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Benzene–Deuteroxyl Exchange over Deuterated γ-Alumina

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The exchange reaction between benzene and a large excess of deuteroxyl on deuterated γ-alumina was investigated as a possible test reaction for evaluating the Lewis acid sites on the alumina surface. The kinetics were first order in adsorbed benzene, but approached zero order in total benzene when tested in the saturation portion of the adsorption isotherm. Preferential retention of deuterium on the alumina is attributed to an equilibrium isotope effect. This is consistent with related equilibria.

The rate of the exchange was very sensitive to minor changes in the pretreatment technique probably because of the resulting small variations in surface structure and catalytic activity. This complicates use of the reaction as a probe for surface Lewis acidity.

INTRODUCTION

The hydrogen/deuterium exchange between hydrocarbons and a deuterated catalyst surface has been studied by several investigators (*1–3*). Generally, paraffin hydrocarbons have been employed in view of the relevance of these materials to catalytic cracking.

In seeking to evaluate acid properties of 500°C outgassed γ-alumina, we decided to investigate the utility of this exchange as a test reaction. Benzene was selected as reagent because it is thermally stable at elevated temperatures, and its π-basicity should give rise to significant interaction with the Lewis acid sites on the alumina. Such sites are presumed to be electron-accepting anionic vacancies, sparsely distributed over the surface. The number and strength of these sites might influence the kinetics of the exchange. As a preliminary to studying the effects of catalyst variations, it was desirable to establish the kinetics with a standard alumina surface, outgassed and deuterated under closely-controlled conditions.

EXPERIMENTAL METHODS

The exchange reactions,

$$C_6H_{6-n}D_n + {>}Al\text{-}O\text{-}D \xrightarrow{k_{n+1}} C_6H_{5-n}D_{n+1} + {>}Al\text{-}O\text{-}H, \quad (1)$$

between benzene vapor and deuterated γ-alumina surfaces were carried out in a static 270-ml quartz reactor connected to a Bendix time-of-flight mass spectrometer. The alumina, described previously (*4*), was in the form of $\frac{1}{16}$-in. spheres and had a surface area of 175 m^2/g. A 1-g sample was spread out in a single layer on the bottom of the vessel which was maintained at test temperature by an external electric heater. The upper 8 in. of the vessel was maintained at a lower temperature to provide mixing by convection. Tests made by consecutive addition of benzene and cyclohexane showed that complete mixing was achieved in less than 5 sec.

The benzene introduction system consisted of a side-arm into which sealed and weighed capillaries containing the benzene were loaded and broken by a magneticallydriven hammer. A deuterium doser permitted a known volume of deuterium gas to be exchanged with the γ-alumina in order to estimate total hydroxyl by the usual isotopic dilution technique. After this determination, additional deuterium gas was repeatedly injected and the vessel was pumped out to obtain complete exchange. This operation was done at 500°C after the alumina had been previously outgassed at 500°C for 3 hr. The reactor was then evacuated for 0.5 hr and cooled to test temperature before introduction of the benzene and start of the test.

The mass spectrometer was connected to the reactor via a commercial ½-mil gold leak, which could be throttled by adjusting a screw-mounted stainless steel ball element from a ball-point pen. This leak gave negligible sample depletion from the reaction chamber and negligible time delay. It could be easily repaired if clogged or damaged and could be rapidly adjusted to any desired leak rate.

The spectrometer gave analyses for the 7 benzene species; necessary overlap and C_{13} isotope corrections were made by a matrix programmed for computer solution.

In addition to benzene species distribution, the amount of benzene in the vapor phase could be determined by summation of initial peak heights. This required a calibration of the mass spectrometer response to a known benzene charge (usually 11.0 μmoles) in the empty reactor immediately following each run.

RESULTS

Table 1 lists the results of 14 exchange experiments run at 200°C. Each experiment was made with a fresh loading of 1 g of alumina. The corresponding hydroxyl loading, S, averaged 900 μmoles. A scatter of ±10% about this mean is attributed to errors in the isotope dilution measurement or small departures from the standard pretreatment. The number is subject to further adjustment, as discussed below, if a correction for isotope effect in the isotope dilution is applied.

