

## Hexene-1 Isomerization Catalyzed by Alumina-Supported Triosmium Clusters

X.-J. LI,<sup>1</sup> J. H. ONUFERKO, AND B. C. GATES<sup>2</sup>

*Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19711*

Received January 24, 1983; revised August 1, 1983

Alumina-supported triosmium clusters,  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}$ , were prepared by the reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with surface  $-\text{OH}$  groups of  $\gamma\text{-Al}_2\text{O}_3$ . The material was catalytically active for isomerization of hexene-1 to give *cis*- and *trans*-hexene-2, and infrared spectra of the catalyst under reaction conditions at 1 atm and 50 to 70°C indicated that the osmium was present as  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}$ . The reaction was promoted by hydrogen and was zero-order in hydrogen and in hexene-1 at partial pressures exceeding 0.1 atm. These results suggest that a supported triosmium cluster itself was the catalytically active species, and the effects of  $\text{H}_2$  and  $\text{D}_2$  in reactant mixtures and the characterization of the used catalyst by XPS indicate an insertion mechanism involving hydride ligands on the osmium. When the catalyst was treated at higher temperatures ( $>120^\circ\text{C}$ ), the clusters broke up, giving ensembles consisting of three Os(II) carbonyl complexes. These are similar in their catalytic character to the clusters, as indicated by the kinetics of the isomerization reaction, but they are only half as active as the supported clusters at 70°C.

### INTRODUCTION

Supported metals prepared from molecular metal clusters offer the prospects of materials having new, controllable catalytic activities and selectivities. One of the challenges is to discover combinations of metals and supports providing new surface structures which are stable enough to allow systematic investigation of the surface chemistry and catalysis characteristic of metal species with simple structures. The combinations of osmium carbonyl clusters and metal-oxide supports have been recognized to be especially useful in this regard (1-11), and it has been concluded from the stoichiometry of the surface synthesis reactions (2, 3) and spectroscopic characterizations of the surfaces (2-9) that  $[\text{Os}_3(\text{CO})_{12}]$  and related clusters react with the  $-\text{OH}$  groups terminating the surfaces of metal oxides to give the bound clusters  $\text{HOs}_3$

$(\text{CO})_{10}-\text{O}-\text{M}$  (where M is Si, Ti, etc.). These clusters break up at temperatures of  $\geq 120^\circ\text{C}$ , giving surface-bound mononuclear Os(II) complexes having 2 or 3 CO ligands (2-7); the stoichiometry of the surface reaction leading to cluster breakup on  $\eta\text{-Al}_2\text{O}_3$  has been determined (3). The complexes are evidently present in ensembles consisting of three Os atoms (6, 10). The clusters and ensembles have been observed by high-resolution transmission electron microscopy (6, 11).

Although the clusters break up readily on the supports to give the ensembles, there is evidence that the intact clusters themselves are the catalytically active species for some reactions: triosmium clusters on MgO have been implicated in catalysis of CO hydrogenation at 300°C (7); triosmium clusters on  $\text{SiO}_2$  in catalysis of ethylene hydrogenation (12) at 70 to 100°C and butene-1 isomerization at 50 to 90°C (1); and triosmium clusters on  $\gamma\text{-Al}_2\text{O}_3$  in catalysis of hexene-1 isomerization (10). The work summarized here was intended to provide a quantitative characterization of metal-oxide-supported

<sup>1</sup> Permanent address: Chemistry Department, Sichuan University, Chengdu, People's Republic of China.

<sup>2</sup> To whom correspondence should be addressed.

triosmium clusters as catalysts of the olefin conversion reactions and to provide a comparison of the catalytic activities of the clusters and the ensembles derived from them. Isomerization and hydrogenation of hexene-1 were investigated with  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported triosmium cluster catalysts, which were characterized by infrared and X-ray photoelectron spectroscopies. The results provide evidence that hydridocarbonyl clusters of triosmium are catalytically active for hexene-1 isomerization at temperatures  $\leq 70^\circ\text{C}$ , and the clusters are more active than the ensembles.

#### EXPERIMENTAL

**Materials.** The catalyst support,  $\gamma$ - $\text{Al}_2\text{O}_3$  (Ketjen, surface area  $185\text{ m}^2/\text{g}$ ; particle size  $<100$  mesh), was dried at  $120^\circ\text{C}$  in air and then calcined in flowing oxygen at  $400^\circ\text{C}$  for 4 hr. The sample was transferred to a desiccator and stored over anhydrous  $\text{CaSO}_4$  until it was used in catalyst preparation. The solvent *n*-heptane (Fisher, Reagent Grade) was purified by distillation from sodium/benzophenone under nitrogen. Hexene-1 (Aldrich, 99%, containing *trans*-hexene-2 and *n*-hexane impurities—identified by GLC) was used as received. The osmium carbonyl  $[\text{Os}_3(\text{CO})_{12}]$  (Strem) was also used as received. Helium (Airco, 99.995%), hydrogen (Airco, 99.995%), and deuterium (MG Scientific Gases, CP Grade), were purified by flow through traps containing supported copper catalyst and zeolite 5A to remove traces of oxygen and water, respectively.

