JOURNAL OF CATALYSIS 13, 404–412 (1969)

# Deuterogenolysis of 2-Bromopropane on Ni and Pd and Deuterogenolysis and Dehydrobromination of 2-Bromobutane on Ni and Pt

ISAO MATSUZAKI* AND ROBERT L. BURWELL, JR.

*From the Department of Chemistry, Northwestern University, Evanston, Illinois 60201*

AND

TSUYOSHI NAKAJIMA†

*From the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan*

Received October 15, 1968

Previous workers have shown that reaction of alkyl halides on Pd and Pt in the presence of hydrogen results solely in hydrogenolysis, whereas on Ni both hydrogenolysis and dehydrohalogenation are observed. We have studied the reactions mentioned in the title at temperatures of 70–270°C on Pd, 100°C, on Pt, and 27-150°C on Ni. On Pd and Pt hydrogenolysis with the formation of highly deuterated alkanes occurs, while on Ni, olefins as well as deuterated alkanes are observed. We conclude that the same basic mechanism is operative on all the catalysts and that variations in the relative rates of the several steps in the overall mechanism lead to the observed difference. Direct dehydrobromination was observed on Pt and Ni films in the absence of $H_2$.

## INTRODUCTION

Previous work (*1–3*) has shown that the catalyzed hydrogenolysis of alkyl halides on Pd and Pt gives only alkane but that Ni leads to formation of both alkane and alkene. This paper is concerned with experiments designed to determine the origin of these differences.

Two different mechanistic explanations may be offered for the observation that two catalysts exhibit different catalytic behavior under similar reaction conditions. In one, the mechanisms are basically different. In the other, the *reaction structures* are different but the basic mechanism is the same. The term "mechanism" is defined here as a set of elementary steps and the term "reaction structure" is defined as a mechanism in which the relative rates of the constituent elementary steps are specified. In the latter case, the observed differences in catalytic behavior result from variations in the relative rates of the constituent elementary steps but the two catalysts do not differ fundamentally in their chemical reactivities. For instance, if Ni is capable, but Pt is inherently incapable, of forming diadsorbed alkane from alkyl halides, production of olefins from alkyl halides will be possible on Ni but impossible on Pt, i.e., this would be a case of different mechanism. If both Ni and Pt are capable of forming diadsorbed alkanes but under the influences of concurrent progress of the other elementary steps the desorption of diadsorbed alkanes as olefins takes place on Ni but hardly at all on Pt, the phenomenon described above with respect to olefin production from alkyl

* Present address: Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan.

† Present address: Institute of Chemistry, Faculty of Fisheries, Hokkaido University, Hakodate, Japan.

halides would appear, i.e., this would be a case of different reaction structures.

If the different catalytic behavior observed on two catalysts under the same conditions of reaction results from different mechanisms, one could not obtain identical catalytic behavior by making the conditions of reaction different. If the different behavior results from different reaction structures, this may be possible. Therefore, when alteration of reaction conditions has given rise to similar behavior, one may conclude that the previously observed different catalytic actions result from different reaction structures and that the catalysts are not inherently different. This is the conceptual basis underlying the present experiments.

In the present experiments, deuterogenolysis, which furnishes more information than hydrogenolysis, was first investigated using 2-bromopropane and 2-bromobutane as the substrates and Ni, Pd, and Pt as the catalysts. The results led to the conclusion that the different catalytic behavior of Ni, Pt, and Pd results from different reaction structures and in consequence Ni, Pt, and Pd are not inherently different in chemical reactivities insofar as the hydrogenolysis of alkyl halides and related reactions are concerned. In order to confirm this conclusion, catalyzed dehydrohalogenation of alkyl halides was then investigated using 2-bromobutane on Ni and Pt to see whether both catalysts could behave similarly. Both the catalysts were, indeed, found capable of catalyzing dehydrobromination. This supports the conclusion given above.

## EXPERIMENTAL

### *Deuterogenolysis*

**Materials.** The Pd catalyst used was 200–250 mesh Pd black prepared according to Willstätter and Waldschmidt-Leitz (*4*).

The Ni-silica catalyst used was 150–200 mesh prepared by crushing and sieving granules of commercial Harshaw 0101 Ni-silica catalyst (Ni content 42%).

