

The Hydroisomerization of *n*-Butenes

2. The Reaction of 1-Butene over Mercury-Poisoned Rhodium-Silica Catalysts

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The influence of adsorbed mercury upon the rates of hydrogenation, isomerization and olefin exchange over silica-supported rhodium catalysts has been studied in the temperature range 0-69°, using deuterium and radioactive tracer techniques. The results show that whereas the rates of hydrogenation and 1-butene exchange decrease uniformly with increasing mercury coverage, the rate of isomerization is virtually independent of mercury coverage up to $\theta_{\text{H}_2} > 80\%$. The results are interpreted in terms of a model in which hydrogenation and olefin exchange occur directly on the metal, while isomerization involves the migration of adsorbed 1-butene from the metal to the support followed by isomerization on the silica.

INTRODUCTION

There are a number of reports of the inhibition of hydrogenation reactions over Group VIII metal catalysts poisoned by small amounts of heavy metals (1). Campbell and Thomson (2) investigated the poisoning of evaporated nickel films for the hydrogenation of cyclopropane and propylene using radioactive mercury as the poison. Subsequently, Bond and Wells (3) showed that mercury was also a poison for the hydrogenation of acetylene over alumina-supported palladium catalysts. Campbell and Hislop (4) have recently reported upon the poisoning action of mercury for the hydrogenation of cyclopropane over nickel-pumice and palladium-pumice catalysts.

The poisoning action of heavy metals has usually been interpreted in terms of the physical obstruction of the surface for the adsorption of the reactants, although as the toxic metals are those with filled *d* orbitals, electron donation to the *d*-band

vacancies of the metal may be significant in a manner analogous to the catalytic behavior of Hume-Rothery alloys (5).

In a previous paper (6) we suggested that over alumina- and silica-supported rhodium catalysts the isomerization of 1-butene proceeds via a 1-methyl- π -allyl intermediate, and consequently isomerization and hydrogenation of 1-butene are independent of each other. In order to examine this postulate further, we have studied the influence of adsorbed mercury upon the rates of isomerization, hydrogenation and olefin exchange in the reaction between 1-butene and deuterium over silica-supported rhodium catalysts. The results of this study are presented in this paper.

EXPERIMENTAL

Materials. The preparation of 5% Rh/silica catalyst has been described previously (6). 1-Butene, from Matheson Co. Inc., contained 0.4% isobutene as impurity. However, tests showed that at this level, the impurity had no effect upon the reaction and consequently the 1-butene was merely degassed before use. Cylinder deuterium of isotopic purity ≥ 99.7 at.% D,

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from I.C.I. Ltd., was used without further purification.

Radioactive mercury (^{197}Hg , ^{203}Hg) was supplied by the Isotope Production Unit, AERE, Harwell in batches containing *ca.* 50 mCi of ^{203}Hg ($t_{1/2}$, 47 days) and *ca.* 700 mCi of ^{197}Hg ($t_{1/2}$, 65 hr). Each batch was allowed to stand for at least 4 weeks so that the activity of the short-lived isotope became negligible. The radioactive mercury was then diluted to the required activity with normal mercury and vacuum distilled before use.

Apparatus and methods. The general features of the apparatus and reaction procedure have been described previously (6). The principal feature in the design of the apparatus was that the entire system was mercury free, thus preventing any possibility of unintentional contamination of the catalyst by mercury vapor.

The catalyst (2.0–12.5 mg) was placed in the shallow well situated in the base of the Pyrex glass reaction vessel (volume *ca.* 100 ml) shown in Fig. 1. The vessel and side-arm were evacuated, tap T_2 closed and the catalyst activated in 150 mm deuterium at 220°C for 1 hr.

The adsorption of mercury was carried out as follows: The reaction vessel was evacuated and tap T_1 closed; mercury vapor was then allowed to diffuse via tap T_2

from the ampoule C, which was maintained at a constant temperature, usually 0°, into the catalyst vessel. The extent of adsorption was followed by means of an end-window Geiger-Muller counter (Mullard MX 168/01) mounted immediately below the reaction vessel. The window of the counter was fitted with a lead disc of thickness 87 mg cm^{-2} to increase the count rate by the photoelectric effect with γ radiation. At the required time the adsorption was stopped and a series of reactions was performed. Using this procedure, the effect of the progressive poisoning of the catalyst was investigated.