The supported osmium catalyst was prepared [as described in detail previously (10)] by refluxing a *n*-heptane solution of  $[\text{Os}_3(\text{CO})_{12}]$  with  $\gamma$ - $\text{Al}_2\text{O}_3$  at  $98^\circ\text{C}$  under nitrogen. The osmium content of the catalyst was determined by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y., to be 0.91 wt%.

**Catalytic reaction experiments.** The catalytic isomerization of hexene-1 was carried out at atmospheric pressure and 50 to  $110^\circ\text{C}$  in a flow microreactor interfaced to a

gas chromatograph. After charging of the catalyst (about 0.50 g in glass wool) into the reactor and purging of the system with dried and deoxygenated hydrogen or helium for at least 2 hr at room temperature, the catalyst was heated to the reaction temperature in flowing hydrogen, deuterium, or helium. The stream of gas (hydrogen and/or helium) was then diverted to a thermostated vaporizer containing the liquid reactant, hexene-1. The gas bubbled through the hexene-1, and analysis by GLC indicated that the stream was saturated with the vapor under the conditions of the kinetics experiments. The partial pressure of hexene-1 in the reactant stream varied from 0.072 to 0.15 atm; the partial pressure of hydrogen varied from 0.23 to 0.93 atm. The product stream was analyzed periodically by GLC, as described previously (10).

The determination of the kinetic isotopic effect was carried out with the reactor thermostated at  $90^\circ\text{C}$ . The partial pressures of hexene-1 and deuterium were 0.23 and 0.77 atm, respectively. The liquid product was collected in a trap at liquid nitrogen temperature. NMR spectra of these liquid products were measured with a Bruker Spectrospin Model WM 250. The  $^1\text{H}$ -NMR and  $^1\text{H}$ -decoupled NMR spectra of the products were recorded in the absence of solvent.

**Spectroscopic characterization of catalysts.** The catalyst was characterized by infrared spectroscopy, the equipment consisting of a quartz cell interfaced to a vacuum and gas handling system (1) and a Nicolet 7199 Fourier transform infrared spectrometer. Catalyst samples were pressed into wafers, as described elsewhere (10).

Spectra of samples in the carbonyl region were recorded at 50 to  $90^\circ\text{C}$  under reaction conditions, i.e., with the catalyst in the presence of hydrogen and hexene-1 in the cell (rates of catalytic reaction were too low to determine in these experiments). The used catalysts were also characterized with the same apparatus; the samples were exposed to air during the transfer to the cell.

Pressed wafers were also used to obtain X-ray photoelectron spectra of the fresh and used catalysts, recorded with a Physical Electronics Model 550 spectrometer having a Mg X-ray source ( $h\nu = 1253.6$  eV). A binding energy of 74.1 eV for the Al 2*p* level was used as an internal standard.

## RESULTS AND DISCUSSION

### *Catalysis by Supported Triosmium Clusters*

The infrared spectra of the initially prepared catalysts (10) demonstrate that  $[\text{Os}_3(\text{CO})_{12}]$  had reacted with surface  $-\text{OH}$  groups to give the surface-bound carbonyl cluster  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}\langle$ , as expected (2-4). When this material was placed in the flow reactor, it catalyzed the isomerization of hexene-1 in the presence of helium to give hexene-2 at 120°C (10). When the catalysis experiment was attempted at 70°C in the presence of helium, however, only a negligible activity was observed.

When the hexene-1 isomerization was carried out in the presence of hydrogen and the alumina-supported cluster,  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}\langle$ , at atmospheric pressure and temperatures from 50 to 73°C, however, a much greater rate of reaction was ob-

served, the hexene-1 being converted into *cis*- and *trans*-hexene-2. An induction period was observed in each experiment begun with a fresh catalyst sample, followed by a steady-state activity of the catalyst (Fig. 1). The induction period decreased with increasing temperature, being about 5 hr at 50°C and 2 hr at 73°C. The observation of an induction period is in agreement with the results of Barth *et al.* (1) for the silica-supported cluster,  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Si}\langle$ , and suggests that the catalytically active species were formed slowly from the original, coordinatively saturated cluster.

Infrared spectra of the catalysts used in the absence of hydrogen at 120°C (10) demonstrate that the surface-bound clusters broke up; as the Os-Os bonds were broken, the osmium was oxidized, forming ensembles consisting of three Os(II) complexes (1-6), which are less active catalytically than the supported clusters (10). The activities observed in this work at lower temperatures (with hydrogen in the feed)—which are higher than those of the ensembles formed from the cluster—suggest that triosmium clusters themselves might have been catalytically active species—as was inferred by Barth *et al.* (1) for the silica-supported catalysts prepared from  $[\text{Os}_3(\text{CO})_{12}]$ .