The Pt-alumina catalyst used was 100–140 mesh prepared by crushing and sieving granules of commercial Baker 5% Pt-alumina catalyst.

The 2-bromopropane and 2-bromobutane were Phillips Petroleum Co., pure grade purified by distillation.

Deuterium of over 99.5% purity was obtained in cylinders from the General Dynamics Co. It was purified by passage through Ni-kieselguhr at 350°C, $CaCl_2$, Molecular Sieve 4A, Ni-kieselguhr at room temperature, and a trap cooled in liquid nitrogen.

**Apparatus.** The apparatus used is shown schematically in Fig. 1. $RV_1$ is a static

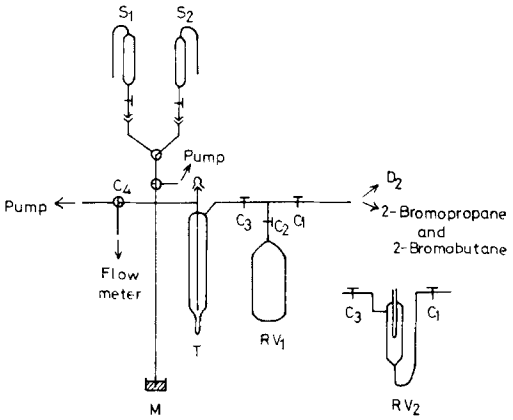



FIG. 1. Apparatus used for the deuterogenolysis experiments.

reactor which was employed in all the experiments except for two runs with Pd black at 214° and 270°C in which case the flow reactor $RV_2$ was used. The volume of $RV_1$ is 150 cc and that of trap T, 50 cc. The cap on trap T permits withdrawl of liquid samples condensed at the bottom. The reactor $RV_2$ is 10 cm long and 0.6 cm in diameter with a thermocouple well of 3.5 cm in depth and 0.3 cm in diameter. Its volume is approximately 2 cc. M is a mercury manometer of 2 mm capillary tubing. $S_1$ and $S_2$ are sampling vessels each with a side tube for collecting condensable substances.

**Procedure using the static reactor $RV_1$.** A measured quantity of the catalyst was put in the reactor. After evacuation of the whole apparatus, the reactor was heated electrically to 200°C and the trap was cooled in a methanol-$CO_2$ bath. Deuterium was then admitted to atmospheric pressure. The reduction of the catalyst at 200°C was

continued with intermittent addition of deuterium until no deuterium consumption could be observed. Reduction required 1 week for the Ni-silica catalyst and 2 days for the Pt-alumina catalyst. After evacuation, either 2-bromopropane (vapor pressure, 240 torr at 27°C) or 2-bromobutane (vapor pressure, 80 torr at 29°C) was introduced into both the reactor and the trap to a pressure a little lower than the vapor pressure at room temperature. Deuterium was then added to a predetermined pressure, the stopcock $C_2$ closed, all the parts but the reactor evacuated, and the trap immersed in liquid nitrogen. Reaction was initiated by heating the reactor using an oil bath, a metal bath, or an electric furnace.

At a selected time, the reaction mixture was expanded through the trap immersed in liquid nitrogen into $S_1$, thus providing a sample of hydrogen. The hydrogen remaining in the trap and reactor was slowly evacuated through the stopcock $C_4$, all the other components being collected in the trap. The mixture of the components collected was separated into three fractions—olefin plus alkane, hydrogen bromide, and alkyl bromide—by dipping the trap successively in methanol cooled at suitable temperatures.

The amount of hydrogen bromide, which should be equal in moles to the sum of alkane and olefin produced, was determined by measuring the pressure developed in the trap when it was allowed to warm to room temperature after the evacuation of hydrogen. The ratio of alkane to olefin produced was determined gas chromatographically.

**Procedure using the flow reactor $RV_2$.** Experiments with the flow reactor involved the following changes from experiments with the static reactor. The reactor was filled with a selected weight of the Pd catalyst dispersed in 2 cc of 40-mesh glass beads. This mixture was contained between plugs of glass wool. A known flow of deuterium was established through the reactor by means of a soap-film flow meter and to this flow 2-bromopropane was added at known rate by a motor-driven syringe which discharged at a warm spot in the flow path.