The benzene loading, M, varied from 14 to 44 μmoles/g of catalyst. The initial distribution of benzene between the vapor phase and solid, estimated from total peak

TABLE 1

EXCHANGE OF C_6H_6 WITH DEUTERATED[a] γ-Al_2O_3 AT 200°C

μmoles/g of cat.									
M	M_S	M_V	ϕ_∞	k' (sec^{-1} $\times 10^3$)	$k'M$ (μmoles sec^{-1} g^{-1} $\times 10^3$)	$k_1 = k'M/M_S$ (sec^{-1} $\times 10^3$)	k_ϕ (sec^{-1} $\times 10^3$)	$k\phi/k'$	$\alpha(1)$[b]
41.10	14.4	26.7	3.75	4.0	164	11.4	4.4	1.10	0.43
43.86	14.5	29.4	3.75	3.6	158	10.9	3.8	1.06	0.47
37.25	15.3	22.0	4.00	4.9	183	13.0	5.8	1.17	0.49
35.71	14.6	21.1	4.00	4.4	157	10.7	4.9	1.12	0.47
33.23	13.9	19.3	4.22	5.6	186	13.3	5.9	1.05	0.55
33.22	13.6	19.6	4.22	5.7	189	13.9	5.7	1.00	0.54
28.61	12.9	15.7	4.35	5.9	169	13.1	6.0	1.02	0.52
28.36	12.2	16.2	4.37	6.2	176	14.4	6.5	1.05	0.53
28.80	12.7	16.1	4.34	6.1	176	13.9	6.6	1.08	0.52
21.47	11.0	10.5	4.58	7.0	150	13.7	7.4	1.06	0.49
21.71	10.8	10.9	4.64	8.7	189	17.4	8.9	1.02	0.53
20.20	9.7	10.5	4.68	6.8	137	14.2	7.1	1.04	0.51
13.84	10.1	3.7	5.03	8.8	122	12.0	8.9	1.01	0.53
13.86	10.1	3.7	5.06	9.1	126	12.5	—	—	0.56
Mean					162	13.1		1.06	0.51

[a] Outgassed 3 hr at 500°C, deuterated at 500°C.

[b] Computed from S_{corr} = 750 μmoles OH/g of catalyst.

TABLE 2

EXCHANGE CASCADE FOR 3.3 μmoles C_6H_6 WITH 0.8 g DEUTERATED γ-ALUMINA AT 250°C

Time (min)	Total peak hts.[a]	Mole fraction of deuterated benzenes							
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	ϕ
1	24.2	0.554	0.337	0.086	0.015	0.007	0.001	—	0.587
2	25.8	0.323	0.380	0.207	0.066	0.021	0.003	—	1.091
3	28.0	0.193	0.353	0.265	0.134	0.043	0.009	0.003	1.520
4	28.1	0.118	0.258	0.302	0.202	0.092	0.022	0.006	1.982
5	27.1	0.063	0.207	0.299	0.255	0.128	0.038	0.010	2.332
6	26.1	0.036	0.160	0.267	0.286	0.174	0.064	0.013	2.646
7	25.3	0.016	0.106	0.239	0.307	0.218	0.093	0.021	2.968
8	25.0	0.006	0.076	0.213	0.300	0.255	0.126	0.024	3.196
9	24.3	0.001	0.053	0.171	0.290	0.284	0.169	0.032	3.438
10	23.3	0.000	0.039	0.137	0.259	0.311	0.195	0.058	3.657
11	22.6	0.000	0.027	0.110	0.250	0.321	0.223	0.069	3.810
12	22.2	0.000	0.008	0.092	0.226	0.326	0.259	0.089	4.003
13	22.0	0.000	0.005	0.066	0.205	0.323	0.296	0.104	4.151
14	21.5	0.000	0.009	0.052	0.182	0.319	0.315	0.123	4.248
15	21.6	0.000	0.000	0.039	0.158	0.317	0.337	0.149	4.399
16	20.6	0.000	0.003	0.030	0.130	0.289	0.371	0.177	4.526
17	20.0	0.000	0.000	0.022	0.107	0.283	0.372	0.216	4.653
18	19.8	0.000	0.000	0.016	0.099	0.270	0.372	0.243	4.727
19	19.7	0.000	0.000	0.004	0.101	0.260	0.390	0.245	4.771
20	19.5	0.000	0.000	0.007	0.077	0.243	0.402	0.271	4.853
21	19.0	0.000	0.000	0.004	0.060	0.211	0.428	0.297	4.954
22	18.8	0.000	0.000	0.003	0.056	0.224	0.398	0.319	4.974
23	18.0	0.000	0.000	0.007	0.047	0.186	0.412	0.348	5.039
24	17.9	0.000	0.000	0.000	0.042	0.199	0.398	0.361	5.078
25	17.8	0.000	0.000	0.000	0.036	0.178	0.406	0.380	5.130
26	17.7	0.000	0.000	0.000	0.022	0.165	0.417	0.396	5.187
27	17.2	0.000	0.000	0.000	0.026	0.157	0.405	0.412	5.203
28	16.9	0.000	0.000	0.000	0.021	0.138	0.407	0.434	5.254
29	16.8	0.000	0.000	0.000	0.007	0.143	0.386	0.464	5.307
30	16.5	0.000	0.000	0.000	0.009	0.115	0.388	0.488	5.355
35	16.0	0.000	0.000	0.000	0.000	0.085	0.381	0.534	5.449
40	14.9	0.000	0.000	0.000	0.000	0.075	0.342	0.583	5.508
45	14.0	0.000	0.000	0.000	0.000	0.053	0.319	0.628	5.575
∞	—	—	—	—	—	—	—	—	5.64[b]