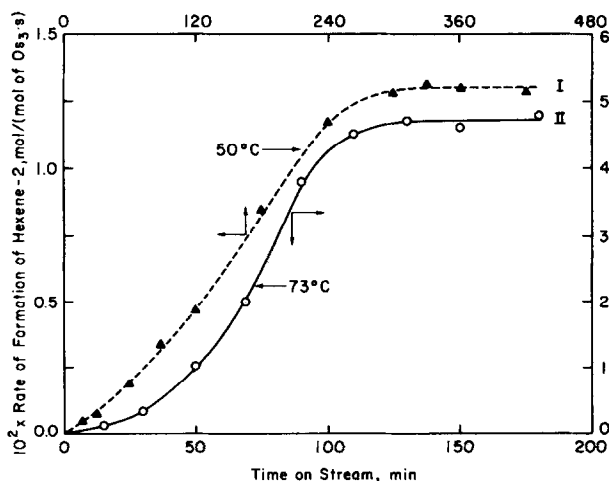


FIG. 1. Break-in in the activity of  $\gamma\text{-Al}_2\text{O}_3$ -supported triosmium clusters initially present as  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}\langle$ . Reaction conditions:  $P_{\text{Hexene-1}} = 0.072$  atm;  $P_{\text{H}_2} = 0.93$  atm; mass of catalyst = 0.5 g.

The dependence of the catalytic activity on the presence of hydrogen suggests that there was an interaction between hydrogen and the surface osmium carbonyl, forming osmium hydride species. Some osmium carbonyl clusters in solution are readily converted into hydridocarbonyl clusters in the presence of hydrogen, the latter having higher catalytic activities than the original carbonyl clusters (13–16).

As a test of the hypothesis that the clusters themselves were the catalytically active species, infrared spectra of the catalyst were measured under reaction conditions at 50 and 70°C (Figs. 2 and 3). The frequencies and intensities of the bands in the carbonyl region indicate the presence of  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}$ ; the spectrum indicating this surface-bound cluster did not change during the induction period or during the period of steady-state activity. Consistent with these results, the spectrum of the catalyst which had been used in the flow reactor at 70°C for 6 hr (spectrum 4, Fig. 3) is al-

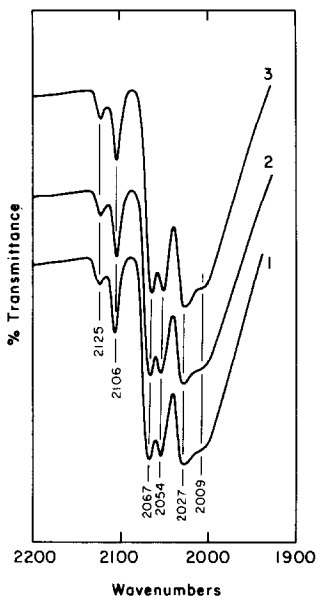


FIG. 2. Infrared spectra of the catalyst at 50°C in the presence of flowing hydrogen ( $P_{\text{H}_2} = 0.93$  atm) and hexene-1 ( $P_{\text{hexene-1}} = 0.072$  atm). (1) Fresh catalyst; (2) after 6 hr on stream; (3) after 10 hr on stream.

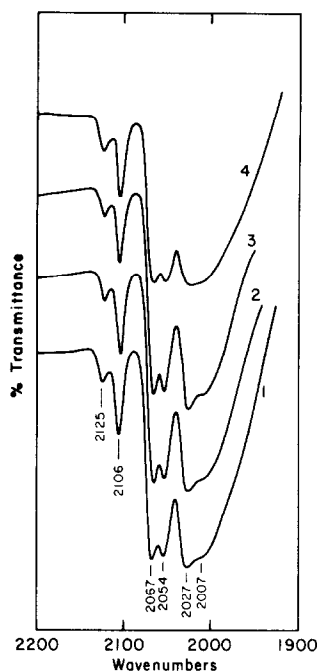


FIG. 3. Infrared spectra of the catalyst at 70°C in the presence of flowing hydrogen ( $P_{\text{H}_2} = 0.93$  atm) and hexene-1 ( $P_{\text{hexene-1}} = 0.072$  atm). (1) Fresh catalyst; (2) after 3 hr on stream; (3) after 7.5 hr on stream; (4) after catalyst had been used in the flow reactor for hexene-1 isomerization for 6 hr.

most identical to that of the fresh catalyst (spectrum 1).

These results demonstrate that the predominant form of the supported osmium catalyst consisted of the triosmium clusters—we infer that the cluster framework did not break up to a significant degree during the low-temperature catalysis and that the triosmium clusters themselves catalyzed the isomerization of hexene-1. The inference is in agreement with that drawn by Barth *et al.* (1) for the silica-supported triosmium clusters used to catalyze isomerization of butene-1 under nearly the same conditions, and it provides a contrast to the results observed with the alumina-supported catalyst at 120°C—which showed that the clusters had broken up to give less active catalytic species, which were ensembles consisting of three mononuclear Os(II) complexes (10).

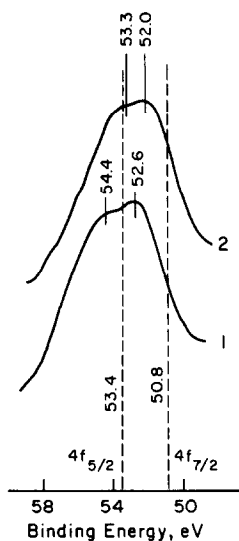


FIG. 4. X-Ray photoelectron spectra of the catalyst. (1) Fresh catalyst; (2) catalyst after use for 6 hr in hexene-1 isomerization at 70°C with  $P_{H_2} = 0.93$  atm and  $P_{\text{hexene-1}} = 0.072$  atm.