The amount of hydrogen bromide formed was determined from the decrease in the flow rate at the flow meter.

**Method of analysis.** The hydrogen was analyzed mass spectrometrically for isotopic composition using an ionization voltage of 68 V.

The alkyl bromide fraction was subjected to gas chromatographic analysis to determine whether any change in the alkyl bromides had occurred, such as isomerization or disproportionation, and to mass spectrometric analysis for deuterium distribution. In the former analysis, 20 ft of TCP-on-firebrick column at 80°C was used and in the latter, the ionization voltage was 68 V.

The olefin and alkane fraction was separated by means of a gas chromatograph using 20 ft of TCP-on-firebrick column at room temperature and each component was subjected to mass spectrometric analysis.

The deuterium distributions of propane, propene, *n*-butane, butenes, 2-bromopropane, and 2-bromobutane were determined from the mass spectra as follows: the cracking pattern of each deuterated compound was derived from that of the nondeuterated species on the approximation that a C–D bond would be ruptured as easily as C–H; butenes were subjected to the analysis as a mixture and the mass spectra obtained were analyzed on the approximation that the mixture would be *trans*-2-butene because gas chromatographic analysis had revealed that the mixture were largely *trans*-2-butene.

*Dehydrobromination*

**Materials.** The nickel and platinum wires used for the preparation of evaporated films were supplied by the Tanaka Noble Metal Co., Tokyo, the purities and diameters of both the wires being 99.99% and 0.5 mm, respectively.

The 2-bromobutane (99.5%) was used as supplied by the Tokyo Chemical Industry Co., Tokyo.

**Apparatus.** The apparatus shown schematically in Fig. 2 was connected to an oil diffusion pump backed by a rotary oil pump.

The reaction vessel RV is 15 mm in diameter and 15 cm long and it contained 15 cm of the wire for producing evaporated films. The circulation pump CP consists of a cylinder and a glass piston which encloses an iron core. It was dirven magnetically by means of solenoids surrounding the cylinder.

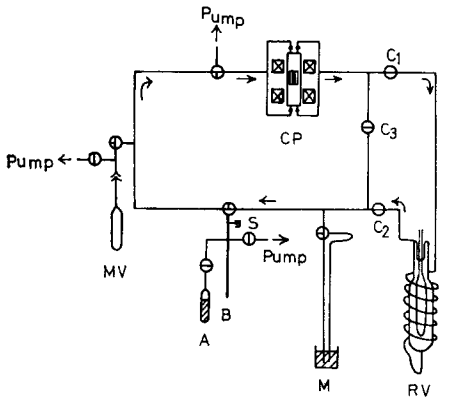



FIG. 2. Apparatus used for the dehydrobromination experiments.

MV is a vessel containing 2-bromobutane. M is a mercury manometer of 3-mm capillary tubing. A is a vessel containing barium hydroxide to remove hydrogen bromide from samples of reaction mixtures. S is a silicon rubber disc through which the gas confined in B was withdrawn by means of a syringe. All stopcocks were lubricated with a grease which was tested for absorption of 2-bromobutane, butenes, and hydrogen bromide. A maximum of 3% of the first and third components was absorbed.

**Procedure.** After evacuating the apparatus to $\sim 10^{-6}$ torr, the reaction vessel was thermostated at 400°C during evacuation for about 15 hr, during which period the wire was heated by a current of 5 amp to dull redness. The temperature of the reactor oven was then raised to 500°C and evacuation continued for 2 hr. The oven was then replaced by an ice-water bath, the current through the wire was gradually raised to 9.5 amp (yellow-red), and maintained there for 30 min to develop an evaporated film. The film thus formed was stabilized by sintering at 460°C for 30 min.

The 2-bromobutane in MV was outgassed several times by alternate freezing and thawing during evacuation. With the reaction vessel closed and immersed in a thermostated oil bath at 150°C, the vapor of the bromide was expanded into the apparatus until the vapor pressure measured on the manometer reached the saturation value at room temperature. The vapor was then circulated and reaction was initiated by switching the stopcocks $C_1$, $C_2$, and $C_3$ to allow the vapor to circulate through the reaction vessel. The progress of the dehydrobromination was followed by measuring the pressure with the manometer. To check on dehydrobromination being the only reaction, the reaction mixture was analyzed as follows: at the end of a run reaction mixture was condensed in vessel A by means of liquid nitrogen; all components other than hydrogen bromide were then transferred to the part B; and a sample was withdrawn through S. The sample was subjected to gas chromatographic analysis using a column containing 225 cm of TCP + 150 cm of DC-550. The temperature of the column was room temperature for butene and 80°C for bromobutanes.

