order of magnitude lower than the value which would have been expected with $k_{sv}' = k_{sv}$ and with c_{max} similar to the values derived from previous studies of the catalysis of ionic reactions in PVS solutions.[2c,d] On the other hand, curve B is clearly qualitatively different from the experimental data. There can be no doubt that these data prove that no significant counterion exchange takes place over the short lifetime of the excited uranyl ion. While this may have been expected

in view of previous estimates of counterion exchange rates,[22-24] the method employed in the present study to substantiate this conclusion should be of some interest, since it is applicable to exchange rates which are much too fast to be investigated by conventional techniques.

(22) F. T. Wall and P. F. Grieger, *J. Chem. Phys.*, **20**, 1200 (1952).
(23) F. T. Wall, P. F. Grieger, J. R. Huizenga, and R. H. Doremus, *ibid.*, **20**, 1206 (1952).
(24) G. Geuskens, A. DePauw, and C. David, *Eur. Polym. J.*, **4**, 316, 365 (1968); **5**, 125 (1969).

Isotopic Exchange Reactions Involving Alcohols, Ketones, and Deuterium on Silica, on Palladium/Silica, and on Alumina

William R. Patterson and Robert L. Burwell, Jr.*

Contribution from the Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received April 18, 1970

Abstract: The following two reactions, (I) i-C$_3$H$_7$OD + butanone = i-C$_3$H$_7$OH + butanone-d and (II) alcohol–ketone interchange, 2-propanol + butanone = acetone + 2-butanol, were catalyzed by a commercial silica at impurity centers, perhaps Al^{3+}. Reaction I is about 100 times as fast as (II) at 100–150°. Reaction II involves a rate-limiting hydride transfer as tested by use of 2-propanol-2-d. Reactions I and II are very much slower on pure silica. Both reactions occurred on a commercial palladium/silica catalyst at roughly the same rate as on commercial silica. The reactions must occur in part on the support, but palladium metal is also active for reactions I and II. In addition, isotopic exchange between deuterium and the hydroxyl hydrogen atoms of ethanol, 2-butanol, and *tert*-butyl alcohol on palladium/silica is about as rapid as reaction I. Isotopic exchange between butanone and deuterium is nearly as rapid. The rate of dehydrogenation of 2-butanol to butanone is only about 0.0001 that of formation of ROD. In addition, skeletal exchange of 2-butanol occurs on palladium/silica at a rate about 0.01 that of formation of ROD. Compared with platinum and nickel, palladium appears to have a low tendency to cleave the H–COH bond of secondary alcohols but a high tendency to cleave the HCO–H bond.

$\mathbf{I}$n recent years, alcohol–ketone interchange reactions have been reported to occur upon passage of the vapors of alcohol–ketone mixtures over various metal and metal oxide catalysts. For example, Malinowski and Kobyliński[1] observed the conversion of a mixture of isovaleraldehyde and ethyl alcohol to isoamyl alcohol and acetaldehyde on several metals supported on pumice. High conversions were obtained with nickel and with copper at 200–300°. 2-Propanol was a better hydrogen donor than ethanol which in turn was better than methanol. Similar interchange accompanied hydrogenation and dehydrogenation in 2-propanol–butanone mixtures passed over unsupported copper catalysts at 115–150°.[2] The reaction was also observed in preliminary experiments on a palladium/alumina catalyst at 96–130°.[2] We decided to extend the study of palladium catalysts because the low activity for hydrogenation of alkyl ketones on palladium permits one to observe reactions in the ketone–alcohol system which are hidden by hydrogenation on most group VIII metals. We started with palladium/silica catalysts because we feared that the interchange observed on palladium/alumina might have occurred on the support.

Initial work disclosed that both the interchange reaction and isotopic exchange between ROD and ketone occurred on commercial silica gel. Accordingly, these reactions were further investigated on palladium/silica, commercial silica gel, pure silica gel, and alumina. Silica gels and aluminas are widely used as supports for catalytically active metals and oxides. It has long been recognized that the catalytic characteristics of alumina can influence the total catalytic behavior of catalysts using alumina as a support. Silica gels, on the other hand, have usually been considered inert. For certain reactions, we will show that commercial silica gels have substantial catalytic activity but that pure silica gel is indeed inert or almost so.

Experimental Section

Materials. Ethanol, 2-propanol, 2-butanol, *tert*-butyl alcohol, and butanone were purified by fractional distillation and were chromatographically homogeneous. 2-Propanol-*O*-*d* was prepared by mixing isopropyl alcohol with deuterium oxide, salting out the alcohol, and distilling it. 2-Propanol-2-d of 98.5% isotopic purity (Volk Radiochemical Co.) was used without further purification.