The X-ray photoelectron spectra provide further evidence of the role of hydrogen in the catalytic reaction; we emphasize that the results determine only qualitative trends, since the peaks were not well resolved. The spectra show the binding energies at 50.8 and 53.4 eV of the  $4f_{7/2}$  and  $4f_{5/2}$  core levels of zero-valent Os, respectively, which were measured with a mechanical mixture of  $[Os_3(CO)_{12}]$  and  $\gamma\text{-Al}_2O_3$ . The  $4f_{7/2}$  and  $4f_{5/2}$  levels shifted 1.8 and 1.0 eV, respectively, toward higher binding energies as the clusters were bonded to the  $\gamma\text{-Al}_2O_3$  support, forming the freshly prepared catalyst (Fig. 4).<sup>3</sup> The shifts suggest that the Os in the unused catalyst is partially oxidized, as would be expected for the surface-bound triosmium cluster  $[HOs_3(CO)_{10}-O-Al<]$ , which is formed in an oxidative addition reaction of  $[Os_3(CO)_{12}]$

<sup>3</sup> There are a few differences between these results and those reported by Knözinger *et al.* (6), reflecting the different choices of the reference binding energy. A value of 73.5 eV for the Al 2p binding energy was used by Knözinger *et al.*, whereas a value of 74.1 eV was used in this work.

with surface —OH groups, the cluster becoming bonded to the surface via an edge-bridging oxygen ligand (2, 3).

The XP spectra show that the  $4f_{7/2}$  and  $4f_{5/2}$  levels shifted toward lower binding energies after the catalyst had been used in the olefin isomerization in the presence of hydrogen (Fig. 4, spectrum 2). This result indicates a partial reduction of the osmium by hydrogen, consistent with the aforementioned conclusion that an osmium carbonyl species with hydride ligands had formed, and in agreement with the results observed by Knözinger *et al.* (6).<sup>4</sup>

The catalytic kinetics measurements, which were carried out during periods of steady-state activity, show that hydrogenation of hexene-1 occurred simultaneously with the isomerization, confirming earlier reports (14, 17). The major products of the catalytic reaction were *cis*-hexene-2 and *trans*-hexene-2 (the *cis/trans* ratio being 0.4 to 0.5); the rate of hydrogenation was much less than that of isomerization (Fig. 5).

The kinetics of the isomerization reaction was determined in experiments carried out with systematic variation of the partial pressures of hexene-1 and hydrogen, sometimes with helium diluent. The rate of isomerization of hexene-1 to give hexene-2 is nearly independent of the partial pressure of hexene-1 (typical data are shown in Fig. 6) and also nearly independent of the partial pressure of hydrogen (data not shown). The kinetics parameters are summarized in Table 1 and in the Arrhenius plot of Fig. 7.

There is a clear curvature in the upper line of the Arrhenius plot for the isomerization reaction in the range of temperatures investigated (50 to 80°C). The activation energy is  $11.5 \pm 0.5$  kcal/mol in the range 50 to 70°C and  $20 \pm 1$  kcal/mol in the range 70 to 80°C. The change in the activation energy at about 70°C suggests that the catalyst

<sup>4</sup> It might be argued that the shift to lower binding energies resulted from a loss of carbonyl ligands during irradiation. However, the infrared spectrum of the sample after the XPS analysis was indistinguishable from that observed prior to the XPS analysis.

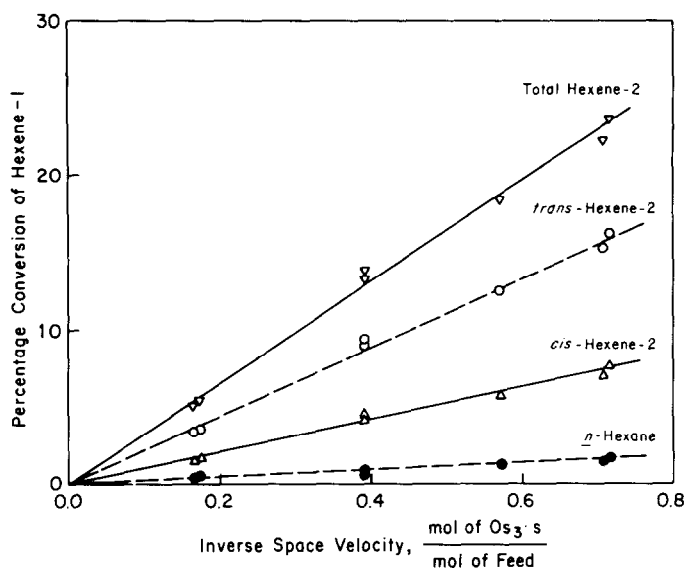


FIG. 5. Differential conversion of hexene-1 catalyzed by  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported triosmium clusters  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}$ . Reaction conditions:  $60^\circ\text{C}$ ;  $P_{\text{H}_2} = 0.93$  atm;  $P_{\text{hexene-1}} = 0.072$  atm.