## RESULTS AND DISCUSSION

### *Comparison of the Catalytic Character of Pd, Pt, and Ni*

The deuterogenolysis experiments were made using the following combinations of substrates, catalysts, and reaction temperatures:

| | | | |
|---|---|---|---|
| Pd | 2-bromopropane | 70–270°C | Table 1 |
| Pt | 2-bromobutane | 100°C | |
| Ni | 2-bromopropane | 27–150°C | Table 2 |
| Ni | 2-bromobutane | 150°C | |

Let us first compare the low-conversion runs on Pd and Pt, at 70° and 214°C on Pd and at 1 min on Pt. The runs differ only in absolute rate and in the deuterium distributions of propane and *n*-butane. In both runs one observes (1) hydrogenolysis as the only chemical reaction, (2) production of multiply deuterated alkanes, (3) no isomerization of substrates, (4) no formation of deuterated substrates, and (5) predominant initial formation of HD rather than $H_2$. It is therefore readily concluded that the mechanisms of catalytic hydrogenolyses of alkyl halides on Pd and Pt are similar.

Let us now compare the 1 min run on Pt with those on Ni in Table 2, all of which are at low conversions. As seen from Tables 1 and 2, in contrast to the case of Pd, results on Ni are very dependent on the temperature, i.e., with increasing temperature (1) dehydrobromination becomes predominant

TABLE 1

DEUTEROGENOLYSIS OF 2-BROMOPROPANE ON Pd AND OF 2-BROMOBUTANE ON Pt

| Catalyst: | | Pd | | | Pt | |
|---|---|---|---|---|---|---|
| Catalyst weight: | | 386 mg | 50 mg[a] | 50 mg[b] | 1 g[a] | 1 g[b] |
| Reactor used: | | Static | Flow | Flow | Static | Static |
| React. temp. (°C): | | 70° | 214° | 270° | 100° | 100° |
| Initial press. (torr): | 2-Bromopropane | 253 | 253 | 253 | — | — |
| | 2-Bromobutane | — | — | — | 49 | 49 |
| | Deuterium[c] | 507 | 507 | 507 | 254 | 258 |
| Contact time: | | 1 day | 9 sec | 9 sec | 1 min | 10 min |
| Comp'n of reaction mixture sampled (torr): | 2-Bromopropane | 237 | 249.2 | 118 | | |
| | 2-Bromobutane | | | | 45.4 | 3 |
| | Propane | 16 | 3.8 | 135 | | |
| | *n*-Butane | | | | 3.6 | 46 |
| | Hydrogen | 491 | 503.2 | 372 | 250.4 | 212 |
| | Hydrogen bromide | 16 | 3.8 | 135 | 3.6 | 46 |
| | | Propane | Propane | Propane | *n*-Butane | *n*-Butane |
| Deuterium distribution in propane or *n*-butane: | $D_0$ | 7.9% | 5.1% | 5.6% | 1.4% | 3.6% |
| | $D_1$ | 6.7 | 3.9 | 6.1 | 7.6 | 14.5 |
| | $D_2$ | 7.1 | 7.7 | 10.3 | 18.7 | 21.0 |
| | $D_3$ | 2.0 | 9.0 | 14.3 | 14.7 | 17.1 |
| | $D_4$ | 0 | 7.2 | 14.1 | 13.0 | 12.7 |
| | $D_5$ | 12.0 | 7.3 | 17.8 | 11.2 | 10.7 |
| | $D_6$ | 12.5 | 13.0 | 20.1 | 9.0 | 8.4 |
| | $D_7$ | 20.3 | 21.0 | 8.8 | 7.4 | 5.6 |
| | $D_8$ | 31.5 | 25.8 | 2.9 | 6.1 | 3.1 |
| | $D_9$ | | | | 7.0 | 2.4 |
| | $D_{10}$ | | | | 3.9 | 0.9 |
| | $D_{av}$ | 5.56 | 5.43 | 4.2 | 4.54 | 3.57 |
| Isomers of 2-bromopropane or 2-bromobutane: | | None | None | None | None | None |
| Deuterated 2-bromopropane or 2-bromobutane: | | None | None | None | None | None |
| Comp'n of hydrogen (%): | $H_2$ | 5.4 | 2.3 | 34.8 | 2.5 | — |
| | HD | 13.2 | 9.0 | 45.6 | 9.0 | — |
| | $D_2$ | 81.4 | 88.7 | 19.6 | 88.5 | — |
| | D content | 88.0 | 93.2 | 42.4 | 93.0 | — |

