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ISOTOPIC EXCHANGE BETWEEN H_2 AND D_2 BY THE RIDEAL-ELEY MECHANISM

Ralph D. GILLESPIE, Robert L. BURWELL, Jr. * and Tobin J. MARKS *

Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, IL 60208, U.S.A.

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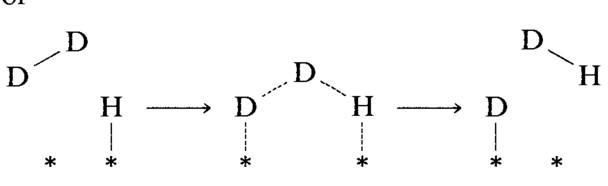
The rate of the reaction, $H_2+D_2 \rightarrow 2HD$, is very rapid at −160 °C on the catalyst $Cp'_2Th\text{-}(CH_3)_2$/dehydroxylated Al_2O_3, activated in H_2+D_2 and believed to contain supported Cp'_2ThH^+ ($Cp' = \eta^5$-pentamethylcyclopentadienyl). Even at −195 °C, the turnover frequency is greater than 0.1 sec^{-1} at $P_{H_2+D_2}=1$ atm. Strong evidence is adduced that the exchange proceeds by a Rideal-Eley process, i.e. by a four-center transition state involving Th-H + D-D.

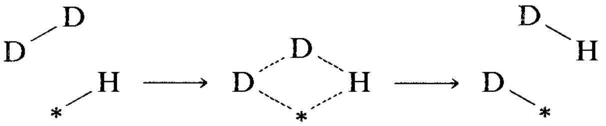
Keywords: Rideal-Eley mechanism, hydrogen-deuterium exchange, organoactinide complexes, bis(pentamethylcyclopentadienyl)thoriumdimethyl

1. Introduction

Isotopic exchange between H_2 and D_2 on heterogeneous catalysts has usually been represented as proceeding through the Bonhoeffer-Farkas (B-H) mechanism [1–3] which involves the dissociative adsorption of hydrogen and deuterium followed by associative desorption of HD. In the alternative Rideal-Eley (R-E) mechanism [1–3] (eq. (1) or (2)), dissociative adsorption does not occur, and one of



(1)



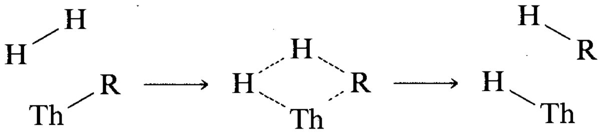
(2)

the atoms in D_2 (or HD or H_2) is never directly bonded to a surface atom. Although the R-E mechanism has been proposed for a number of particular cases, a recent example of which occurs in ref. [4], few if any of these proposals have been generally accepted. However, some of the proposed applications of the R-E mechanism may well turn out to be correct. The reaction depicted in eq. (3)

$$H_2 + D_2 \rightarrow 2HD \tag{3}$$

has too few handles easily to permit strong support for the R-E mechanism or, indeed, for any mechanism. In most cases, only rate data have been available and rate data alone can rarely restrict possible mechanisms to just one. The B-H mechanism has been more appealing chemically, and developments in surface science have tended to support it as the mechanism of exchange on metals. We present here an instance of the heterogeneous catalysis of eq. (3) where we believe that the arguments favoring a R-E mechanism are strong and not dependent upon detailed kinetic analysis.

It has been shown [5–7] that $Cp'_2Th(CH_3)_2$ ($Cp' = \eta^5$-$(CH_3)_5C_5$) [8] undergoes reaction with highly dehydroxylated γ-Al_2O_3 (DA) to transfer one CH_3^- to a coordinatively unsaturated surface Al^{3+} (Al^{3+}(cus)) and to leave $Cp'_2ThCH_3^+$ bound to the surface by electrostatic forces and/or by coordination to a surface oxide ion. Only about 4% of the $Cp'_2ThCH_3^+$ species are sufficiently unencumbered to adsorb CO [9]. Such materials are among the more active known catalysts for the hydrogenation of propylene and are also very active catalysts for the polymerization of ethylene [5,9]. The bulky Cp′ ligands of such a species bound to the surface make it unlikely that a pair of Th atoms are involved in these reactions. Furthermore, oxidative addition of H_2 to, and reductive elimination of alkane from, ThH(R) are also unlikely since Th(IV) is very difficult to oxidize or reduce and Th(VI), the necessary product of oxidative addition, is unknown chemically. There is thus a strong argument that hydrogenation involves insertion of olefin into a ThH bond followed by hydrogenolysis of the resulting ThR bond via a 4-center transition state [5–7,10] (eq. (4)).



(4)

In view of the close resemblance between eqs. (2) and (4), the catalytic activity of $Cp'_2Th(CH_3)_2$/DA for eq. (3) was investigated. The observed activity of supported $Cp'_2Th(CH_3)_2$ exceeded expectations.