The 0.3% palladium/silica catalyst (Baker and Co., Inc.) was crushed and sieved to 60–80 mesh. It was diluted with three to four times its weight of Pyrex beads of the same mesh size. Before used it was treated in a stream of hydrogen at 350° for about 10 hr. The following silicas were employed: (1) 60–200 mesh Davison Chemical Co., Grade 950 silica gel, washed with water and then dried; (2) Filtros FS-140-L (Filtros Incorporated, East Rochester, N. Y.), a low-area (~1 m²/g), large-pore silica reported

(1) S. Malinowski and T. Kobyliński, *Actes Congr. Int. Catal., 2nd, 1960*, 2689 (1961); see also S. Malinowski, *Oesterr. Chem. Ztg.*, **68**, 1 (1967).
(2) J. Newham and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **86**, 1179 (1964).

Table I. Isotopic Exchange between Alcohols and Deuterium on Palladium/Silica Gel Catalyst

Run	G_{61}	G_{92}	G_{14}		G_{54}^e		G_{73}	G_{76}
Alcohol	—Ethanol—			2-Butanol			—tert-Butyl alcohol—	
Temp, °C	102	133	109		130		101	131
L_{alc}^a	8.8	0.9	8.7		0.70		8.8	0.72
OD, %^{b}	35.1	75.4	42.4		81.0		13.0	91.0
			Me^d	Et^d	Me^d	Et^d		
D_0, %^{c}		98.3	99.4	99.4	94.4	90.6	100.0	
D_1, %^{c}		1.6	0.3	0.3	5.2	8.2	0.0	
D_2, %^{c}		0.0	0.3	0.3	0.5	1.2	0.0	

^{a} Flow rate of alcohol in millimoles per hour per gram of catalyst. The flow rate of deuterium was 11 to 12 times greater except in run G_{14}, in which case it was 14 times greater. ^{b} Per cent exchange of hydroxylic hydrogen atom by ir analysis. ^{c} Per cent exchange of skeletal hydrogen atoms. D_0 is % d_0 in skeletal positions of product alcohol. OD was converted to OH before mass spectroscopy; see under Analysis. ^{d} Me means exchange in MeCHOH$^+$ ion; Et means exchange in EtCHOH$^+$ ion; see under Analysis. ^{e} Run G_{53}, 130°, L_{alc} = 8.3, % OD = 46.7, % butanone = 0.006. At 102°, L = 8.3; G_{52}, % OD = 29.4; G_{55}, % OD = 29.9.

to contain 0.21% alumina (X-ray diffraction shows the material to be at least partially crystalline); (3) 60–140 mesh silica gel prepared by hydrolysis of purified ethyl orthosilicate by G. L. Haller in these laboratories. All samples of silica gel were initially treated overnight *in situ* in a stream of nitrogen at 150°.

Apparatus. A flow system devoid of greased stopcocks was used.[3] Hydrogen and deuterium were purified by passage over charcoal at −195°. One of these gases as the carrier gas was passed through a short column of 30–60 mesh Chromosorb G saturated with the compound to be volatilized. The column was maintained at that temperature which gave the desired ratio of partial pressures of compound to carrier gas. The stream from the saturator passed through the catalyst vessel which was immersed in a fluidized bath of Carborundum powder, the temperature of which was controlled to ±1° by means of a Thermocap relay. Samples for analysis were condensed in a trap held at −78°.

The catalyst was usually held in hydrogen overnight at the next reaction temperature and then purged for 1 hr with deuterium when that gas was to be employed. The reactant stream was started and maintained for at least 0.5 hr before sampling. All experiments with palladium/silica were run on the same sample, 0.881 g of catalyst dispersed in 3.14 g of glass beads. In most cases, the steady-state activity of the catalyst was stable for many runs. Occasionally the catalyst was regenerated by treatment with hydrogen at 350°. This produced a material with two to three times the usual activity, but this activity rapidly declined to the usual steady-state activity. All listed runs refer to the steady-state catalyst.

Analysis. Contents in ROD and ROH were determined with a Beckman IR9 infrared spectrometer using cells of the Connecticut Instrument Co. with windows of Eastman Kodak Co. Irtran. The OH and OD stretching bands at about 3400 and 2500 cm^{-1} were employed. With alcohols, a 10% solution in carbon tetrachloride was employed. Mixtures resulting from the use of the azeotrope of butanone and 2-propanol were analyzed without solvent. The analytical procedure was calibrated with synthetic mixtures. We estimate the accuracy to be ±2.5 percentage units in OD.