[a,b] Runs *a* and *b* were made with the same charge of catalyst. Preliminary runs indicated that the catalyst was more or less poisoned by catalyzing the reaction, so it was reactivated by reduction in deuterium between run *a* and *b*.

[c] Found mass spectrometrically: $H_2$ 2.4%, HD 2.7%, and $D_2$ 94.8%, the D content being 96.2%. The decrease in the D content of the source deuterium was due to residual hydrogen in the Ni-kieselguhr in the purification train which had been reduced in hydrogen.

over hydrogenolysis, (2) the deuterium content in both propane and propene decreases, and (3) formation of deuterated 2-bromopropane becomes detectable. One can predict, from the data of Table 2, that one could find some temperature lower than 27°C at which results similar to those on Pt would be found. 2-Bromobutane and 2-bromopropane behave very similarly on Ni at higher temperatures.

We conclude, thus, that the mechanisms of the catalytic hydrogenolysis on Pd, Pt, and Ni are basically the same and that there are two extreme reaction structures, one for Pd (70-214°C), Pt (100°C), and Ni (lower temperatures) and the other for Ni (higher temperatures). Details of the reaction structures will be given later.

### *Dehydrobromination by Ni and Pt*

A blank was run before studying the catalytic dehydrobromination. 2-Bromobutane at 30 torr was circulated through the reaction system. The reaction vessel, which

TABLE 2

DEUTEROGENOLYSIS OF 2-BROMOPROPANE AND 2-BROMOBUTANE ON Ni

| | | | | | | |
|---|---|---|---|---|---|---|
| React. temp. (°C): | | 27 | 70 | 100 | 150 | 150 |
| Catalyst[a] wt (g): | | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Initial press. (torr): | 2-Bromopropane | 253 | 253 | 253 | 253 | |
| | 2-Bromobutane | | | | | 58 |
| | Deuterium[b] | 507 | 507 | 507 | 507 | 285 |
| React. time: | | 2 days | 2 hr | 20 min | 3 min | 5 min |
| Comp'n of reaction mixture sampled (torr): | 2-Bromopropane | 225.5 | 203.7 | 221.5 | 223.0 | — |
| | Propane | 17.2 | 12.3 | 3.5 | 4.0 | — |
| | Propene | 10.3 | 37.0 | 28.0 | 26.0 | — |
| | 2-Bromobutane | — | — | — | — | 48.5 |
| | *n*-Butane | — | — | — | — | 0 |
| | Butenes | — | — | — | — | 9.5[c] |
| | Hydrogen | 489.8 | 494.7 | 503.5 | 503.0 | 285 |
| | Hydrogen bromide | 27.5 | 49.3 | 31.5 | 30.0 | 9.5 |