[a] Arbitrary units; surge at 3–4 min is attributed to thermal transient of initial adsorption.

[b] Calculated.

height as described above, is given in columns headed M_V and M_S, respectively.

Table 2 gives the isotopic benzene distribution for a complete exchange cascade obtained at 250°C. The low loss leak used in the 200°C experiments was not used, and there was some reduction in the benzene inventory as indicated by drop in total peak height. The distribution of benzene between vapor and adsorbed phases was not determined, nor was a value of ϕ_∞ directly measured.

Kinetics

The first order exchange plots of log $[C_6H_6]$ vs time were made to represent the drop in concentration of the undeuterated species, d_0. These plots were linear to 80–90% disappearance of C_6H_6. The range of linearity tended to increase with lower benzene loading. The first order constants, k', calculated from the slope of these plots, are given in Table 1, Column 5, while the initial conversion rate μmoles of benzene/g of catalyst-sec, are given in Column 6. The conversion appeared to follow zero order kinetics with respect to overall benzene concentration, since there was no strong correlation with benzene loading. However, a plot of the conversion rate ($k'M$) vs the amount adsorbed (M_S) suggests that the conversion is first order in adsorbed benzene (Fig. 1).

The rate equation for reaction (1), $n = 0$, may therefore be written:

$$-\frac{d(Md_0)}{dt} = k_1(M_S d_0).$$

The average value of k_1 for the 14 experiments was 13.1×10^{-3} sec^{-1} with a standard deviation of 0.5×10^{-3}, 5.7% of the mean.

The rate equation indicates that if the benzene adsorption is in the Henry's Law portion of the isotherm, where M_S is proportional to M, the reaction would be first order in total benzene concentration. The tendency toward zero order kinetics arises because a large number of the experiments were made in the saturation portion of the isotherm.

The average deuterium content per molecule of benzene, ϕ, defined as $\phi = \Sigma n d_n$, where d_n is the mole fraction of the species $CH_{6-n}D_n$, was calculated for all analyses. The equilibrium value, ϕ_∞, was obtained by shutting off the leak to the mass spectrometer after the disappearance of C_6H_6 and rescanning about 21 hr later. The plots of $\log(\phi_\infty - \phi)$ vs time were linear to at least 40% of equilibrium exchange. The initial slopes yielded values of k_ϕ, the rate constant for initial appearance of deuterium in the benzene. Kemball's "*M*" test was then applied (*5*).