underwent a structural change at temperatures  $\approx 70^\circ\text{C}$ . The infrared spectra of Fig. 8 show that the catalyst was decarbonylated

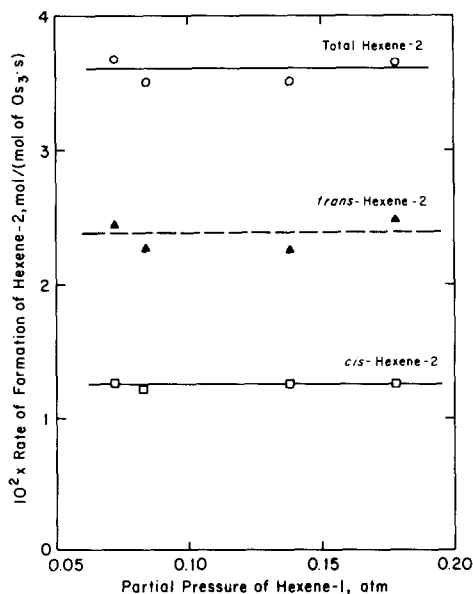


FIG. 6. Rates of isomerization of hexene-1 to give *cis*- and *trans*-hexene-2 at  $70^\circ\text{C}$  and 1 atm. The reactant mixture contained hexene-1 and hydrogen. The predominant form of the catalyst was the  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported cluster  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}$ .

much more rapidly at  $80^\circ\text{C}$  than at  $70^\circ\text{C}$ ; after 2 hr at  $80^\circ\text{C}$ , the intensities of the carbonyl bands at  $2066$  and  $2054$   $\text{cm}^{-1}$  had decreased markedly, and simultaneously a new band started to appear at about  $1940$   $\text{cm}^{-1}$  (spectrum 2). This change became clearer after 4 hr (spectrum 3). The results are similar to those observed by Barth *et al.* (1) for silica-supported osmium carbonyl clusters catalyzing butene-1 isomerization. We infer

TABLE I  
Rate Constants for Hexene-1 Isomerization  
Catalyzed by Alumina-Supported Triosmium  
Clusters<sup>a</sup>

$T$ ( $^\circ\text{C}$ )	mol/(mol of $\text{Os}_3 \cdot \text{s}$ )		
	$10^2 \times k_1$	$10^2 \times k_2$	$10^2 \times k$
50	0.89, 0.86	0.43, 0.43	1.32, 1.29
60	1.55, 1.41	0.71, 0.70	2.26, 2.17
70	2.75, 2.65	1.15, 1.11	3.90, 3.76
73	3.47, 3.50	1.46, 1.56	4.93, 5.06
81	6.74, 6.90	2.72, 2.75	9.46, 9.65

<sup>a</sup> The parameters  $k_1$ ,  $k_2$ , and  $k$  are the zero-order rate constants for hexene-1 conversion to *trans*-hexene-2, *cis*-hexene-2, and total hexene-2, respectively.

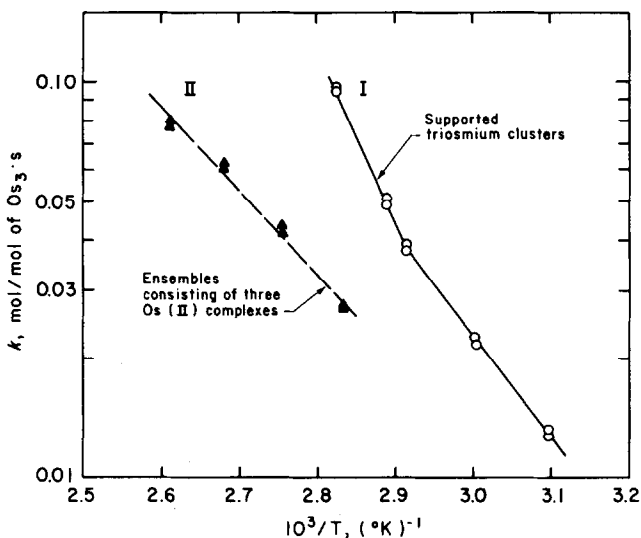


FIG. 7. Arrhenius plot: zero-order rate constants for isomerization of hexene-1 catalyzed by  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported triosmium clusters and by ensembles consisting of three Os(II) complexes formed by breakup of the supported clusters.

that a more active, coordinatively unsaturated, osmium hydride species formed as a result of the decarbonylation.

