

Butene Isomerization Catalyzed by Supported Metals in the Absence of Molecular Hydrogen

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Alumina-supported nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum are active at 100°C for butene isomerization in the absence of molecular hydrogen, and for an isotopic exchange reaction between gaseous hydrogen and hydrogen atoms associated with the support. Relative isomerization activities have been determined qualitatively and, with the exception of platinum, the activity sequence is independent of the phase of alumina used as support. Nevertheless, the alumina support appears to be an essential constituent of the catalyst if butene isomerization is to be achieved. Mechanism is not studied in detail, but it is likely that hydrogen atoms which migrate from the support to the metal initiate butene isomerization at the metal surface.

In a previous communication we have shown that isomerization of butenes (i.e., double bond migration and *cis*-*trans* isomerization) proceeds in the *absence* of molecular hydrogen when cobalt wire, or cobalt-alumina are used as catalyst (1). Cobalt powder is also active. Furthermore, *cis*-*trans* isomerization of deuterium-labeled *cis*-1,3-pentadiene takes place at the surface of cobalt-alumina by an abstraction-addition mechanism (2). The advantages of being able to examine olefin isomerization without the reactant being consumed by hydrogenation have been stressed (2).

Having established the activity of cobalt, it was of interest to us to determine whether other Group VIII metals are active under similar conditions. There are no obvious reasons why cobalt should possess unique properties, but there are reports in the literature that nickel is inactive for butene isomerization in the absence of hydrogen (3). Indeed, such negative findings have been accommodated in discussions of mechanism (3, 4). Thus, our first

objective was to establish whether other Group VIII metals were active for 1-butene isomerization, and to this end we have conducted a qualitative survey of the activities of alumina-supported Ni, Ru, Rh, Pd, Os, Ir, and Pt for this reaction. Conditions were quickly found under which these preparations were catalytically active and so, as a second objective, we examined the effect of changing the phase of alumina used as support.

NOMENCLATURE AND DEFINITIONS

The following nomenclature will be used in this paper.

The term *hydrogen* will be used only when no isotopic differentiation is necessary. H and D will be referred to as protium and deuterium, respectively, when isotope differentiation is important. The catalytic interconversion of butene isomers will be called *isomerization* when the process occurs in the absence of molecular hydrogen, and *hydroisomerization* when it proceeds in the presence of molecular hydrogen. The process whereby protium atoms associated with the catalyst support exchange with gaseous deuterium to form

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deuterated support and gaseous HD and H₂ will be termed *the hydrogen exchange reaction between the support and the gas phase*, or, more briefly but less accurately, *the support-deuterium exchange reaction*.

The *protium number* of a hydrogen sample is the average number of protium atoms present per molecule (i.e., x in H₂D_(2-x)).

The *extent of 1-butene isomerization* is defined as $(100 - y)/(100 - z)$ where y is the measured percentage of 1-butene in samples extracted from the vessel, and z is the percentage 1-butene that would be present in an equilibrium mixture at the relevant temperature.

EXPERIMENTAL

Apparatus and materials. The high-vacuum and GLC analysis apparatus have been described (2). 1-butene (Matheson) contained no impurities detectable by GLC or mass spectrometry. Hydrogen and deuterium were purified by diffusion through heated palladium thimbles.

Catalysts are designated using an M-X code, where M is the chemical symbol of the metal, and X(=A,B,C,D) denotes the support. Support A was a mixture of boehmite and amorphous alumina (Type A alumina marketed by Peter Spence Ltd.). This material had the nominal formula Al₂O₃·H₂O and was used as 8–16 mesh granules. Support B was a 1:1 mixture of α - and κ -Al₂O₃ (ICI Agricultural Division), and was used as cylindrical pellets (3 mm long; 3 mm in diameter). Support C was 8–16 mesh granules of α -Al₂O₃ (ICI Agricultural Division). Support D was granular pumice. X-Ray analysis confirmed the natures of the aluminas. Catalysts were prepared by the usual impregnation technique, followed by calcination in the case of nickel only, and reduction in hydrogen. Rh-A, Pd-A, Pt-A, and Ir-A were made by Johnson, Matthey and Co. Ltd.; Rh-C, Pd-C, and Ir-C by ICI Agricultural Division; and the remainder by workers in this laboratory. The nickel catalysts were made using the nitrate, whereas the other catalysts were made using chlorine-containing salts as the

source of metal. All catalyst samples weighed 0.40 g except Ni-A (0.33 g); other details are given in Table 1.*