We employed a Consolidated 21-130 mass spectrometer, provided this department by a grant from the National Science Foundation, and used an ionizing voltage of 15 V with alcohols, 68 V with ketones. Parent ions were used with ketones but, with alcohols, the parent peak is very small. The ion CH_3CHOH^+ was used with 2-propanol, and this ion and $C_2H_5CHOH^+$ with 2-butanol. It is known that fragmentations to these ions are unattended by isotopic rearrangements.[4,5] The parent ion was used for ethanol, the $CH_3COHCH_3^+$ ion for tert-butyl alcohol. Direct analysis of 2-propanol-*O-d* showed that about 35% of the deuterium in ROD was lost by exchange in the mass spectrometer. For this reason, before mass spectrographic determination of skeletal deuterium, all hydroxyl deuterium was removed by passage through a gas chromatographic column containing diglycerol. This was usually combined with separation of a reaction mixture into its components before mass spectroscopy. For this purpose a dual column was employed: 6 ft of Carbowax 20M followed by 12 ft of 20% diglycerol, both on Chromosorb P.

(3) K. Schrage and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **88**, 4549 (1966).
(4) L. Friedman and J. Turkevich, *ibid.*, **74**, 1669 (1952).
(5) K. Mislow, R. E. O'Brien, and H. Schaefer, *ibid.*, **84**, 1940 (1962).

The infrared method for assessing the degree of formation of ROD appears to be more reliable than mass spectrographic methods because of difficulties in allowing for the degree of exchange in the inlet systems of a mass spectrometer.

Results

Isotopic Exchange between Deuterium and Alcohols on Palladium/Silica Gel.

Exchange between deuterium and the hydroxyl hydrogen atoms of ethanol, 2-butanol, and tert-butyl alcohol occurred rapidly on the palladium/silica catalyst at 100–130°. As shown in Table I, skeletal exchange of ethanol and 2-butanol was much slower than hydroxyl exchange and that of tert-butyl alcohol was too slow to be detected.

Dehydrogenation of 2-butanol became evident only at high degrees of OH exchange. Thus, in run G_{54} of Table I, 0.05 mol % butanone was formed. It was isolated and analyzed mass spectrometrically (Table II). Its degree of exchange was much greater than that of the skeletal exchange of the butanol (Table I).

Table II. Isotopic Exchange between Deuterium and Butanone on Palladium/Silica Gel Catalyst

Run	G_{54}^c	G_{82}^d	G_{83}^e	G_{41}^f	G_{42}^f
Reactant^a	2-Butanol	—Butanone—		—Mixture—	
Temp, °C	130	131	131	135	135
L^b	0.72	17.4	1.8	3.9	0.95
D_0, %	5.6	86.0	35.5	47.4	28.0
D_1, %	7.6	12.6	32.2	36.4	36.2
D_2, %	8.0	1.2	21.5	12.4	24.8
D_3, %	11.2	0.2	9.6	2.9	9.2
D_4, %	19.2	0.0	1.9	0.6	1.7
D_5, %	42.5		0.3	0.2	0.2
D_6, %	3.2		0.0	0.0	0.0
D_7, %	1.6				
D_8, %	1.2				

^{a} Reactant fed. Mixture is 73% butanone + 27% 2-propanol. ^{b} Flow rate of organic reactants in millimoles per hour per gram of catalyst. In runs G_{82} and G_{83}, deuterium flow rate is 5 times greater, in runs G_{41} and G_{42}, 8.3 times greater. ^{c} See Table I. The analysis is for the 0.05% butanone formed. ^{d} No detectable butanol formed. ^{e} 0.06% butanol formed. ^{f} The analysis is for the butanone fraction.

Exchange between Butanone and Deuterium on Palladium/Silica Gel.

Butanone in deuterium was also passed over the catalyst (Table II), as was a mixture of butanone and 2-propanol (mole ratio about three) in deuterium.