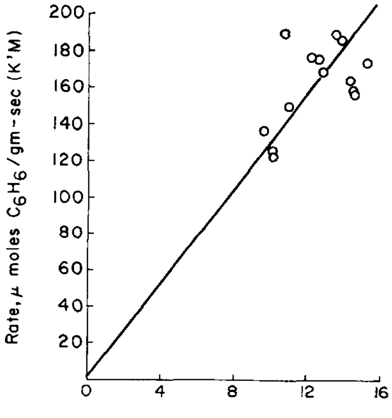

FIG. 1. Exchange rate: $C_6H_6 + {>}AlOD \rightarrow C_6H_5D + {>}AlOH$.

The experimental value of k'/k_ϕ ranged from 1.0 to 1.17, with an average of 1.06. A ratio of unity has been taken to indicate stepwise exchange. This is not necessarily true if fast redistribution of the deuterium occurs between isomers, independently of the exchange with deuteroxyl. Such redistribution, or "scrambling" indeed did occur very rapidly, when equal mixtures of C_6H_6 and C_6D_6 were charged.

Larson and Hall (*3*) found in the exchange of deuteromethane with alumina at 135°C an initial rapid exchange followed by a slow exchange. The deuterium which exchanged at or near catalytic sites did not mix readily with the pool of surface hydrogen since it could be recovered by back exchange. At 200°C we expect that surface diffusion is faster and that the exchanged hydrogen will mix rapidly with the pool of surface deuterium. This pool is assumed to comprise an aggregate of mobile, undifferentiated species. This picture is consistent with Peri's infrared spectrogram (*7*) of 500°C outgassed deutero-alumina, which shows a broad adsorption band indicating extensive deuterium bonding.

The curvature of the $\log(\phi_\infty - \phi)$ vs time plot suggests that at 200°C some diffusion control remains. The situation appears to be improved in the 250°C exchange data listed in Table 2. A value of $\phi_\infty = 5.64$ was used to linearize the log $(\phi_\infty - \phi)$ vs time plot to 98% conversion. This compared to a value of 5.81 based on statistical distribution of D between benzene and deuteroxyl; or to a somewhat higher value if losses of benzene hydrogen from the system were taken into account.

The ln d_0 vs time plot from Table 2 was linear to 98% conversion and gave $k' = k_1(M_S/M) = 9.3 \times 10^{-3}$ sec^{-1}. The value of k_1 would depend on the fraction of benzene adsorbed, which was not determined.

Equilibria

The experimental values of ϕ_∞, M, and S may be used to calculate an equilibrium isotope effect, $\alpha(1)$, for reaction (1). The computation formula was derived from Harris' (*6*) general treatment of the bimolecular equilibrium for exchange:

$$\frac{\alpha(1)}{\alpha(1) - 1} = \frac{M\phi_\infty}{(6M + S) - 6S/\phi_\infty},$$

$\alpha(1)$ is defined (*9*) as:

$$\alpha(1) = \frac{(\mathrm{D/H})\text{benzene}}{(\mathrm{D/H})\text{alumina}}.$$

In applying this formula it is legitimate to question whether the value of S as conventionally determined should be used, or whether an isotope effect correction should be applied. The complete computation formula for surface hydroxyls, S, from isotope dilution is:

$$S = \mathrm{D}Q\left[1 - \frac{\alpha(2) - 1}{\alpha(2)} \cdot \frac{Q}{Q + 1}\right],$$

where D is the initial charge of deuterium, Q is the final equilibrium hydrogen/deuterium ratio in the gas phase, and $\alpha(2)$ is the isotopic equilibrium for the exchange reaction (2):

$$\mathrm{HD} + {>}\mathrm{AlOH} \rightleftharpoons {>}\mathrm{AlOD} + \mathrm{H_2}. \qquad (2)$$

In the absence of isotope effect, $\alpha(2) = 1$ and the formula reduces to the usual simple form, $S = \mathrm{D}Q$.

Work in these laboratories indicates that $\alpha(2)$ does not differ greatly from $\alpha(3)$, the isotopic equilibrium for the exchange reaction (3):

$$\mathrm{HD} + \mathrm{HOH} \rightleftharpoons \mathrm{HOD} + \mathrm{H_2}. \qquad (3)$$

At 500°C $\alpha(3) = 1.4$ (*8*). Since most isotopic dilution experiments were run under conditions where $Q \cong 1$, the correction factor is 0.86. A corrected value of $S = 750$ μmole/g was used to calculate values of $\alpha(1)$ shown in the last column of Table 1. The average value was 0.51.