TABLE 1
DETAILS OF THE CATALYSTS USED

Catalyst	Percentage metal by weight	Reduction temperature (°C)	BET surface area (m ² g ⁻¹)
Ni-A	10	420	193.2 ± 2.0
Ni-B	10	485	15.1 ± 0.6
Ni-D	10	300	0.4
Rh-A	0.5	205	202.2 ± 5.0
Rh-B	0.5	205	15.5 ± 0.1
Rh-C	5.0	400	2.3 ± 0.2
Ir-A	0.5	205	201.2 ± 2.0
Ir-B	0.5	205	16.5 ± 0.1
Ir-C	5.0	400	3.0 ± 0.1
Ru-A, Pd-A, { Os-A, Pt-A }	0.5	205	Not measured
Pd-C, Pt-C	5.0	400	Not measured
Support A	—	—	183.0 ± 4.0
Support B	—	—	13.7 ± 0.9

Standard procedure for the survey. Samples of reduced catalyst were taken from stock and sealed into reaction vessels of 120-ml capacity; surface oxygen was removed by hydrogen treatment at 200°C for 1 hr. The vessel was then pumped down to normal high vacuum and the temperature was lowered to 100° or 150°C.

The support-deuterium exchange reaction was investigated by admitting 100 mm of deuterium to the vessel and the gas was extracted for mass-spectrometric analysis after 5 min (A.E.I. M.S.3., electron beam energy, 60 eV). To check the result it was, of course, necessary to admit successive portions of protium to the vessel in order to remove deuterium that had

* At one stage we hoped that, by varying the metal loadings per unit area of support as shown in Table 1, we would discover whether isomerization activity was dependent upon mean metal crystallite size. However, the results show that any such dependence was obscured by a more important effect (hydrogen atom mobility between support and metal) and thus our original intentions in varying metal loadings were not realized.

become associated with the support, before deuterium was admitted. Butene isomerization was then investigated by admitting 50 mm of 1-butene to the evacuated vessel. After 10 min the butene was withdrawn for GLC analysis and the vessel was again pumped. This procedure was repeated several times to check the result.

Exchange was studied first and isomerization second to avoid any interference or participation of hydrocarbon residues in the exchange reaction.

Neither reaction was accompanied by a pressure change and hence no simple means of following reactions was available. The reactions times of 5 and 10 min referred to above are those for which as many catalysts as possible gave moderate reaction rates.

RESULTS AND DISCUSSION

Preliminaries

The effect of varying the length of the pumping time before butene admission, and the constancy or otherwise of isomerization activity from one run to the next, were studied thoroughly using Rh-B (see Table 2). Other catalysts were examined less extensively; they behaved similarly except that reaction rates were sometimes less

cedure (i.e., heating the catalyst in hydrogen at 200°C, and then pumping it under high-vacuum conditions while the temperature was reduced to 100°C). The small yield of butane observed in the first few reactions was a trivial feature; a small quantity of butene either disproportionated at very active sites or was saturated by hydrogen that had been occluded in the metal during catalyst preparation.

Over Rh-B at 100°C the initial rate of isomerization was independent of the initial 1-butene pressure (initial pressure was varied from 25 to 100 mm), which indicates that virtually full surface coverage of 1-butene was achieved under these conditions. This is to be expected by comparison with studies of butene hydroisomerization using the C series of catalysts (5).

Supports A and B were inactive at 152°C both for butene isomerization and for the support-deuterium exchange reaction. At 225°C they showed low activities for both reactions, i.e., about 10% of that shown by Rh-C at 100°C (see Fig. 1). Pure supports C and D were not available for study; however, by comparison with the behavior of supports A and B, we expect that support C had no inherent activity for either reaction at 152°C.

TABLE 2
PRELIMINARY EXPERIMENTS USING Rh-B AT 100°C^a

Experiment No.	1	2	3	4	5	6	7	10	15
Pumping time between reactions (min)	15	15	15	15	30	120			
Extent of 1-butene isomerization ($\times 10^2$)	61	60	59	59	58	58	57	55	54
Butane yield (% total products)	2	1	1	Trace	0	0	0	0	0

^a Initial 1-butene pressure, 50 mm.

reproducible. Table 2 shows that butene isomerization activity declined slowly during the course of 15 experiments and that activity was independent of pumping time. The origin of this decline in activity is not known; some butene may have disproportionated slowly to give gaseous butane and dehydrogenated residues that were too strongly adsorbed to be removed by pumping. This is supported by the observation that the original activity was restored by repeating the reduction pro-

The Survey

Results of the survey are shown in Table 3 and in Fig. 1. Table 3 also contains values for the butene composition at thermodynamic equilibrium at 151°C, and for the isotopic composition of the hydrogen gas for a protium number of 1.776 (6).