The presence of 2-propanol seems slightly to increase the degree of exchange of butanone, runs G_{41} and G_{42} vs. G_{82} and G_{83}. Added tert-butyl alcohol reduces

Table III. Deuterium Transfer in 2-Propanol-O-d Plus Butanone in Hydrogen

Run	Pd/SiO₂c			Grade 950d,e			Pure SiO₂e,f Gel
	H₇₂ᵍ	H₇₃ʰ	H₇₄	J₉₁	J₉₂	J₉₃	J₁₆₂
Temp, °C		135			101		103
Lᵃ	7.7	3.6	52.3	1.8	7.3	25.9	0.4
OD, %	Negligibleⁱ	Negligibleⁱ	28.5	Negligibleⁱ	39.6	60.2	69.1
D₀, %ᵇ	86.0	87.4	93.7	73.9	90.9	93.5	97.0
D₁, %ᵇ	12.8	11.5	5.7	22.3	8.4	5.7	2.1
D₂, %ᵇ	1.1	1.0	0.5	3.2	0.7	0.7	0.6
D₃, %ᵇ	0.2	0.1	0.1	0.4	0.2	0.0	0.2
D₄, %ᵇ	0.0	0.0	0.0	0.2	0.0	0.0	0.1

ᵃ Flow rate of mixture in millimoles per hour per gram of catalyst. The flow rate of hydrogen was 6.5 times greater. ᵇ Exchange pattern of butanone separated from product. ᶜ 0.881 g of catalyst. i-PrOD was 70.7% labeled. The deuterium balance showed that there was substantial formation of HD. ᵈ 2.01 g of catalyst. i-PrOD was 70.7% labeled. ᵉ The deuterium balance showed that there was negligible formation of HD. ᶠ 3.11 g of catalyst. i-PrOD was 73.4% labeled. ᵍ 1.5% acetone and 2.2% butanol formed. ʰ 2.2% acetone and 3.2% butanol formed. ⁱ Zero within experimental error.

both the rate of exchange of butanone and that of its hydrogenation to butanol.

Exchange between 2-Propanol-O-d and Butanone. Table III presents the results of experiments in which hydrogen carrier gas containing butanone plus 2-propanol-O-d (mole ratio about three) was passed over palladium/silica gel, over Davison Grade 950 silica gel, and over pure silica gel.

The Alcohol–Ketone Interchange Reaction. During passage of 2-propanol–butanone in hydrogen or deuterium over the palladium/silica catalyst at 110–160°, we observed substantial formation of 2-butanol. Thus, in runs G₄₁ and G₄₂ of Table II, 2.5 and 8.8% of 2-butanol were formed and nearly equal amounts of acetone. In the absence of 2-propanol, runs G₈₂ and G₈₃, mere traces of butanol were formed.

However, the interchange reaction appeared to be almost as fast on a commercial silica gel (Davison Grade 950). Accordingly, the reaction was investigated on Grade 950 and on a Harshaw alumina.⁶ Further, since G. L. Haller in these laboratories had found that commercial silica catalyzed the isomerization of 1-hexene at 100° but that pure silica gel did not, we also investigated pure silica gel. Typical results appear in Table IV. No detectable reaction occurred on pure

Table IV. The Alcohol–Ketone Interchange Reaction on Commercial Silica and Alumina

Run	Temp, °C	Lᵃ	Acetone, %	Butanone, %	2-Propanol, %	2-Butanol, %
On Grade 950 Silica Gel of Table III						
J₆₁	118	1.59	0.8	75.0	23.0	1.0
J₁₃₂ᵇ	134	1.09	1.7	75.2	21.9	1.2
J₆₄	162	0.56	8.1	64.8	15.6	11.3
J₇₃ᶜ	162	0.60	1.5	76.7	19.0	2.8
J₇₄ᵈ	162	2.00	2.0	77.2	18.1	2.7
On 3.005 g of Alumina						
K₂₁	105	1.4	7.8	61.3	22.4	8.5
K₂₂	132	1.4	17.2	51.1	14.0	17.8
K₂₅	146	3.1	18.2	49.5	10.0	22.3

ᵃ Flow rate of 2-propanol + butanone in millimoles per hour per gram of catalyst. The flow rate of the carrier gas was eight times greater. The carrier gas was hydrogen except in run J₁₃₂. ᵇ The carrier gas was nitrogen, and a different sample of Grade 950 silica gel was employed, 2.240 g. ᶜ 2-Propanol-2-d, 98.5% labeled. ᵈ As in c but 22.1% labeled.