2. Experimental

Activity for isotopic exchange was measured in a batch reactor. Since only ca. 15 μmol of $Cp'_2Th(CH_3)_2$ was employed and since this furnished only an upper limit of ca. 0.5 μmol of actual catalyst, the system is potentially very sensitive to poisoning. In fact, O_2, H_2O, and CO are very strong poisons with large sticking coefficients. Extreme measures are thus needed to avoid serious poisoning. In general, the techniques of ref. [5] were used to minimize poisons and to reduce any O_2 in the $H_2 + D_2$ to $\leqslant 3 \times 10^{-6}$ mol%. Pentane was distilled from Na/K alloy and then distilled from bulb to bulb immediately prior to use. DA was prepared by dehydroxylating γ-Al_2O_3 to < 0.12 OH per nm^2 in flowing He at 950 °C for 0.5 h and stored in an airtight tube until use. H_2-D_2 mixtures were provided from a 500 cm^3 bulb initially filled with 350 Torr each of H_2 and D_2. All procedures were effected on a high vacuum line or in a nitrogen-filled glove box in which contents in O_2 and H_2O were in the low ppm range [6]. $Cp'_2Th(CH_3)_2$ was prepared and purified using high vacuum line techniques [8]. H_2,HD,D_2 mixtures were analyzed on a quadrupole or a VG 70-SE high resolution mass spectrometer.

The reactor unit consisted of two 50 cm^3 bulbs (each provided with a magnetic stirbar) joined top and bottom by Solv-Seal joints to a tube containing a fritted disk. The disk was by-passed by a tube containing a valve. Attached to the tube containing the fritted disk was a side tube connected to a valve and then to a joint for attachment to the high vacuum line. The unit was first flamed and evacuated and then placed in the glove box. One bulb was loaded with $Cp'_2Th(CH_3)_2$ and the other with DA. The reactor unit was then reattached to the vacuum line with the Al_2O_3-containing bulb up, evacuated, the complex-containing bulb was cooled, and 5 cm^3 of pentane transferred onto the complex. After the complex had dissolved, the reactor unit was rotated 180° consequent to which the solution passed through the frit onto the DA. The slurry was stirred for 2 h and the reactor unit was again rotated by 180°. The catalyst was then located on top of the frit. It was known from previous studies that $Cp'_2Th(CH_3)_2$ rapidly and strongly adsorbs on DA. The system was evacuated, the upper bulb was cooled so that the pentane distilled to the upper bulb and returned to the lower bulb washing the catalyst in so doing. The pentane was now evaporated, the reactor unit was inverted so that the catalyst lay at the bottom of its bulb, and the catalyst was exposed to the reaction mixture for 0.25–0.50 h at 25 °C, a pretreatment which from results of previous hydrogenation experiments [5,9] should convert adsorbed $Cp'_2ThCH_3^+$ to adsorbed Cp'_2ThH^+. The reaction system was then evacuated and the catalyst was cooled to the desired reaction temperature (slush baths or liquid N_2). During this period, a valved side tube attached to the bulb containing the catalyst was connected to the high vacuum apparatus. The reaction unit was now filled with the H_2, D_2 mixture. After a desired interval, usually 5 min, a sample of the gas phase was removed for analysis via the side tube connected to the catalyst-containing bulb. The system was then evacuated and refilled with reaction mixture. This was usually repeated once again. Results are given in table 1. Fifteen μmol of $Cp'_2Th(CH_3)_2$ and 0.23 g of DA was used except at -195 °C where 17.5 μmol and 0.40 g was employed.

3. Results

As shown in table 1, DA alone gives no significant activity for exchange at −160 ° C. In this experiment the reactor unit was attached to the high vacuum line with the Al_2O_3 bulb down. The pentane was distilled onto the Al_2O_3 and then removed by evaporation. After evacuation, the reaction mixture was added. Alumina is well known to be a catalyst for the exchange reaction at higher temperatures, but significant activity is not expected at −160 ° C [11].

Table 1 lists observed values of $[HD]^2/([H_2][D_2])$. The equilibrium values of this ratio are 2.28 at −160 ° C and 1.85 at −195 ° C [12]. Exchange runs were made at 0, −78, −131, −160 and −195 ° C. Equilibrium was attained within 5 min at the three higher temperatures and nearly so at −160 ° C. Reaction was only partial at −195 ° C, but, even so, reaction was extremely rapid when one considers that 435 kJ bonds are broken and reformed. Probably only Pt exhibits a catalytic activity for exchange which is near that of $Cp'_2Th(CH_3)_2/DA$ [3], but comparable data for exact comparison are unavailable.