The support-deuterium exchange reaction. All of the metal-alumina samples were active catalysts for the hydrogen exchange reaction between the support and

the gas phase. This exchange reaction has been reported before, first by Hall and Lutinski (7) and later by Yates, Sinfelt, *et al.* (8); both groups of workers used

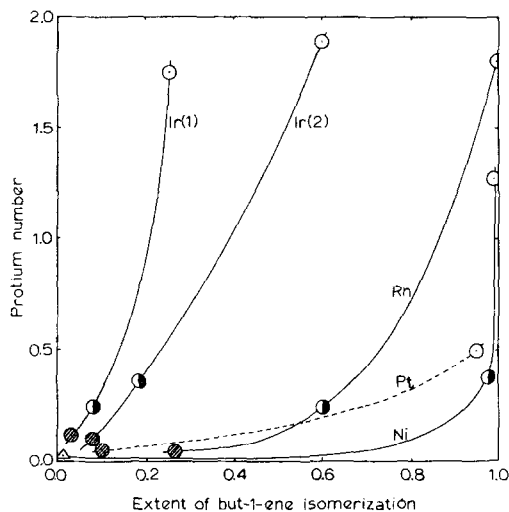


FIG. 1. Protium numbers, and extents of butene isomerization measured during the survey by the standard procedure. Temperatures: Ir(1), Rh, and Pt, 100°C; Ir(2) and Ni, 150°C. Catalysts: A series, open circles; B series, half-filled circles; C series, hatched circles; Ni-D, triangle.

alumina and platinum-alumina. More recently, we have reported the reaction using cobalt supported on alumina support A (2). Rh-A (like Co-A) contained 10^{21}

that the hydrogen atoms so exchanged are originally present in hydroxyl groups bonded to the alumina. In our experiments, the support-deuterium exchange reaction was observed only when metal was present on the support; that is, each metal greatly enhanced the exchange rate. In this respect our results differ somewhat from those of previous workers. Yates, Sinfelt *et al.* observed an exchange reaction at 150° using alumina alone; furthermore, they observed an increased exchange rate when metallic platinum was present, and a decreased rate when chloride was present (8). Hall and Lutinski (7) had previously reported the inhibiting effect of chloride on the exchange; in their system, platinum-alumina (prepared by impregnation using chloroplatinic acid) gave a slower rate of exchange than the pure support. All of our catalysts were prepared using halogen-containing salts as the sources of the metals, with the exception of Ni-A and Ni-D, for which the nitrate was used. Consequently, the accelerative effect of metal far outweighed any inhibiting effect of chloride in our system.

The support-deuterium exchange reaction was most rapid for the A series of catalysts, substantially less rapid for the B series, and slow for the C series and Ni-D. Thus, the exchange rate is proportional to the

TABLE 3
TYPICAL RESULTS OBTAINED FOR Pd-A, Pd-C, Ru-A, AND Os-A
USING THE STANDARD SURVEY PROCEDURE

Catalyst	Temp. (°C)	Hydrogen composition (%)			Protium number	Butene composition (%)		
		H ₂	HD	D ₂		1-Butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene
Pd-A	97	33	47	20	1.13	8.1	60.1	31.8
Pd-A	150	78	20	2	1.67	9.9	57.8	31.4
Pd-C	150	1	8	91	0.10	10.9	57.5	31.6
Ru-A	97	18	44	38	0.80	8.2	62.9	28.9
Ru-A	151	80	18	2	1.78	10.2	57.2	32.6
Equilibrium	151	79.02	19.60	1.38	1.776	9.6	61.7	28.8
Os-A	97	19	46	35	0.84	96.5	2.0	1.5

exchangeable hydrogen atoms per gram of catalyst; this number agrees with the value quoted by Hall *et al.* for some of their preparations (7). It is generally agreed

number of hydrogen atoms that are expected to be associated with the catalysts [the conversion of support A to C and of B to C can be achieved by progressive heat

treatment accompanied by dehydration (9)]. Furthermore, we expect the weakly bound hydrogen associated with support A to exchange more rapidly than the more strongly bound hydrogen associated with supports B and C. The observed relative exchange rates of the three series of catalysts are thus qualitatively interpreted. We suppose that the metal exerts this accelerative effect on the exchange rate because deuterium is able to dissociate into atoms at its surface; these atoms must then migrate to the support where the exchange with protium atoms occurs, followed by the back-migration of protium atoms to the metal, where combination to give gaseous protium and HD takes place. The mechanism of the actual exchange process itself is not revealed by this work. The various metals, when supported on a given form of alumina, exhibit approximately the same efficiency in promoting the exchange reaction. This shows that the actual exchange process is rate-determining and that hydrogen chemisorption and desorption are always relatively fast.