#### Catalysis by Ensembles Formed by Breakup of Supported Triosmium Clusters

When the alumina-supported triosmium clusters were pretreated at  $120^\circ\text{C}$  in flowing hydrogen, and the temperature was then decreased to  $70^\circ\text{C}$  and the flow of hexene-1 in hydrogen begun, the induction period was no longer observed, but the activity of the catalyst was markedly less than that observed in the experiments mentioned

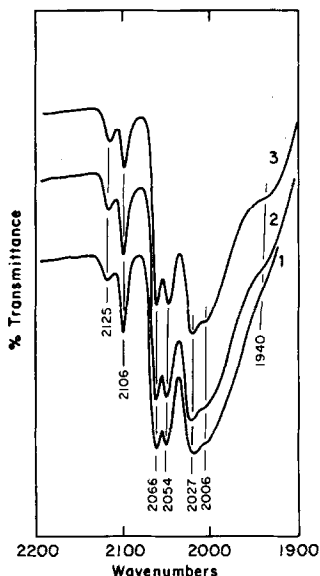


FIG. 8. Infrared spectra of the supported triosmium cluster catalyst at  $80^\circ\text{C}$  in the presence of flowing hydrogen ( $P_{\text{H}_2} = 0.93$  atm) and hexene-1 ( $P_{\text{hexene-1}} = 0.072$  atm). (1) Fresh catalyst; (2) after 2 hr on stream; (3) after 4 hr on stream.

TABLE 2

Dependence of Catalytic Activity for Isomerization of Hexene-1 on Time of Catalyst Pretreatment at  $120^\circ\text{C}$  in Hydrogen<sup>a</sup>

Time of pretreatment (hr)	$10^2 \times \text{rate, mol}/(\text{mol of Os}_3 \cdot \text{s})$		
	$r_1$	$r_2$	$r$
0	2.75, 2.65	1.15, 1.11	3.90, 3.76
1.5	1.93, 1.91	1.01, 1.02	2.94, 2.93
3	1.03, 0.99	0.65, 0.59	1.68, 1.58

<sup>a</sup> The rates were measured at  $70^\circ\text{C}$  with a partial pressure of hexene-1 of 0.072 atm;  $r_1$ ,  $r_2$ , and  $r$  are the rates of formation of *trans*-hexene-2, *cis*-hexene-2, and total hexene-2, respectively.

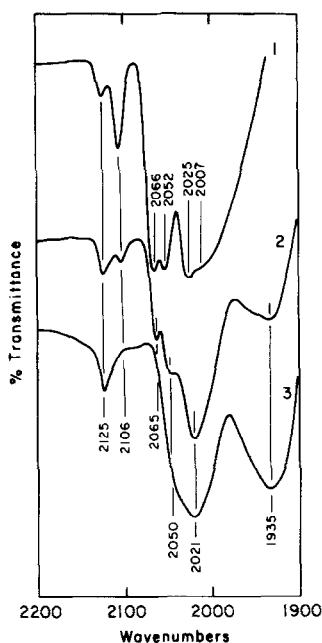


FIG. 9. Infrared spectra of the catalyst. (1) Fresh catalyst; (2) after use for 3 hr in hexene-1 isomerization at 70°C (the catalyst had been pretreated in flowing hydrogen at 120°C for 1.5 hr), (3) after use for 2 hr in hexene-1 isomerization at 70°C (the catalyst had been pretreated in flowing hydrogen at 120°C for 3 hr).

above. The loss of activity depended on the duration of the catalyst pretreatment—and, we infer, on the degree of decarbonylation and cluster breakup; the catalytic reaction rate data of Table 2 and the infrared spectra of Fig. 9 show that the longer the catalyst was held at 120°C, the more carbonyl ligands were lost and the lower was the catalytic activity. For example, the activity of the catalyst pretreated at 120°C for 3 hr was less than half that of the fresh catalyst.

There are many results now supporting the contention that the edge-bonded triosmium carbonyl cluster  $\text{HOs}_3(\text{CO})_{10}-\text{O}-\text{Al}$  decomposes to give mononuclear osmium carbonyl complexes (2–5), and it has been suggested (1, 6, 10) that the transformation proceeds as the edge-bonded cluster bends over to interact with the surface, forming a face-bonded cluster. Spectrum 3 (Fig. 9) is typical of the broken-up clusters (consisting of ensembles of three

Os complexes), and we suggest that spectrum 2 of this figure represents an intermediate face-bonded cluster, in which the osmium has not yet been oxidized to the divalent state and which is not so completely decarbonylated as the osmium in an ensemble. We suggest that the Os–Os bond in the decarbonylated face-bonded species had not broken, but that the original triangular structure was only slightly deformed and the Os–Os bonds weakened. As carbonyl ligands were lost from the osmium in this process (3), and each of the three osmium atoms was bonded to oxygen atoms of the alumina surface, the Os–Os bond broke and the formal oxidation state of the osmium increased [presumably to +2 (2–5)] and the catalytic properties of the material changed markedly.

Further evidence of structure–activity relations is provided by catalysis experiments done at 80 to 110°C with a catalyst which had been first held at 120°C in flowing helium for 3 hr to cause complete breakup of the cluster (10). After this pretreatment the temperature was decreased to the desired value with hydrogen flowing, and the hexene-1 was introduced. The kinetics data, summarized in Table 3 and Figs. 7 and 10–12, show that in the presence of the ensembles formed upon cluster breakup, the isomerization reaction is still zero-order in hexene-1 and in hydrogen partial pressure, but the activity is less than that of the clus-

TABLE 3

Kinetics Parameters for Isomerization of Hexene-1 Catalyzed by the Partially Decarbonylated Triosmium Cluster on  $\gamma\text{-Al}_2\text{O}_3$