| | | Propane | Propene | Propane | Propene | Propane | Propene | Propane | Propene | Butenes |
|---|---|---|---|---|---|---|---|---|---|---|
| Deuterium distribution | $D_0$ | 5.7% | 30.0% | 15.2% | 45.0% | 7.6% | 60.0% | 2.5% | 89.5% | 81.6% |
| in propane, propene, | $D_1$ | 12.7 | 41.5 | 37.3 | 40.5 | 38.2 | 33.5 | 51.8 | 7.5 | 17.6 |
| and butenes: | $D_2$ | 21.3 | 21.0 | 21.3 | 11.5 | 25.7 | 4.2 | 21.0 | 2.0 | 0.73 |
| | $D_3$ | 15.6 | 5.5 | 9.6 | 2.3 | 8.2 | 1.8 | 9.0 | 1.0 | 0.07 |
| | $D_4$ | 14.0 | 1.5 | 4.9 | 0.7 | 0.4 | 0.5 | 2.4 | 0 | 0 |
| | $D_5$ | 12.4 | 0.5 | 5.8 | 0 | 10.0 | 0 | 6.1 | — | — |
| | $D_6$ | 7.4 | 0 | 0.2 | — | 0 | — | 0.1 | — | — |
| | $D_7$ | 8.0 | — | 4.3 | — | 5.7 | — | 4.5 | — | — |
| | $D_8$ | 2.9 | — | 1.4 | — | 4.2 | — | 2.6 | — | — |
| | $D_{av}$ | 3.4 | 1.1 | 2.0 | 0.73 | 2.4 | 0.49 | 2.1 | 0.15 | 0.19 |
| Isomers of 2-bromopropane or 2-bromobutane: | | None | | None | | None | | None | | None |
| Deuterated 2-bromopropane or 2-bromobutane: | | None | | Almost none | | $D_0$ 95%, $D_1$ 5% | | $D_0$ 93%, $D_1$ 7% | | $D_0$ 91.6%, $D_3$ 0.06 $D_1$ 7.8, $D_4$ 0.07 $D_2$ 0.47, $D_{av}$ 0.092 |
| Comp'n of hydrogen (%): | $H_2$ | 4.2 | | 3.8 | | 3.6 | | 2.9 | | 4.9 |
| | HD | 10.7 | | 13.4 | | 10.1 | | 9.8 | | 15.1 |
| | $D_2$ | 85.1 | | 82.8 | | 86.3 | | 87.3 | | 80.0 |
| | D content | 90.5 | | 89.5 | | 91.4 | | 92.2 | | 87.6 |

[a] The same charge of catalyst was used. For the same reason as mentioned in the footnote *a*, *b* of Table 1, it was reactivated by reduction in deuterium after each run.

[b] See footnote *c* of Table 1 for the composition.

[c] Consisting of 1-, *trans*-2-, and *cis*-2-butene in an approximately equilibrium composition.

contained no evaporated film, was heated to 150°C. No pressure increase was observed in 72 hr and the gas chromatographic analysis indicated no change in the reaction mixture.

Catalytic dehydrobromination runs with 2-bromobutane were made on both Ni and Pt at 150°C and an initial pressure of 30 torr. Dehydrobromination was found to occur on both metals as shown in Fig. 3. At the end of each run, 1-, *trans* 2-, and *cis*-2-butene were present in approximately their equilibrium proportions.

In confirmation of the conclusions of the preceding section, we have, thus, established that Ni and Pt metals as such both catalyze dehydrobromination.

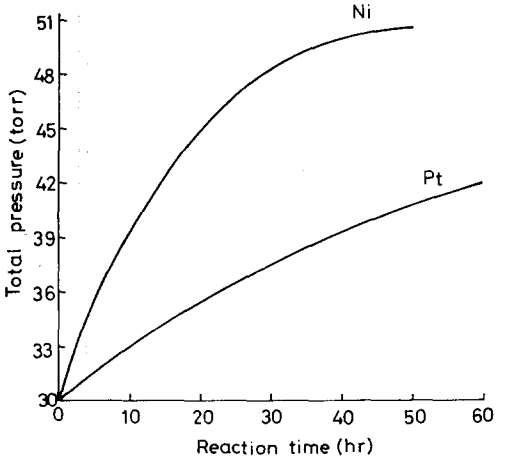
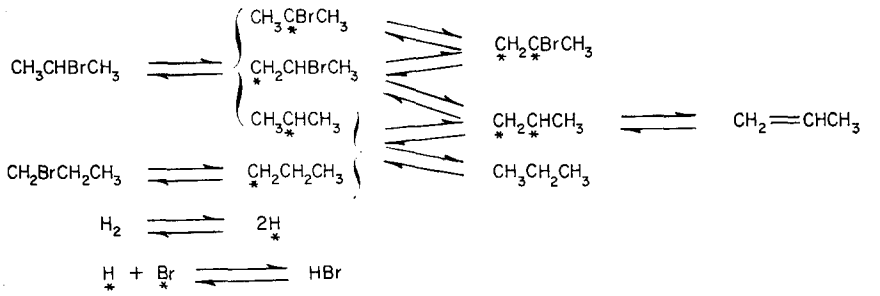



Fig. 3. Dehydrobromination of 2-bromobutane on Pt and Ni evaporated film at 150°C.