The very occurrence of the support-deuterium exchange reaction demonstrates that the migration of hydrogen atoms from support to metal and *vice versa* proceeds at a measurable rate, and this must be taken into account when consideration is given to the role of adsorbed hydrogen in reactions catalyzed by supported metals.

The initial rates of both the support-deuterium exchange reaction and of butene isomerization declined exponentially as temperature was lowered. The lowest temperature at which each reaction could be conveniently studied over the most active catalysts (Rh-A, Ru-A, and Pd-A) was 20°C.

I-Butene isomerization. The activity for butene isomerization varied from metal to metal, but the following activity sequences for the three series of catalysts exhibit common relationships:

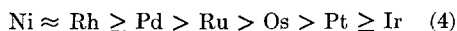
A series: Ni \approx Rh \approx Pd \approx Ru \approx Pt \gg Ir > Os (1)

B series: Ni > Rh > Ir (2)

C series: Pd > Rh > Pt > Ir (3)

The activity of nickel in these sequences is that measured at 150°C, whereas the activities of the other metals are those measured at 100°C. The A series of catalysts were so active that, with the exception of Ir and Os, equilibrium or near-equilibrium proportions of the butenes were obtained under the conditions of the standard procedure, and hence differences between the activities of Ni, Rh, Pd, Ru, and Pt cannot be discerned. Pt-C and Ir-C both exhibit low isomerization activity but, remarkably, Pt-A is very active whereas Ir-A shows only moderate activity. This relatively high activity of Pt-A may be due to the platinum being more efficiently distributed than iridium over the high-area alumina.

In some respects, sequences (1), (2), and (3) above resemble the sequence for butene hydroisomerization activity at 100°C, which is (10)



If the isomerization activity of Pt-A in sequence (1) is considered to be exceptional, each sequence shows that the metals of the third transition series are significantly poorer catalysts than those of the second transition series and nickel.

The Role of the Support in Isomerization

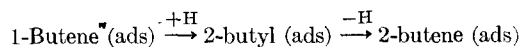
Mellor and Wells have observed that unsupported osmium, iridium, and platinum powders are inactive for butene isomerization at 100°C in the absence of molecular hydrogen, and that rhodium exhibits only an extremely low activity at this temperature (11). These, and other such negative findings recorded in the literature, must be regarded with caution, in view of the established activity of unsupported cobalt (1, 2). However, there can be no doubt (i) that the alumina supports used in this work actively assisted isomerization, and (ii) that alumina is superior to pumice in this respect.

The correlation between isomerization activity and exchange activity demonstrated in Fig. 1 is of the first importance. For each metal, changes in support which cause an increase (or decrease in support-

deuterium exchange activity also cause an increase (or decrease) in 1-butene isomerization activity. There is no doubt that hydrogen atom migration from support to metal crystallites occurs during the exchange reaction. There is, therefore, a *prima facie* case for considering this process to be important in butene isomerization, with the necessary qualification that the actual surface concentration of hydrogen atoms on the metal crystallites must have been much lower during isomerization than during exchange.

The Mechanism of Isomerization

The observations (i) that the activity sequences for isomerization and hydroisomerization are similar, and (ii) that the alumina support plays a positive role, strongly suggest that 1-butene isomerization over these metals proceeds by the addition-abstraction mechanism:



Here we envisage that the hydrocarbon species are adsorbed at sites on the metal surface and that the hydrogen atom which initiates the process has migrated from the surface of the oxide support to the metal surface. Butene isomerization is then a self-sustaining straight-chain reaction. Alternatives to this mechanism are (i) concerted hydrogen switch mechanisms akin to those proposed for butene hydroisomerization over nickel (3a, 12) and (ii) an abstraction-addition mechanism [involving adsorbed C_4H_7 as an intermediate (13)] analogous to those proposed by us for the isomerization of butene and of 1,3-pentadiene over cobalt (1, 2). These alternatives are unlikely; if either was operative butene isomerization could be a self-initiated process (so that the presence of the support would appear to be unnecessary) and the similarity between the isomerization and hydroisomerization activity sequences would be fortuitous. However, the present work does not permit a detailed mecha-

nistic analysis to be made; it was designed only to explore the general descriptive features of the reaction. Experiments designed specifically to reveal reaction mechanisms will be reported in a later paper.

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