Product	$10^2 \times$ zero-order rate constant at 90°C, mol/(mol of $\text{Os}_3 \cdot \text{s}$ )	Activation energy (kcal/mol)
<i>trans</i> -Hexene-2	3.14	$10.4 \pm 0.9$
<i>cis</i> -Hexene-2	1.67	$8.1 \pm 0.6$
Total hexene-2	4.81	$9 \pm 1$



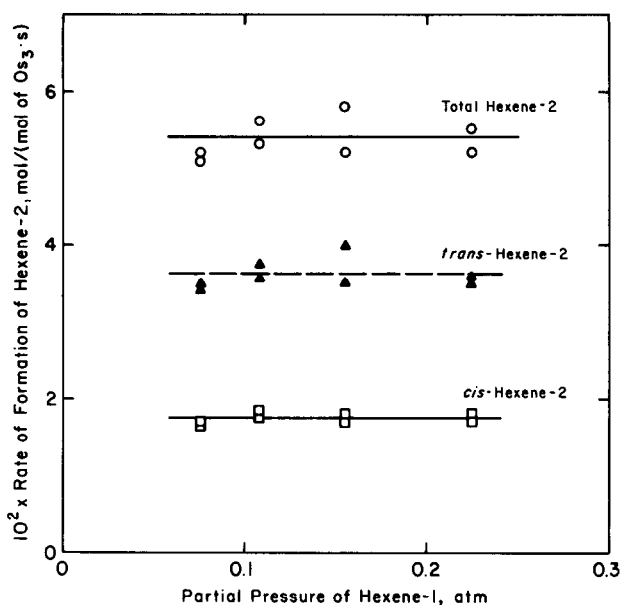


FIG. 10. Rates of isomerization of hexene-1 at 90°C and 1 atm catalyzed by the ensembles consisting of three Os(II) complexes on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The partial pressure of hydrogen was 0.39 atm.

ters, and the activation energy for total hexene-2 formation is different from the values characteristic of the clusters in the two apparent states of decarbonylation (Fig. 7). This comparison illustrates further how the catalytic properties depend on the degree of

decarbonylation and the changes in bonding and oxidation state of the osmium. We recognize that there is a complex role of CO in this chemistry; CO is not a simple inhibitor of the catalytic reaction—it can also cause significant changes in the structure of the

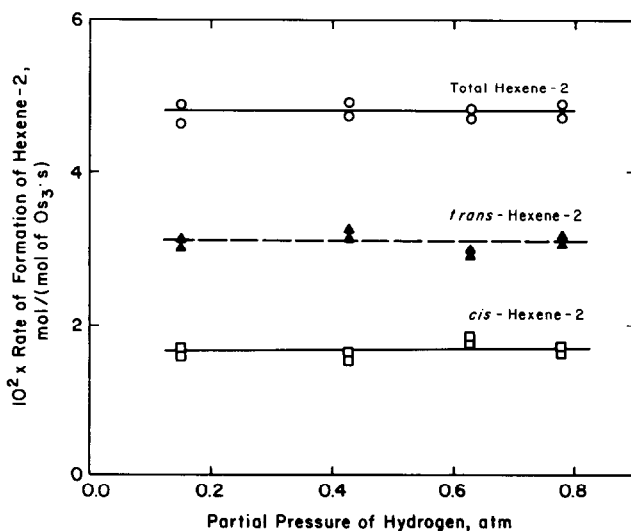


FIG. 11. Rates of isomerization of hexene-1 at 90°C and 1 atm catalyzed by the ensembles consisting of three Os(II) complexes on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The partial pressure of hexene-1 was 0.23 atm.

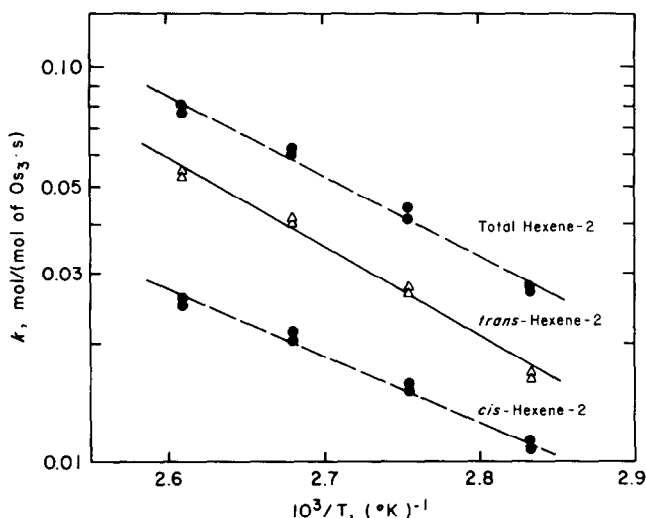


FIG. 12. Arrhenius plot: zero-order rate constants for isomerization of hexene-1 catalyzed by the  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported ensembles consisting of three Os(II) complexes.

osmium species and the oxidation state of osmium.

Like the supported clusters, the ensembles formed by cluster breakup were catalytically more active when hydrogen was added to the hexene-1 feed; the rate of the isomerization reaction occurring in the presence of hydrogen is about 6 times that of the reaction occurring in the presence of helium at 100°C. It is clear that hydrogen plays a significant role in the activation of the surface osmium carbonyl species.

