a manner similar to that which operates during multiple exchange of the corresponding alkane itself.

It is useful to compare the distributions of deuteroalkanes formed by ring opening, with the corresponding alkane. Table 9 compares mean deuterium numbers and kinetic parameters for the formation of deuteropropanes by the two processes.

The most striking feature is the much higher mean deuterium number for the "propane" formed from the cyclopropane reaction on both nickel and tungsten. On rhodium and palladium, on the other hand, the mean deuterium numbers are very similar for the two processes. There are no propane exchange data for platinum for comparison. Since we have shown that cyclopropane was considerably more strongly adsorbed than was propane, the proportion of deuterium on the surface in the presence of cyclopropane would be considerably less than in the presence of propane. Now there is good evidence that in ethane and propane exchange reactions, the mean deuterium number increases as the deuterium pressure is reduced (*17*, *18*), provided this pressure reduction is not large enough to allow appreciable isotopic dilution of the deuterium to occur. This is understandable if, for instance, one or more extra bare sites are required to transform an adsorbed hydrocarbon residue into a configuration required for multiple exchange. We suggest therefore that the relatively lower surface deuterium concentration in the presence of cyclopropane is responsible for the enhanced mean deuterium numbers on nickel and tungsten. Clearly, if the propane exchange already gives very high mean deuterium numbers, as on rhodium and palladium, there is little room for further enhancement in this way. That the σ-bonded species (C) did not propagate exchange further to give polydeuterocyclopropane is probably a consequence of the short lifetime of (C) due to rapid reconversion to (A) followed by desorption or conversion to (B).

The activation energies for the overall cyclopropane reaction are somewhat lower than for propane exchange on all metals, as shown in Table 9. Although the major surface species in these two reactions are likely to be very similar [e.g., (B)], the surface concentration of hydrocarbon residues is probably lower in the propane exchange reaction, so that the relative positions of the potential energy curves for adsorption (i.e., for chemisorption as (B) relative to the physically adsorbed or π-adsorbed precursors) will not necessarily be the same for the two systems.

Ring opening in methylcyclopropane gives varying proportions of *n*-butane and isobutane, depending whether the analogue of (B) is ($B_i$) or ($B_{ii}$)



Remembering that ($B_{ii}$) may be formed by the rupture of two possible equivalent bonds, we may use the data of the relative proportions of *n*-butane and isobutane to calculate the relative bond rupture probabilities given in Table 10. For convenience the value for ($CH_2$–$CH_2$) has been set at unity.

In each case the relative bond rupture probabilities are somewhat temperature-dependent, but the values recorded in Table 10 refer to about the middle of the indicated temperature range. However, if the temperature range is very large, variation in the proportion of the different modes of ring opening may become substantial, as the data in Fig. 3 show.

The methyl group of methylcyclopropane has previously been considered (*3*) to exert an inductive or hyperconjugative effect on the cyclopropane ring so as to increase the electron density in the π orbitals. This increased electron density would be expected to be greatest at the carbon–carbon bonds adjacent to the methyl group, so that ring opening should occur in a manner to favor the formation of isobutane rather than *n*-butane. This is generally in accordance with the results. However, the influence of π-bonding to the metal must be considered: dative π-bonding from the ring to the metal, as suggested for (B), would exert a leveling effect to reduce the influence of the methyl group on the bond orders.

TABLE 10

BOND RUPTURE PROBABILITIES IN THE REACTION OF METHYLCYCLOPROPANE

| | ($CH_2$-$CH_2$) | (CH-$CH_2$) |
|---|---|---|
| Tungsten (−23° to 48°C) | 1.0 | 1.0 |
| Nickel (−46° to 0°C) | 1.0 | 0.04 |
| Palladium (−46° to −8°C) | 1.0 | 0.09 |
| Platinum (−78° to −23°C) | 1.0 | 0.01 |