(6) Kindness of Professor H. Pines. It is a nonacidic γ-alumina. See H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82**, 2471 (1960).

silica gel at up to 175° nor on the Filtros at 250°. Generally, yields of acetone were somewhat below those of 2-butanol, presumably because of preferential loss of the lower boiling acetone during sampling.²

To test for the effect of pretreatment by acid or base, Davison Grade 950 silica gel was washed with 0.1 M hydrochloric acid, washed with water, and dried. Another sample was washed with 0.1 M sodium hydroxide, washed with many changes of water, and dried. Both exhibited nearly the same catalytic activity as the standard gel. The untreated silica was tested after pretreatment at temperatures ranging from 150 to 476°. At a reaction temperature of 152° and flow rates of 8.8 mmol of hydrogen hr⁻¹ g⁻¹ and 1.36 of 2-propanol plus butanone, the yield of butanol rose slowly with increasing activation temperature. The per cent butanol in the product rose from 4.6% at a pretreatment temperature of 150° to 7.0% at one of 476°.

Alumina is considerably more active as a catalyst, but it also forms moderate amounts of higher boiling substances of sharp odor. Gas chromatography indicated that at least five compounds were present. On the basis of retention times, one was tentatively identified as diacetone alcohol. The matter was not further investigated. The results in Table IV are based only upon the C₃ and C₄ compounds.

The interchange reaction was investigated on the standard silica gel using 2-propanol-2-d and hydrogen as the carrier gas, runs J₇₃ and J₇₄ of Table IV. Mass spectral results appear in Table V.

Table V. Isotopic Distributions in the Products of Runs J₇₃ and J₇₄

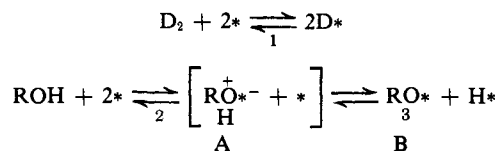| Run	Alcohol	D₀, %	D₁, %	Ion used for analysis
J₇₃	2-Propanol	1.70	98.30	MeCHOH⁺
	2-Butanol	10.00	90.00	MeCHOH⁺
		7.39	92.61	EtCHOH⁺
J₇₄	2-Propanol	77.22	22.78	MeCHOH⁺
	2-Butanol	88.29	11.71	MeCHOH⁺
		88.30	11.70	EtCHOH⁺

The 2-propanol and 2-butanol from runs on palladium/silica with deuterium carrier, G₄₁ and G₄₂ of Table II, were also analyzed mass spectrometrically, but the similar run G₃₃ at lower conversions (Table VI) is more informative with respect to initial behavior.

Table VI. 2-Propanol Plus Butanone in Deuterium on Palladium/Silica at 112.5°, Run G_{33}, $L = 2.3^a$

OD, %	2-Propanol	Butanone	2-Butanol	
	58		(58)	
$\%^b$	25.0	72.4	1.3	
Ion^c	MeCHOH$^+$	Parent$^+$	MeCHOH$^+$	EtCHOH$^+$
D_0, %	99.0	81.6	84.1	81.8
D_1, %	0.8	14.9	13.4	15.0
D_2, %	0.2	2.8	1.9	2.5
D_3, %		0.7	0.4	0.8
D_4, %		0.0	0.2	0.0

^{a} Millimoles of alcohol + ketone per hour per gram of catalyst. The flow rate of deuterium was 6.6 times greater. ^{b} % in product. ^{c} Ion used in mass spectrometric analysis.

The 2-propanol may have been even less exchanged than shown because of imperfect separation from 2-butanol.

Runs with $CH_3CDOHCH_3$ like runs J_{73} and J_{74} of Tables IV and V were also made on palladium/silica. Results were very nearly the same as on Grade 950 silica gel: the same kinetic isotope effect, the same formation of 2-butanol-d_1. Runs at lower temperatures and conversions gave nearly the same results, although 2-butanol-d_0 was slightly larger.

Discussion

Reactions on Silica. Two reactions were found to occur on a standard commercial silica gel, Davison Grade 950, Tables III and IV.

$$(CH_3)_2CHOD + CH_3COC_2H_5 =$$
$$(CH_3)_2CHOH + CH_3COC_2H_5\text{-}d \quad (I)$$
$$(CH_3)_2CHOH + CH_3COC_2H_5 =$$
$$(CH_3)_2CO + (CH_3)(C_2H_5)CHOH \quad (II)$$

At temperatures in the vicinity of 100–120°, reaction I is relatively fast, roughly 100 times faster than reaction II. At higher temperatures, reaction II can lead to substantial conversions; for example, run J_{64} of Table IV had proceeded more than half-way to equilibrium. The alcohol–ketone interchange reaction, reaction II, proceeds at about the same rate with nitrogen, hydrogen, or deuterium as the carrier gas and, when deuterium was used, no isotopic exchange could be detected. Further, no loss of deuterium to form HD occurs in reaction I with hydrogen carrier, nor is deuterium lost when alcohols labeled at carbon atom 2 are used. With such alcohols, as shown by run J_{73} of Tables IV and V, the interchange reaction proceeds as follows

The 2-propanol-2-d reacts distinctly more slowly than 2-propanol and, in run J_{74} with a mixture of labeled and unlabeled alcohol, the ratio of reactivities of labeled to unlabeled was 1/2.