The absolute amount of mercury adsorbed on the catalyst was determined in the following way. After the final series of reactions on the poisoned catalyst, the latter was boiled with *ca.* 50 ml of 12 *M* nitric acid solution for 30–40 min to dissolve the adsorbed mercury. The resulting solution was evaporated to *ca.* 5 ml and then accurately diluted to 10 ml with distilled water. The solution was counted in a liquid Geiger-Muller counter and the count rate compared with that obtained from a similar solution containing a known weight of radioactive mercury of the same specific activity as that used for the adsorption. This gave an apparent specific activity which, together with the count rates observed with the external counter, was used to calculate the weight of mercury adsorbed on the catalyst at any given time.

Analysis. Gas chromatography was used (i) to estimate quantitatively the relative concentrations of the hydrocarbon products and (ii) to separate the hydrocarbon products into individual fractions for mass spectrometric analysis. Both of these functions were achieved using a 20 ft column consisting of 40% w/w 2,5-hexadione supported on 60–80 mesh Silocel firebrick. The column was operated at ambient temperature and nitrogen was used as carrier gas. The corrected retention volumes were 200, 385, 525 and 650 ml, respectively, for *n*-butane, 1-butene, *trans*-2-butene, *cis*-2-butene. On elution the products were condensed out of the carrier gas stream

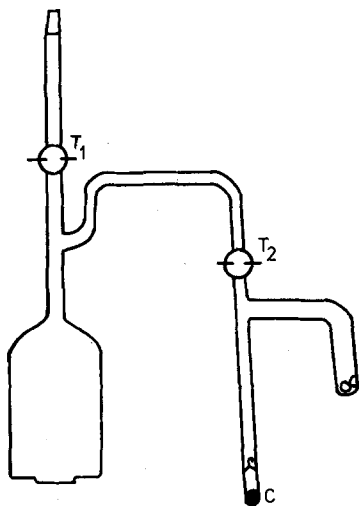


Fig. 1. Reaction vessel used for mercury adsorption.

separately into receivers cooled in liquid nitrogen. Each sample was then transferred to the mass spectrometer for analysis for deuterium content.

The deuterated hydrocarbons were analyzed using a A.E.I. MS10 mass spectrometer operated at an electron beam voltage of 12.0 eV. The true parent ion intensities, and hence the deuterio distribution, were obtained by correcting the measured positive ion currents for fragmentation and ^{13}C contributions.

The residual deuterium was analyzed at 70 eV to determine the isotopic purity using the untreated gaseous mixture extracted from the reaction vessel.

RESULTS

Adsorption of mercury on Rh/silica catalysts. The characteristics of the adsorption of mercury were investigated in a three-stage continuous adsorption using 10.6 mg of catalyst. The relationship between the extent of adsorption and the time for which the adsorption had proceeded is shown in Fig. 2.

During steps 1 and 2, the mercury source was maintained at 0°C while the catalyst was kept at $12 \pm 1^\circ$ and $18 \pm 0.5^\circ$, respectively. For stage 3, the catalyst temperature was $27 \pm 1^\circ$, while the mercury source was at $22 \pm 0.5^\circ$. Blank experiments showed that under the conditions used, the count rate due to mercury in the gas phase was negligible and thus the increase in count rate from stage 2 to 3 is due to an increase in the amount of mercury adsorbed on the catalyst.

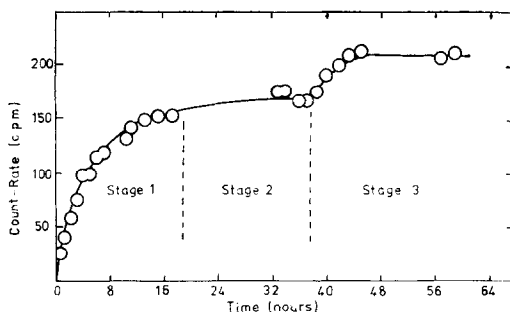


FIG. 2. Adsorption isotherm for mercury on Rh/SiO₂ catalysts.

Since it was intended to investigate the hydroisomerization of 1-butene on partially poisoned catalysts at various temperatures, it was necessary to investigate the effect of temperature upon the adsorbed mercury. This was carried out as follows. Radioactive mercury was absorbed onto a 5.2 mg sample of catalyst until no further increase in count rate was observed (*ca.* 8 hr). The catalyst vessel was then continuously evacuated as the temperature was slowly increased to 120° , this being the maximum temperature at which the Geiger-Muller counter could be operated. Up to 120° the count rate remained constant showing that no mercury desorption had occurred. However, after the catalyst had been heated to 300° with continuous evacuation, and cooled again to 25° , the count rate had fallen from an initial value of 117.5 cpm to 18.2 cpm. Thus, between 120 and 300° , 84.5% of the mercury had been desorbed.

