Isotopic Exchange Reactions Involving Alcohols, Ketones, and Deuterium on Copper Catalyst

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Abstract: At 135°, addition of acetone, 2-butanol, or *tert*-butyl alcohol at 0.1 atm to a mixture of hydrogen and deuterium at 1 atm reduces the rate of formation of HD on copper containing 1% nickel to one-fifth of its initial value. Removal of the organic compound rapidly restores the initial rate. Desorption of HD is fast enough to keep the ratio $*D/*H$ large during exchange between deuterium and 2-butanol under similar conditions. Relative rates are 1.00 for exchange at carbon 2, 0.2 for exchange at hydroxyl, about 0.05 for exchange at carbons 1 and 3, and 0.4 for dehydrogenation. Ethanol behaves similarly in exchange, but *tert*-butyl alcohol exchanges more rapidly although only at OH. We suggest that the slow step in dehydrogenation of 2-butanol at low conversions is the cleavage of the O–H bond either in $RHO*$ or $*\underset{\text{H}}{\text{C}}\text{–O}*$ and that optically active 2-butanol is racemized by roll-over of the second surface species. Butanone deactivates the catalyst much more rapidly than the other compounds. Initially, 2-butanone plus deuterium gives –CDOH– in which the OH is only 20% D labeled. Total deuterium in CH_3 and C_2H_5 of butanone and the 2-butanol about equals that in –CDOH–. This suggests that 2ketone(adsorbed) = $*\underset{\text{H}}{\text{C}}\text{–O}*$ + enolate(adsorbed). Adsorbed enolate is also involved in isotopic exchange of ketone.

A number of papers have dealt with the mechanism of the heterogeneous catalytic reactions which occur among secondary alcohols, ketones, and hydrogen or deuterium.[1–5] Most of these studies have involved group VIII metals. Copper has received little attention despite its importance in the hydrogenation of ketones, an importance which results mainly from its low rate of hydrogenolysis of the carbon–oxygen bond. For this reasons we have been interested in copper;[6] but copper also has a special interest because, in bulk metal, its d band is filled, and the catalytic consequences of this have been the subject of continuing controversy.

Since there have been many more mechanistic studies related to the hydrogenation of alkenes than to that of ketones, some comparisons of the latter reaction with the former may be helpful. Table I gives values of ΔH and $\Delta G°$ for the hydrogenations of acetone and its analog, isobutylene.

Table I

Reaction	ΔH, kcal	Temp, °C, for $\Delta G° = 0$
$(CH_3)_2C{=}O + H_2$	−14	200
$(CH_3)_2C{=}CH_2 + H_2$	−28	700

As may be seen, the equilibrium constant for hydrogenation of isobutylene becomes unity at about 700°. It is not surprising that, at 100°, alkene is very much more strongly adsorbed than alkane. However, at 100–150°, the equilibrium constant for the hydrogenation of acetone is not greatly larger than unity, and we may suspect that ketone and alcohol will be adsorbed about equally strongly. Further, at 100–150°, the hydrogenation of isobutylene is essentially irreversible; practically, we cannot observe the dehydrogenation of alkane. On the contrary, both the hydrogenation of ketones and the dehydrogenation of alcohols can be measured. This feature permits the use of mechanistic probes not possible in the hydrogenation of olefins, but it may also increase the complexity of the actual mechanism.

Our previous study[6] of interactions in mixtures of deuterium, alcohols, and ketones gave data which were principly of a stereochemical and of an isotopic tracer nature. In its interpretation we explicitly assumed, in analogy with work on other metals,[2a] that exchange of the hydrogen atom of a hydroxyl group would be fast compared with other reactions. However, in further work, this assumption always seemed to cause difficulty in mechanistic interpretations. Accordingly, we have experimentally investigated this assumption for copper catalysts. It is incorrect. We have also run a number of isotopic tracer reactions of other types. We now present a new interpretation to supplant the previous one.[6]

Experimental Section

Procedure generally followed those in the previous paper[7] except in the studies involving the reaction

$$H_2 + D_2 = 2HD \qquad (I)$$

Here, hydrogen and deuterium were passed separately through heated 75% palladium–25% silver alloy, mixed, and then passed through a saturator packed with a porous siliceous material, Filtros FS-140-L (Filtros Inc., East Rochester, N. Y.). In changing liquids in the saturator, it is much easier completely to pump off alcohols or ketones from Filtros than from the Chromosorb G used previously.[7]

Copper oxide containing 1% nickel oxide was prepared[6] from the coprecipitated carbonates. The oxide, 40–60 mesh, was mixed with about ten times its weight of glass beads of the same size and reduced overnight in flowing hydrogen at about 220° (100 mesh and

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

[2] (a) C. Kemball and C. T. H. Stoddart, *Proc. Roy. Soc., Ser. A*, **241**, 208 (1957); (b) *ibid.*, *A*, **246**, 521 (1958).

[3] D. Cornet and F. G. Gault, *J. Catal.*, **7**, 140 (1967).

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

[5] G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962, Chapter 14. This surveys this area.

[6] J. Newham and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **86**, 1179 (1964).

[7] W. R. Patterson and R. L. Burwell, Jr., *ibid.*, **93**, 833 (1971).