We have run no experiments aimed at ascertaining what impurity in commercial silica is responsible for this catalytic activity. However, in isomerization of 1-hexene by commercial silica, the effective impurity seems to be aluminum ion,[7] and it may well be the effective impurity for reactions I and II. Further, at least one alumina is a catalyst for the interchange reaction (Table IV) and a much more active one than commercial silica. However, it also catalyzes the formation of condensation products.

(7) G. L. Haller, P. B. West, and R. L. Burwell, Jr., unpublished.

Similarly, 0.02% alumina, added as a aluminum nitrate during hydrolysis of ethyl orthosilicate, conveys substantial activity for dehydration of alcohols at 190°.[8]

Since the interchange reaction on impure silica clearly involves a "hydride" transfer from alcohol to ketone, and since it probably involves a surface aluminum ion, the reaction might well be considered to be a heterogeneous Meerwein–Ponndorf–Oppenauer equilibration, and coordination of ketone to aluminum as in the conventional mechanism[9] may be involved.

The coordination number of the aluminum(III) in this structure is uncertain.[9] The observed kinetic isotope effect suggests that the hydride-transfer step is rate limiting, unlike the situation in the usual Meerwein–Ponndorf reaction.[9] The near identity in rates on silica gel extracted with acid and on gel treated with base suggests that a proton acid is not involved. Although some process like that just suggested is clearly required, considerable further work might be needed to establish the details.

Filtros is inactive for the interchange reaction even though it is reported to contain a small amount of aluminum. However, its surface area is very low and it is crystalline.

Impurities, probably aluminum ion, might be responsible for some of the reactions which have been reported to occur on silica, for example, isomerization of m-dioxanes to β-alkoxy aldehydes at 300°,[10] polymerization of acetaldehyde,[11] and condensation of acetaldehyde.[12]

At the beginning of the flow of reactants, our experiments showed that both commercial and pure silica gel remove deuterium from $(CH_3)_2CHOD$ presumably by exchange with surface silanol groups.

$$(CH_3)_2CHOD + \equiv\!SiOH = (CH_3)_2CHOH + \equiv\!SiOD \quad (III)$$

The isotopic exchange reaction I appears to involve (III) acting on $\equiv\!AlO^+H_2$ coupled with an acid-catalyzed enolization of the following type.

(8) H. Pines and T. Kobyliński, private communication.
(9) V. J. Shiner, Jr., and D. Whittaker, J. Amer. Chem. Soc., **91**, 394 (1969).
(10) C. S. Rondestvedt, Jr., and G. J. Mantell, ibid., **84**, 3307, 3319 (1962).
(11) V. V. Stelko, L. N. Ganyuk, I. Yu. Kachkurova, and Z. Z. Vysotskii, Proc. Acad. Sci. USSR, Chem. Sect., **145**, 759 (1962).
(12) R. P. Young and N. Sheppard, J. Catal., **7**, 223 (1967).

Whether the small rate of exchange observed on our purest silica (Table III, run J_{162}) results from the acidity of $\equiv$SiOH or from unremoved impurity is not clear.

Reactions on Palladium/Silica. Preparatively, palladium catalysts are well known to be inactive for the liquid-phase hydrogenation of dialkyl ketones.[13,14] Evaporated palladium films are also relatively poor catalysts for the gas-phase hydrogenation. Stoddart and Kemball[15] report that equivalent temperatures for equal rates of hydrogenation of acetone per unit area of film are $-62°$ for platinum, $-17°$ for nickel, and $185°$ for palladium. On the other hand, palladium is slightly more active than either platinum or nickel for isotopic exchange between deuterium and acetone.[16] Further, palladium is reported to be inactive for hydrogenolysis of acetone to propane.[16] This combination of properties makes palladium an interesting material for study of certain reactions in a system composed of alcohol, ketone, and deuterium, since complications resulting from hydrogenation–dehydrogenation and hydrogenolysis are nearly absent. Work in this paper is concerned with 0.3% palladium on a silica support. Except for possible contributions of the commercial silica support to catalytic activity, palladium on silica appears to possess catalytic activity quite similar to that reported for evaporated palladium film.