1-Butene Hydrogenation and Isomerization

Courses of reaction. Series of reactions were carried out, using equal partial pressures (30.0 ± 1.0 Torr) of 1-butene and deuterium, at 0, 21 and 69° using catalyst samples weighing 12.6, 6.4 and 2.0 mg, respectively. The effect of adsorbed mercury upon the course of reaction was studied at each temperature using the following poisoning procedure: With the mercury source at 0°C , the catalyst temperature was raised to 25, 48 or 83° from the reaction temperature of 0, 21 or 69° , respectively, and an amount of mercury was adsorbed onto the catalyst. The catalyst was then allowed to reattain the reaction temperature and a series of reactions carried out. By repeating this procedure a number of times, successive increments of mercury were absorbed onto the catalyst and the variation of the butene distribution with conversion to *n*-butane studied as a function of the adsorbed mercury concentration. As the amount of adsorbed mercury was increased, fewer reactions per series were carried out, since it was observed that the relative poisoning effects on the hydrogenation and isomerization re-

TABLE 1
THE VARIATION OF THE BUTENE DISTRIBUTION
WITH CONVERSION AT VARIOUS CONCENTRATIONS OF ADSORBED MERCURY

$(P_{1-B})_0 = 30.0 \pm 1.0$ mm $(P_{D_2})_0 = 30.0 \pm 1.0$ mm

Temperature = 21°C

θ_{Hg}	% C_4H_{10}	Butene distribution %		
		1-B	<i>trans</i> -2-B	<i>cis</i> -2-B
0.000	10.3	88.9	5.1	6.1
	26.5	68.1	15.5	16.4
	41.1	29.3	41.2	29.5
0.395	10.0	60.9	19.8	19.3
	25.4	13.9	50.4	35.7
	41.1	2.5	72.3	25.2
0.786	11.1	7.9	58.6	33.5
	18.1	2.0	73.4	26.6
0.931	3.8	12.8	54.4	32.7
	6.5	3.1	70.9	25.9

actions were such as to allow the butenes to isomerize to their thermodynamic equilibrium proportions at lower conversions to *n*-butane. A typical set of results, obtained at 21°, is shown in Table 1. Similar series of results were obtained at 0 and 69°.

In this and subsequent tables and figures, the concentration of adsorbed mercury, designated θ_{Hg} , is defined as the ratio of the amount of mercury adsorbed at any time t to the amount adsorbed at t_∞ . The latter corresponds to the plateau region of Fig. 2.

Initial rates of hydrogenation and isomerization. The initial rates of hydrogenation were calculated from the plots of pressure fall against time. The variation in rate of hydrogenation with adsorbed mercury concentration is shown in Fig. 3.

Initial rates of isomerization were calculated from the product analyses as described previously (θ). Plots of the rate of isomerization against adsorbed mercury concentration are shown in Fig. 4.

Comparison of Figs. 3 and 4 shows that over the temperature range studied, whereas the rate of hydrogenation falls regularly with increasing mercury coverage, at 21 and 69°, the rate of isomerization remains virtually constant up to $\theta_{Hg} = 0.90$, al-

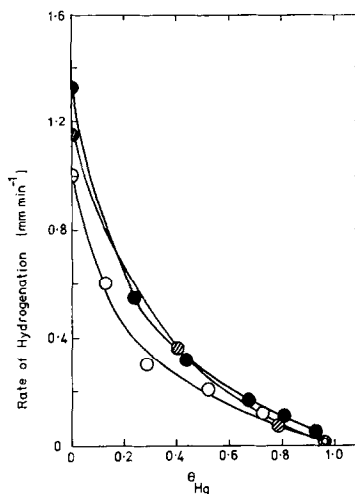


FIG. 3. Variation of rate of 1-butene hydrogenation with mercury coverage, θ_{Hg} (○, 0°C; ◐, 21°C; ●, 69°C).

though at 0° the isomerization rate decreases with increasing θ_{Hg} above $\theta_{Hg} = 0.55$.

Deuterobutene distributions. The products of reactions extracted at $12 \pm 2\%$ conversion to *n*-butane were analyzed for deuterium content, and the deuterobutene distributions determined. Table 2 shows some typical results for reactions carried out at 69°. Similar results were obtained at other mercury coverages and at 0 and 21°.