An alternate calculation which is independent of a predetermined value of S employs a linear form of the computation formula, with M and ϕ_∞ as knowns, S and $\alpha(1)$ as unknowns. A least squares fit of the data in Table 1 leads to $S = 475$ μmoles/g and $\alpha(1) = 0.9$. This value of S appears unacceptably low in view of Peri and Hannan's summary (*10*) of the effect of dehydration temperature of alumina on its residual hydroxyl content. The low value could be due to a small consistent error in the ϕ_∞'s.

The possibility still exists that only a portion of the surface deuterium enters into exchange equilibrium with benzene at 200°C. Hall and Lutinski's data for deuterium/hydroxyl exchange (*11*) suggest this. However, their alumina was pretreated under somewhat more severe conditions than ours, and contained only 570 μmoles/g hydrogen uncorrected for isotope effect.

The value of $\phi_\infty = 5.64$ derived from the 250°C experiment gave $\alpha(1) = 0.5$, in agreement with the results in Table 1.

A value of $\alpha(1)$ may also be calculated from the related equilibria of reactions (2) and (4):

$$\mathrm{HD} + \mathrm{C_6H_6} \rightleftharpoons \mathrm{C_6H_5D} + \mathrm{H_2}. \qquad (4)$$

A short extrapolation of Taylor and Joris' data (*9*) gives $\alpha(4) = 1.5$ at 200°C. At this temperature $\alpha(3) = 2.0$ (*8*). Using this value for $\alpha(2)$, as before,

$$\alpha(1)_{\mathrm{calc}} = \frac{\alpha(4)}{\alpha(2)} = 0.75.$$

This equilibrium lies in the same direction as indicated by our experiments.

The phenomena of incomplete equilibration and isotope effect are not mutually exclusive. Both may be operating to give values of ϕ_∞ lower than the statistical prediction. A study of the reverse exchange should clarify the issue.

Variation of the Surface

It is evident from the variation of k_1 in Table 1 that exceedingly careful control of outgassing and reaction conditions is needed to get reproducible exchange rates. In one experiment the outgassing time was increased from 3 to 16 hr. The rate constant decreased from 13.1×10^{-3} to 3.4×10^{-3} sec^{-1}. In another case where the reverse exchange of $\mathrm{C_6D_6}$ with normal alumina was being studied, the reaction rate dropped in half when the hydrogen pretreatment (analogous to the deuteration step in the forward exchange experiment) was omitted. The first observation suggests that chemisorbed water promotes exchange. The second can be interpreted in the same fashion if it is assumed that the hydrogen (or deuterium) pretreatment reduced residual adsorbed oxygen, adding the corresponding amount of water to the surface.

This effect has been frequently observed in the exchange of hydrocarbon hydrogen with deuterated silica–alumina (*12*). On the other hand, water depresses the catalytic activity of alumina for H_2–D_2 exchange (*13*). The latter reaction, which does not involve the surface itself as a reagent, probably proceeds by a heterolytic disassociative adsorption of gas phase molecules, requiring a Lewis acid site to accept the hydride ion. In the case of exchange of benzene hydrogen with surface deuteroxyl, it is the concentration of highly labile deuterons adjacent to the adsorption sites, i.e., Brönsted acidity, which controls the rate. This concentration will increase with hydration of the surface up to the point where the Lewis sites are themselves eliminated by deuteroxylation.

CONCLUSIONS

The kinetics of exchange of benzene with a large excess of deuterium as surface alumina deuteroxyl may be described as first order in adsorbed benzene. A lower than statistical amount of deuterium appears in the benzene at equilibrium, interpreted as due to an isotopic effect favoring retention of deuterium on the alumina. Such an effect is consistent with related equilibria.

The suitability of the reaction as a test for surface Lewis acidity is diminished by the strong effect of water in promoting the exchange. This, in fact, suggests that Brönsted acidity is rate controlling.

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