As shown in Table I, isotopic exchange between ethanol, 2-butanol, or *tert*-butyl alcohol and deuterium is the fastest reaction of any which we directly observed on palladium. The rate of exchange of *tert*-butyl alcohol is about one-half as fast as those of the other two, possibly because of the greater cross-sectional area of *tert*-butyl alcohol.

The near identity in behavior of *tert*-butyl alcohol with the others strongly indicates that exchange proceeds on palladium *via* the simultaneous progress of the following two reactions.

$$D_2 + 2* \underset{1}{\rightleftharpoons} 2D*$$

$$ROH + 2* \underset{2}{\rightleftharpoons} \left[\underset{H}{\overset{+}{RO}}*^- + * \right] \underset{3}{\rightleftharpoons} RO* + H*$$
$$\qquad\qquad\qquad A \qquad\qquad\qquad B$$

We have not specifically measured the rate of reaction 1, but we assume that it proceeds much more rapidly than reactions 2 + 3, or reaction 4 of Figure 1.

Although few data exist for palladium, exchange between deuterium and alcohols and between deuterium and water is relatively fast on group VIII metals. For example, Smith and Stewart[17] have reported that deuterium exchanges with methanol at 35° on Raney nickel without accompanying exchange of the methyl group. Swain and Kresge[18] report similar results for platinum and nickel.

Butanone exchanges with deuterium to give mainly butanone-d_1. From a comparison of runs G_{53} (Table I, footnote *e*) and G_{82} (Table II), we conclude that the

(13) O. W. Wheeler, "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, p 510.

(14) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, Chapter 15.

(15) C. T. H. Stoddart and C. Kemball, *J. Colloid Sci.*, **11**, 532 (1956).

(16) C. Kemball and C. T. H. Stoddart, *Proc. Roy. Soc., Ser. A*, **241**, 208 (1957).

(17) H. A. Smith and B. B. Stewart, *J. Amer. Chem. Soc.*, **82**, 3898 (1960).

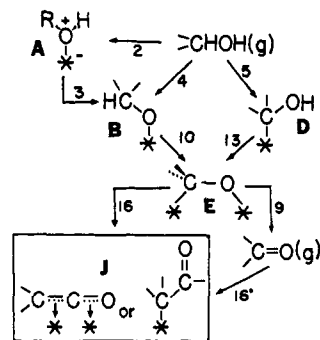(18) C. G. Swain and A. J. Kresge, *ibid.*, **80**, 5281 (1958).

Figure 1. Mechanism.

rate of exchange of butanone is about one-half that of 2-butanol under equivalent conditions.

In mixtures of 2-propanol, butanone, and deuterium, there is little competitive inhibition of the exchange of either alcohol or ketone. At lower conversions, exchanges into butanone and alcohol are about equal. 2-Propanol appears to increase the rate of exchange of butanone a little, but *tert*-butyl alcohol seems to decrease the rate a little. Presumably, then, alcohol and ketone are adsorbed with about equal strength on palladium.

Exchange between ROD and ketone, reaction I, is catalyzed by palladium/silica as well as by commercial silica (Table III). In exchange on commercial silica between ROD and ketone in hydrogen carrier, there is no loss of deuterium from the organic material, but, on palladium/silica, deuterium from ROD goes nearly equally to form butanone-d and HD (run H_{74} of Table III). The HD can be formed only at the palladium.

Skeletal exchange of 2-butanol proceeds at a rate about 0.01 that of exchange of the hydroxyl group (run G_{14} of Table I). The exchange is primarily a single-atom exchange, as is also that of isopropyl alcohol in mixture with butanone. In the succeeding paper,[19] we present strong evidence that this exchange on copper involves primarily formation of $CH_3CDO-HC_2H_5$, but we have no definite evidence as to the location of the exchanged deuterium using palladium/silica. However, the observation that ethanol exchanges about one-sixth as rapidly as 2-butanol, that 2-propanol exchanges much like 2-butanol, but that *tert*-butyl alcohol does not exchange at a detectable rate could be taken to indicate that $-CDOH-$ is the major initial product of skeletal exchange.