### *Reaction Structures*

In this section we shall consider the reaction structures of the hydrogenolysis of alkyl halides using 2-bromopropane as example.

The mechanism of the catalytic hydrogenation of olefins and that of exchange of alkane with deuterium on metallic catalysts have been reasonably well established (*5*). By analogy, the following processes should be considered for reactions of alkyl halides on Ni, Pt, and Pd:



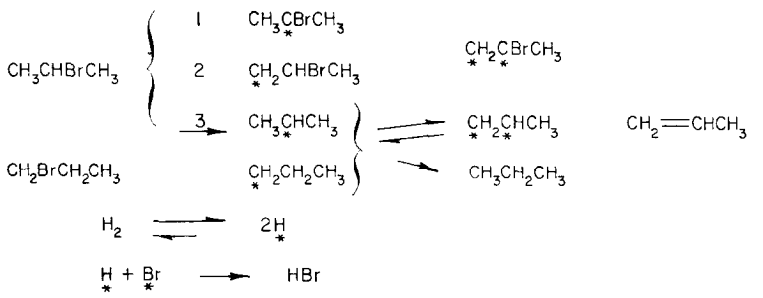

where * represents a site on the catalyst.

### *The Reaction Structure for Ni (Lower Temperatures), Pd, and Pt*

The reaction structure is determined by estimating the relative rates of the elementary steps constituting the above mechanism with the aid of the data in Tables 1 and 2.

The experimental results for Ni (lower temperatures), Pd, and Pt show the following characteristics: (1) formation of HD is much faster than that of $H_2$; (2) highly deuterated alkanes are formed; (3) no isomerization of the substrates occurs; (4) there is no formation of deuterated substrates, and (5) no formation of olefins. Items (1) and (2) indicate that the ratio $D_*/H_*$ on the catalyst surface is large and, thus, that the rates of adsorption of $D_2$ and desorption of HD are large. Item (2) also establishes that the rate of interconversion of mono- and diadsorbed alkane is fast relative to the rate of associative desorption of alkane. Items (3) and (4) indicate that the rate of desorption of alkyl bromide is negligible. Desorbed alkyl bromide might arise from either monoadsorbed alkyl bromide plus D* or from monoadsorbed alkane plus Br*. In either case, an alkyl bromide-*d* should be formed and none is. Item (5) indicates either that there is no desorption of diadsorbed alkane to form olefin (g) or that any olefin so formed readsorbs and goes to alkane at a rate much in excess of that of hydrogenolysis of alkyl bromide. If the former possibility is tenta-

tively taken as correct, the simplest reaction structure which can accommodate the results is




Here, the relative lengths of the arrows indicate roughly the relative rates. The rate of adsorption of alkyl bromide, the rates of desorption of HBr and alkane, and the net rate of adsorption of hydrogen must be identical. The rate of interconversion of mono- and diadsorbed alkane is faster and the rates of adsorption and desorption of $H_2$ are the fastest rates of all. The rates of reactions $-1$ and $-2$ must be zero and we show the rates of 1 and 2 as zero. However, the rates of 1 and 2 might be significant provided that the rate of conversion of the monoadsorbed alkyl bromides to diadsorbed alkane was significant.

In this reaction structure, we implicitly assume that the coverage by H is large enough so that the ratio, (monoadsorbed alkane)/(diadsorbed alkane), is large and that, consequently, the rate of desorption of olefin is negligible. This corresponds to the situation during isotopic exchange of alkane at temperatures of 200°C or less.