The present work was designed primarily only to determine whether $Cp'_2Th(CH_3)_2/DA$ is an active catalyst for H_2/D_2 exchange. However, the data of table 1 also permit one to estimate lower limits of the rate of exchange at −195 °. Dividing the moles of HD produced by the moles of complex and by the reaction time in seconds one obtains 0.21, 0.22, and 0.16 and 0.37 molecules of HD formed per second per molecule of starting $Cp'_2Th(CH_3)_2$. This is necessarily a lower limit, since in the batch reactor, access to the catalyst by $H_2(g)$ and $D_2(g)$ was not fully characterized, but most of the H,D sample analyzed must have come from the catalyst bulb which at −195 ° C contained one-half of the $(H,D)_2$ mixture. However, the discovery that the rate of exchange is remarkably large for a reaction at −195 ° C satisfies the purpose of this investigation.

Table 1

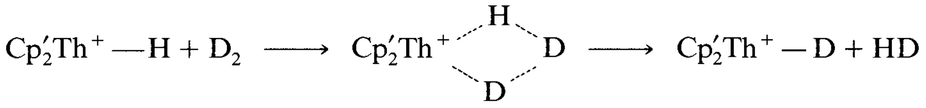
H_2/D_2 exchange data at −160 and −195 ° on Cp'_2ThMe_2/DA [a]

Time (min)	T(° C)	P(Torr)	Mole percent			$\frac{[HD]^2}{[H_2][D_2]}$
			H_2	D_2	HD	
5 (blank)	−160	170	0.391	0.588	0.021	0.002
5	−160	155	0.206	0.337	0.457	3.01
5	−160	135	0.192	0.439	0.369	1.62
10	−160	105	0.199	0.395	0.406	2.10
5	−195	174	0.467	0.237	0.296	0.79
5	−195	230	0.526	0.240	0.233	0.43
5 [a]	−195	230	0.658	0.176	0.166	0.24

[a] The volume of the reactor unit was 250 cm^3 except for the final run in which case it was 750 cm^3. About half of the H_2-D_2 mixture was in the catalyst bulb except during the final run where only about 1/4 was in the catalyst bulb.

4. Discussion

Since oxidative addition to Th(IV) and any reaction involving interaction of two Th atoms can be eliminated with high probability and since the operative catalyst is likely to be Cp'_2ThH^+, the transition state for exchange given in eq. (5) is strongly supported, and the exchange reaction must



$$Cp'_2Th^+{-}H + D_2 \longrightarrow Cp'_2Th^+ \overset{H}{\underset{D}{\diamond}} D \longrightarrow Cp'_2Th^+{-}D + HD \qquad (5)$$

proceed heterogeneously on the supported actinide complex by a Rideal-Eley mechanism in the form of eq. (2).

There is both solution chemical and theoretical support for the proposed surface chemistry. Thus, recently characterized $Cp'_2ThCH_3^+\ B(C_6F_5)_4^-$ [7] models many salient spectroscopic and catalytic properties of $Cp'_2Th(CH_3)_2/DA$. The high activity exhibited for 1-hexene hydrogenation, $N_t = 0.94\ s^{-1}$ at 25 °C in toluene solution, is far in excess of that exhibited by other $Cp'_2ThCH_3^+X^-$ complexes (e.g., $N_t = 1.1 \times 10^{-3}\ s^{-1}$ for $X^- = B(C_6H_5)_4^-$ in toluene solution at 25 °C), demonstrating the marked sensitivity of $Cp'_2ThCH_3^+$ reactivity to counter-ion environment. This behavior is likely to hold for surface-bound species as well. Thus, the few percent of $Cp'_2Th(CH_3)_2/DA$ sites which are highly active for propylene hydrogenation ($N_t = 8\ s^{-1}$ per site active for the adsorption of CO at -45 °C [5]) must be in rather unencumbered environments [13].

In regard to precedents for eq. (5), $[Cp'_2Th(\mu\text{-}H)H]_2$ undergoes facile exchange with H_2 or D_2. For the former process, the bimolecular rate constant determined by NMR line broadening in toluene solution is $7 \times 10^{-4}\ M^{-1}\ s^{-1}$ at -30 °C [8]. In addition, $Cp'_2Th(OR)H$ [8], $[(Me_3Si)_2N]_3ThH$ [14], and Cp'_2ScH [15] complexes are reported to undergo facile exchange with D_2. In all cases, the mechanism is proposed to involve a four-centered transition state. The *ab initio* GVB calculations of Steigerwald and Goddard [16] on $Cl_2Sc\text{-}H$, Cl_2TiH_2, and Cl_2TiH^+ also support the idea of a 4-center transition state for isotopic exchange between M-H and D_2 where there is substantial d-character at the metal in the M-H bond. Similar conclusions have been reached by Upton and Rappe [17] for other 2 + 2 reactions. Four-center transition states have also been proposed on the basis of extended Hückel calculations by Rabaâ, Saillard, and Hoffmann [18] for organo-lanthanides and by Brintzinger [19] for organozirconium complexes.

Acknowledgments

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