Exchange of 2-butanol and that of butanone are accompanied by very slow hydrogenation–dehydrogenation. From run G_{54} of Table I, dehydrogenation proceeds at a rate about 0.0001 that of formation of ROD. From run G_{83} of Table II, hydrogenation proceeds at a rate about 0.0005 that of formation of butanone-d. Dehydrogenation to ketone is so much slower than that of skeletal exchange of alcohol that the observed skeletal exchange of alcohol cannot originate *via* formation of gas-phase ketone followed by its rehydrogenation with deuterium.

The alcohol–ketone interchange reaction, reaction II, goes on palladium/silica at least as well as on commercial silica (Tables II and IV). When deuterium is the carrier gas, the interchange reaction proceeds about

(19) W. R. Patterson, J. A. Roth, and R. L. Burwell, Jr., *ibid.*, **93**, 839 (1971).

0.03 times as fast as isotopic exchange of butanone. Table VI reports data on a reaction in deuterium carrier at a conversion which is very low with respect to interchange but high with respect to exchange to ROD. The degree of exchange of butanone is about equal to that of the skeletal exchange of 2-butanol, but 2-propanol is much less exchanged. Since interchange on palladium/silica between $(CH_3)_2CDOH$ and CH_3-COC_2H_5 gives $(CH_3)(C_2H_5)CDOH$, the 2-butanol formed by interchange from $(CH_3)_2CHOH$ must involve the grouping –CHOD– (or –CHOH–) and the skeletal deuterium content in the 2-butanol must be located in the ethyl and methyl side chains. In all of our experiments, exchange into ethyl slightly preponderated. We conclude that the deuterium content of 2-butanol was mainly that already exchanged into butanone before its conversion to 2-butanol by the interchange reaction.

In this cluster of reactions, exchange between deuterium and alcohol alone and between deuterium and ketone alone occurs only at palladium. However, in mixtures of alcohol and ketone there will be some contribution to exchange by the following processes: exchange of alcohol (or of ketone) at palladium to form ROD (or ketone-d) followed by exchange between ROD and ketone (or between ROH and ketone-d) at impurity sites on silica. At lower conversions, contributions from these processes appear to be small. The interchange reaction itself can occur at impurity sites on the silica support. However, palladium does appear to have some catalytic activity, as judged by experiments with palladium made by evaporating to dryness a slurry of 60–80 mesh glass beads in a solution of palladium chloride. This was then reduced with hydrogen. Per unit mass of palladium, the activity for interchange, while finite, was much less than that of the palladium/silica catalyst. However, the data cannot be intercompared quantitatively because we do not know the metallic surface areas of the two catalysts.

Mechanism. Reactions in the system alcohol–ketone–hydrogen on group VIII metals have been discussed in terms of Figure 1 by several writers.[16,20,21]

Reactions 4, 5, and 13 have been assumed to proceed at substantial rates, but 10 has been assigned a negligible rate for reasons which are not entirely compelling.

On palladium, formation of ROD requires formation of RO* (B) and H*. With *tert*-butyl alcohol, no data require the formation of any other species which lead to chemical reaction. However, RHO+* (A) is attractive as a possible intermediate in the formation of B. The species A should represent rather weak chemisorptions, since alcohol as a base is *hard* and the surface of palladium is a *soft* acid.[22] Similarly, the adsorption of ketone to form E should represent a weaker chemisorption than that of olefin to diadsorbed alkane, and this would also be true if the adsorbed species had a π-complex-like structure. Ketone as a base is hard, olefin is soft. Further, one may note that coordination complexes of ketones with structures resembling π complexes are known only for perfluoro ketones.[19] The rapid exchange between deuterium and ketone on palladium requires J to be readily formed, but we have no evidence for the relative occupancy of the surface by E and J. Under the conditions of our experiments, [E + J] and [A + B] do not competitively inhibit one another.

On palladium, reactions [2 + 3] or 4 and reactions [9 + 16'] or 16 are fast. Reaction 5 is relatively slow for a group VIII metal, about 0.01 times as fast as reaction 4. Reactions [10 + 13] are unusually slow for a group VIII metal, 0.0001 times as fast as reaction 4. It is clear that it is the slowness of 5 and particularly of [10 + 13] which result in the inefficiency of palladium as a catalyst for the hydrogenation of ketones. Palladium appears to be efficient for the reversible dissociative adsorption of RH, where H is somewhat acidic (formation of B and J), but ineffective where H is somewhat hydride-like (formation from alcohol of D or E). No explanation for this is immediately apparent.

(20) D. E. Mears and M. Boudart, *AIChE. J.*, **12**, 313 (1966).

(21) G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962, Chapter 14.

(22) For the application of Pearson's classification of soft and hard acids and bases and for references, see ref 19.