The kinetic isotopic effect provides fur-

ther evidence that hydrogen took part in the reaction catalyzed by the ensembles of supported complexes. When the catalytic isomerization was carried out in the presence of  $\text{D}_2$  instead of  $\text{H}_2$ , the rate was less; at 90°C the rate constant  $k_{\text{H}} = 4.66 \times 10^{-2}$  mol/(mol of  $\text{Os}_3 \cdot \text{s}$ ), and  $k_{\text{H}}/k_{\text{D}} = 1.28$ .

The  $^1\text{H}$ -decoupled NMR spectra of the mixtures of hexene-1 and hexene-2 (Fig. 13) show that some deuterium atoms were incorporated in the products. All the results obtained with deuterium suggest a role of hydrogen in a slow step in the catalytic cy-

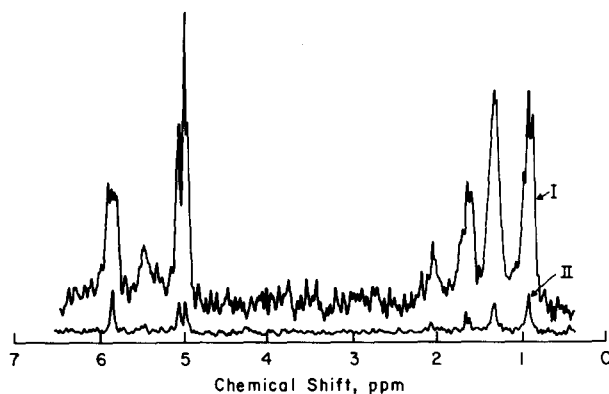


FIG. 13.  $^1\text{H}$ -NMR (I) and  $^1\text{H}$ -decoupled NMR (II) spectra of the catalytic reaction products (a mixture of hexene-1 and hexene-2). Reaction conditions: 90°C;  $P_{\text{hexene-1}} = 0.23$  atm;  $P_{\text{H}_2} = 0.97$  atm; the catalyst was ensembles of Os(II) complexes.

cle. Taking these results together with those presented above, we suggest a catalytic cycle similar to that occurring in the presence of  $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$  for the olefin isomerization (13–15). According to this scheme, the relatively small kinetic isotope effect shows that the possible rate-determining step may be the transfer of hydrogen back to osmium, rather than the transfer of hydrogen to coordinated hexene-1. This suggestion is consistent with the observed zero-order kinetics. It is clear that the catalytic species are different in the catalysts consisting of clusters on the one hand and ensembles on the other, but that the mechanisms of the reactions are similar.

#### ACKNOWLEDGMENT

This work was supported by the National Science Foundation.

#### REFERENCES

1. Barth, R., Gates, B. C., Zhao, Y., Knözinger, H., and Hulse, J., *J. Catal.* **82**, 147 (1983).
2. Smith, A. K., Besson, B., Basset, J. M., Psaro, R., Fusi, A., and Ugo, R., *J. Organometal. Chem.* **192**, C31 (1980).
3. Psaro, R., Ugo, R., Zanderighi, G. M., Besson, B., Smith, A. K., and Basset, J. M., *J. Organometal. Chem.* **213**, 215 (1981).
4. Deeba, M., and Gates, B. C., *J. Catal.* **67**, 303 (1981).
5. Knözinger, H., and Zhao, Y., *J. Catal.* **71**, 337 (1981).
6. Knözinger, H., Zhao, Y., Barth, R., Epstein, R., Gates, B. C., and Scott, J. P., *Faraday Discuss. Chem. Soc.* **72**, 53 (1981).
7. Deeba, M., Scott, J. P., Barth, R., and Gates, B. C., *J. Catal.* **71**, 373 (1981).
8. Besson, B., Moraweck, B., Smith, A. K., Basset, J. M., Psaro, R., Fusi, A., and Ugo, R., *J. Chem. Soc. Chem. Commun.* 569 (1980).
9. Deeba, M., Streusand, B. J., Schrader, G. L., and Gates, B. C., *J. Catal.* **69**, 218 (1981).
10. Li, X.-J., and Gates, B. C., *J. Catal.* **84**, 55 (1983).
11. Schwank, J., Allard, L. F., Deeba, M., and Gates, B. C., *J. Catal.* **84**, 27 (1983).
12. Besson, B., Choplin, A., D'Ornelas, U., and Basset, J. M., *J. Chem. Soc. Chem. Commun.* 843 (1982).
13. Deeming, A. J., and Hasso, S., *J. Organometal. Chem.* **114**, 313 (1976).
14. Keister, J. B., and Shapley, J. R., *J. Amer. Chem. Soc.* **98**, 1056 (1976).
15. Deeming, A. J., and Hasso, S., *J. Organometal. Chem.* **88**, C21 (1975).
16. Deeming, A. J., Hasso, S., and Underhill, M., *J. Organometal. Chem.* **80**, C53 (1974).
17. Freeman, M. B., Patrick, M. A., and Gates, B. C., *J. Catal.* **73**, 82 (1982).