The deuterobutene distributions exhibit several interesting features. The *trans*- and *cis*-2-butene distributions are very similar with a pronounced maximum at $-d_0$. With increasing concentration of adsorbed mer-

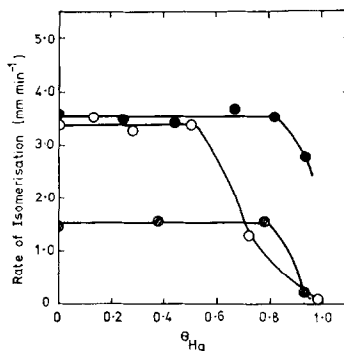


FIG. 4. Variation of rate of 1-butene isomerization with mercury coverage, θ_{Hg} (○, 0°C; ◐, 21°C; ●, 69°C).

TABLE 2
THE VARIATION OF DEUTEROBUTENE DISTRIBUTIONS WITH INCREASING MERCURY COVERAGE

	$(P_0)_{C_4H_8} = 30.0 \pm 1.0$ Torr Conversion = $12 \pm 2\%$			$(P_0)_{D_2} = 30.0 \pm 1.0$ Torr Temperature = 69°C					
	0.000			0.444			0.937 ^a		
θ_{Hg}	1-B	<i>t</i> -2-B	<i>c</i> -2-B	1-B	<i>t</i> -2-B	<i>c</i> -2-B	1-B	<i>t</i> -2-B	<i>c</i> -2-B
$-d_0^b$	96.5	87.5	84.3	80.9	78.8	82.9	84.4	88.2	90.5
$-d_1$	2.9	10.2	12.9	15.8	17.8	12.7	12.6	9.7	7.9
$-d_2$	0.4	1.9	2.3	2.7	2.8	3.1	2.4	1.6	1.3
$-d_3$	0.1	0.3	0.4	0.4	0.6	0.8	0.4	0.3	0.2
$-d_4$	0.1	0.1	0.1	0.2	0.0	0.5	0.2	0.2	0.1
D. N.	0.04	0.15	0.19	0.23	0.28	0.23	0.20	0.14	0.13
H. N.		0.226			0.386			0.088	

^a Conversion = 5.3%.

^b In all cases $-d_5 < 0.1$ and $-d_6, -d_7$ and $-d_8 = 0.0$.

cury, the deuterium number of each butene increased slightly, especially with 1-butene, although the rate of 1-butene exchange, defined as:

$$\text{rate of exchange} = \sum_1^8 (\text{partial pressure of } 1\text{-butene-}d_n) / \text{reaction time,}$$

decreased with increasing mercury coverage (see Fig. 5) at each temperature. Temperature appeared to have little effect upon the deuterobutene distributions.

DISCUSSION

The most striking feature of the results presented above is the marked difference in the effect of adsorbed mercury upon the rates of hydrogenation (Fig. 3), 1-butene

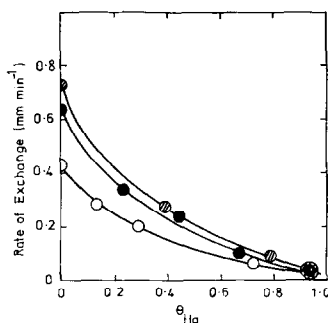
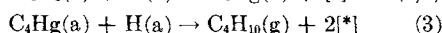
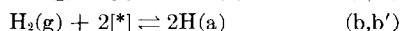


FIG. 5. Variation of rate of 1-butene exchange with mercury coverage, θ_{Hg} (\odot , 0°C ; \ominus , 21°C ; \bullet , 69°C).

isomerization (Fig. 4) and 1-butene exchange (Fig. 5). Of particular interest is the observation that whereas the rates of hydrogenation and 1-butene exchange decrease uniformly with increasing mercury coverage, at 21 and 69° the rate of isomerization is independent of the surface concentration of mercury up to approximately 90% of the monolayer coverage.

In Part I of this series (6) we showed that the kinetics of 1-butene hydrogenation over unpoisoned rhodium-silica catalysts were consistent with the following mechanism:



Evidence was also presented in Part I to suggest that isomerization occurred via a 1-methyl- π -allyl mechanism rather than via an adsorbed 2-butyl intermediate.

On mercury poisoned catalysts the overall kinetics for hydrogenation were of the same form as over unpoisoned catalysts, namely first order in total pressure. This suggests that the mechanism for hydrogenation is similar over poisoned and unpoisoned catalysts, and it is therefore pertinent to examine the effect of adsorbed mercury in the light of the above postulated mechanism.

Considering first the hydrogenation of 1-

butene, the rate of hydrogenation decreased uniformly with increasing mercury coverage, being reduced to zero at $\theta_{\text{Hg}} = 1.00$. It may reasonably be assumed that all the mercury atoms are adsorbed on surface rhodium atoms (5), and thus adsorbed mercury must exert a physical blocking effect upon the adsorption of the reactants. The presence of adsorbed mercury will, therefore, reduce both θ_{H} and $\theta_{1-\text{B}}$.