*The Reaction Structure of Ni (Higher Temperatures)*

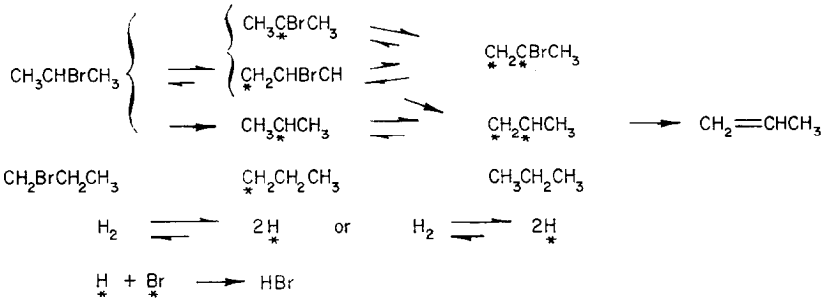
The experimental results in this case are characterized by (1) much faster formation of HD than of $H_2$, (2) predominant formation of olefin of a rather low degree of deuteration, with the small amount of alkane formed being much less highly deuterated than in the previous case, (3) no isomerization of the alkyl bromide, (4) dehydrobromination predominating over hydrogenolysis, and (5) formation of slightly exchanged reactant alkyl halide.

We suggest that the key difference between this case and the former one is that coverage by $H_*$ is much smaller in the present case and that, consequently, the ratio, (monoadsorbed alkane)/(diadsorbed alkane), is small. Thus, the rate of desorption of olefin is large. This corresponds to the situation during the hydrogenation of olefins on palladium and nickel. On platinum, however, the rate of desorption of olefin during the hydrogenation of olefins is slow (*5*, *6*). Item (5) demonstrates that formation and desorption of monoadsorbed alkyl bromides must proceed at a detectable rate although the desorption rate is small relative to that of desorption of olefin. Item (3) demonstrates that the rate of associative desorption from $_*CH_2CH_2CH_3 + Br_*$ is negligible. This suggests that desorption from $CH_3\overset{*}{C}HCH_3 + Br_*$ is also negligible. It does not, however, prove this since the rate of the first reaction could be negligible even though that of the second reaction was significant, if the standard free energy of *n*-propyl bromide was enough less than that of isopropyl bromide.

There are two possible interpretations of item (1). First the ratio $D_*/H_*$ is large and, therefore, the rates of adsorption and desorption of hydrogen (deuterium) are large. If this is correct, the relative rate of interconversion of mono- and diadsorbed alkane is smaller than in the previous case. Alternatively, the ratio $D_*/H_*$ is small, about unity, and, therefore, the rate of desorption of hydrogen is small.* If this is correct, the relative rate of interconversion of mono- and diadsorbed alkane would be larger than the observed isotopic distribution might

* This has some appeal since it would go along with $\theta_{H*}$ being small so that $\theta_{*CH_2CH*CH_3}/\theta_{*R}$ is large.

naively suggest. However, if $D_*/H_*$ is of the order of magnitude of unity, one would expect the initial rate of formation of $H_2$ vs. HD to be larger than we observed. However, the rate of the reaction $H_2 + D_2 = 2HD$ might be large on special sections of the surface of Ni. The reaction structure for Ni at higher temperatures would then be




In this, we omit the effect of the small yields of 2-bromopropane-$d_2$ and propane. We have ignored the adsorption of HBr both in this reaction structure and in the previous one but we have no evidence which indicates that its rate is actually zero.

Some of the uncertainties in the reaction structures could be eliminated by suitable experiments, for example, by determining the effect of alkyl bromide upon the rate of the reaction, $H_2 + D_2 = 2HD$, by studying the rate of exchange between DBr and alkyl bromide, by determination of the degree of isomerization during the hydrogenolysis of 1-bromobutane, etc.

## Acknowledgments

The present authors express appreciation to Mr. Y. Fukuda for his assistance in the dehydrobromination experiment on Ni and to Mr. M. Tachibana for performing the dehydrobromination experiment on Pt.

## References

1. Campbell, J. S., and Kemball, C., *Trans. Faraday Soc.* **57**, 809 (1961).
2. Campbell, J. S., and Kemball, C., *Trans. Faraday Soc.* **59**, 2583 (1963).
3. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 377 (1957).
4. Willstätter, R., and Waldschmidt-Leitz, E., *Ber.* **54**, 113 (1921).
5. See Bond, G. C., "Catalysis by Metals." Academic Press, London and New York, 1962.
6. Hussey, A. S., Keulks, G. W., Nowack, G. P., and Baker, R. H., *J. Org. Chem.* **33**, 610 (1968).