Reactions on nickel, tungsten, and iron resulted in some further fragmentation of the molecules beyond simple ring opening. On nickel and tungsten, cyclopropane gave equimolar amounts of methane and ethane. The proportions were such that on both metals about 80% of the reacting cyclopropanes appeared as "propane," and the reaction was thus limited to the rupture of one further bond beyond ring opening. The behavior of methylcyclopropane on these metals was analogous: the reaction could be almost completely described by the formation of equimolar amounts of methane and propane, and about 80% of the reacting methylcyclopropane appeared as "butane." Reaction beyond ring opening was thus largely limited to rupture of both a (2–3) and a (1–2) ring bond. The tendency to avoidance of rupture of both (1–2) bonds is in agreement with the expected bond orders resulting from the effect of the methyl group. However, on tungsten there was some evidence for rupture of both (1–2) bonds, since a small amount of ethane was produced. The latter is not unexpected in view of the large proportion of ($B_{ii}$) that must have been formed on this metal. On iron, fragmentation of cyclopropane was more extensive since more than twice as much methane than ethane was produced.

We have seen that cyclopropane is more strongly adsorbed than propane, and that the cyclopropane reaction was uninhibited by propane. Thus it is reasonable to conclude that fragmentation beyond ring opening resulted not from the hydrocracking of readsorbed propane, but from a surface residue formed from cycloalkane adsorption. This is in agreement with the conclusion of Taylor *et al.* (*7*).

It should be noted that although there was evidence for self-poisoning in the ring opening and fragmentation reaction with cyclopropane on tungsten, the reaction producing deuterocyclopropane was unpoisoned. The self-poisoning probably resulted from the formation of strongly adsorbed dehydrogenated residues. On this basis we would expect the exchange reaction also to become ultimately poisoned; the reaction was probably not carried out for a sufficiently long time for this to become evident. The greater sensitivity of the ring opening and fragmentation reaction to self-poisoning is probably because the required surface residue (B) occupies two adjacent surface sites, while exchange only requires a single site with residue (C), and for a given overall extent of surface poisoning, the chance of finding two adjacent sites is diminished to a greater extent than the chance of finding a single site. The fact that on tungsten there is a tendency to self-poisoning in the cyclopropane reaction but no such tendency in propane exchange, is probably due to the relatively lower surface deuterium concentration in the cyclopropane reaction.

It is most unlikely that two bonds in the $\pi$-bonded species (A) could be broken simultaneously, and once one bond has been broken, it is reasonable to suppose that (B) is formed. Thus we suggest that fragmentation beyond ring opening proceeds from (B). We note that the 1,3-diadsorbed geometry in (B) fulfills one of the requirements that has previously been suggested for hydrogenolysis (*13*). However, hydrogenolysis reactions of propane(*19*) proceed about 200°C above the corresponding cyclopropane range. This difference may be another consequence of the reduced surface concentration of deuterium in the presence of cyclopropane compared to propane. The mechanism proposed (*13*, *20*, *21*) for hydrocracking in a 1,3-diadsorbed residue requires this residue to be doubly bonded to the surface at least at one carbon atom and this would be expected to be more readily achieved if the surface concentration of deuterium is reduced.

The behavior of iron in forming deuteroalkanes from cyclopropane is noteworthy, because this metal is known not to catalyze the exchange of ethane, and this result can almost certainly be assumed to apply to other alkanes. It is known (*18*), however, that at a sufficiently high temperature a mixture of ethane and deuterium will react over iron to yield deuteromethane. We suggest that this behavior of iron can be rationalized if it is assumed that the initial alkane adsorption has a substantial activation energy. Thus for alkane adsorption to occur at an appreciable rate the temperature must be high, but once on the surface we presume that, at this temperature, dehydrogenation will be rapid. Since the dehydrogenated residue will be very strongly adsorbed, the activation energy for the reverse process will be so high that none of the deuterated parent molecule can be returned to the gas phase. On the other hand, we suggest that species (B) can be established on the iron surface from cyclopropane by an adsorption process with an activation energy low compared to that required for propane. Thus, (B) is formed at a temperature that is low enough for the activation energy barrier to further dehydrogenation to be effective, and exchange can proceed from (B) to yield deuteropropanes. A similar explanation can almost certainly be applied to account for the behavior of ethane exchange on nickel

(*18*). Here exchange first occurs at about 0°C with a low mean deuterium number and on raising the temperature this ceases and is followed by further exchange near 200°C with a much higher mean deuterium number and a much higher activation energy.

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