Assuming that mercury, 1-butene and hydrogen are adsorbed on similar surface sites, the surface concentrations of 1-butene ($\theta_{1-\text{B}}$), and hydrogen (θ_{H}) may be written as:

$$\theta_{1-\text{B}} = b_{1-\text{B}}P_{1-\text{B}}(1 - \theta_{\text{Hg}})/(1 + b_{1-\text{B}}P_{1-\text{B}} + b_{\text{H}_2}^{1/2}P_{\text{H}_2}^{1/2})$$

and

$$\theta_{\text{H}} = b_{\text{H}_2}^{1/2}P_{\text{H}_2}^{1/2}(1 - \theta_{\text{Hg}})/(1 + b_{1-\text{B}}P_{1-\text{B}} + b_{\text{H}_2}^{1/2}P_{\text{H}_2}^{1/2})$$

In the present reaction where 1-butene is relatively strongly adsorbed and hydrogen weakly adsorbed, these equations may be simplified to:

$$\theta_{1-\text{B}} \propto (1 - \theta_{\text{Hg}}) \text{ and } \theta_{\text{H}} \propto b_{\text{H}_2}^{1/2}P_{\text{H}_2}^{1/2}(1 - \theta_{\text{Hg}})$$

Steady-state analysis of the above reaction scheme shows that the rate of hydrogenation (r_h) is

$$\begin{aligned} r_h &= k_3 \cdot \theta_{\text{C}_4\text{H}_8} \cdot \theta_{\text{H}} \\ &= k_1 k_3 \theta_{\text{C}_4\text{H}_8} \theta_{\text{H}}^2 / (k_2 + k_3 \theta_{\text{H}}). \end{aligned}$$

Thus, under conditions where $k_2 \gg k_3 \theta_{\text{H}}$, the rate of hydrogenation is directly proportional to the initial hydrogen pressure and to $(1 - \theta_{\text{Hg}})^3$ which is of a similar form to that observed experimentally (Fig. 3).

The observation that the rates of 1-butene exchange and isomerization show different dependencies upon the extent of mercury coverage suggests that the two processes occur independently of each other. A similar conclusion was reached from a consideration of the kinetics (6).

Assuming that, as the kinetic evidence suggests, the reversal of the formation of adsorbed butyl [step (2)] is rapid relative to the rate of hydrogen atom addition to adsorbed butyl [step (3)], step (2) will give rise to the introduction of deuterium

into the adsorbed but-1-ene. The rate of 1-butene exchange will be given by:

$$\begin{aligned} r_e &= k_2 \theta_{\text{C}_4\text{H}_8} \text{ (assuming step (2) is the rate-determining step)} \\ &= k_1 k_2 \theta_{\text{C}_4\text{H}_8} \theta_{\text{H}} / (k_2 + k_3 \theta_{\text{H}}) \end{aligned}$$

and thus, under conditions where $k_2 \gg k_3 \theta_{\text{H}}$, the rate of 1-butene exchange will be proportional to $(1 - \theta_{\text{Hg}})^2$ in agreement with the experimental observations (see Fig. 5).

From the foregoing discussion it is clear that, while the hydrogenation and 1-butene exchange results obtained using mercury poisoned catalysts are consistent with a mechanism involving the addition and abstraction of hydrogen atoms from adsorbed hydrocarbon species, the dependence of the rate of isomerization upon adsorbed mercury concentration is such as to lead to the conclusion that: (i) as stated above, butene isomerization occurs independently of hydrogenation and olefin exchange; and (ii) butene isomerization occurs on different sites from those involved in the adsorption of mercury.

Two possible explanations of these observations can be postulated. First, assuming that both hydrogenation and isomerization occur on the metal surface, then the adsorption of mercury must be restricted to those surface sites which are active in hydrogenation but not in isomerization. While it is generally accepted that the surfaces of metal catalysts are heterogeneous with respect to hydrocarbon adsorption (9), and it is thus possible that different metal sites are responsible for hydrogenation and isomerization, it seems unlikely that mercury adsorption is specific for only those sites which are active in hydrogenation and olefin exchange. Furthermore, results obtained from studies of mercury adsorption on metal films (10, 12) are most satisfactorily interpreted in terms of a model in which mercury adsorbs randomly on the surface sites.

An alternative explanation of our observations lies in the postulate that while hydrogenation and 1-butene exchange occur on the metal, isomerization occurs on the silica. In a recent study of the reactions of unsaturated hydrocarbons on silica and