Table II. Effect of Alcohol or Ketone upon Isotopic Exchange between Hydrogen and Deuterium

	tert-Butyl alcohol	2-Butanol	Acetone	Butanone[g]	Butanone[h]	Mixture[j]
Temp, °C	134	136	136	136	137	135
D_2 flow[a]	860	1175	450	930	530	500
H_2 flow[a]	960	1030	425	1030	480	475
P, alcohol or ketone, Torr	76	80	65	75	75	71
% HD, A[b]	32.1	37.7	34.4[e]	29.8	35.5	42.0
C_1	7.0	12.3		1.3	8.4	27.0[k]
C_2	7.0	12.6	10.4	0.5	4.7	16.3[l]
C_3	7.2	13.7[d]	11.3[f]	0.6	3.7[i]	9.2[m]
D_1	25.1	31.1	22.2	0.5	2.2	15.1
D_2	34.1	29.0		0.6	7.7	15.1
Activity[c]	0.15	0.21	0.20			

[a] Flow rates of hydrogen and deuterium in millimoles per gram of copper oxide per hour. Total pressure, 750 mm. [b] A is the initial % HD formed. C_1 is % HD in presence of alcohol or ketone. C_2 is the same, 15 min later; C_3, after 15 min more. D_1 is % HD after all alcohol or ketone has evaporated from the saturator; D_2, 15 min later. [c] The ratio of average activity for the exchange reaction in the presence of alcohol or ketone to that in its absence. [d] 3.4% of the alcohol had dehydrogenated to ketone. [e] A_2 was 35.9. [f] C_4 and C_5 were 11.2 and 10.6. 2.1 and 2.2% of the acetone had hydrogenated in C_2 and C_3. [g] The butanone had not been chromatographed. [h] The butanone had been chromatographed. [i] C_4 and C_5 were 3.5 and 2.9. 0.61% of the ketone had been hydrogenated in C_5. [j] Butanone, purified by preparative gas chromatography (65 mol %), and 2-propanol (35 mol %). [k] 31.8% of the 2-propanol converted to acetone; 28.5% of the butanone converted to 2-butanol. [l] 15.8 and 18.3%. [m] 6.8 and 8.9%.

250° in studies of reaction I). At the beginning of each series of runs, the system was evacuated for 2 hr and the catalyst was again subjected to a flow of hydrogen at 220° (or 250°) overnight. In a number of series of runs, particularly with alcohols, constant activity was maintained for many days by this reduction-activation procedure. In others, particularly those employing butanone, activity fell steadily.

Of course, we have no way of knowing whether the copper oxide was completely reduced. The constancy in activity described above suggests but does not prove that the copper surface was completely reduced by our reduction procedure. The use of 1% nickel follows previous work in which we found this necessary to get reproducible activity. Perhaps the nickel reduces the rate of sintering. The use of the nickel introduces some uncertainty but, in our experience, the experiments to be described would be difficult to run without its use. We do not believe that this small amount of nickel substantially affects the activity of copper quantitatively or qualitatively, but we have no formal proof of this.

Results

The Hydrogen–Deuterium Exchange Reaction. To assess the relative degrees of adsorption of hydrogen *vs.* ketone and of hydrogen *vs.* alcohol, the effect of the organic compound upon the hydrogen–deuterium exchange reaction was investigated (Table II). Nearly equal flows of hydrogen and deuterium were passed over the catalyst at about 136°. Space velocities were adjusted so that about 35% HD was made under conditions in which the equilibrium concentration would be 48% if the equilibrium constant for reaction I is 3.5. Analysis was by gas chromatography.[8] The system gave reasonably constant conversions for over 1 hr. During this period the saturator for volatilization of liquid was cooled in liquid nitrogen. The saturator was then rapidly warmed to the desired temperature and conversions were determined over a 30–60-min period. They were lower and constant. After the alcohol of ketone had all evaporated, the conversion was determined again. The catalyst was evacuated at 250° for 1 hr and reduced in hydrogen for 1 hr at 250°, and the reactivity was redetermined. Butanone behaved differently from the other compounds. The activity after the introduction of butanone was much less; it fell progressively, and the recovery after butanone was eliminated was much smaller. This phenomenon was less extreme when the butanone was purified by preparative gas chromatography, but it persisted even when the chromatographed butanone had been distilled in flowing hydrogen through 20 g of copper prepared by reduction of oxide and held at 100°. A few experiments were run with 2-propanol. They resembled those with 2-butanol.

The numbers labeled "activity" in Table II are R/R_0, where R and R_0 are computed after and before the addition of alcohol or ketone, from[9]

$$R = \left(\frac{2L_0}{1 + [(4 - K)/K]\alpha_{eq}}\right) \times \log\left\{\frac{1 + \alpha/[\alpha_{eq} + 2K/(4 - K)]}{1 - \alpha/\alpha_{eq}}\right\}$$

where L_0 is the flow rate, K is the equilibrium constant in reaction I, and α is the fraction HD in total hydrogen plus deuterium. This computation ignores the change in R attendant upon the decrease in the partial pressures of hydrogen and deuterium which results from introducing the vapor of alcohol or ketone. If the reaction is zero order in total pressure of hydrogen and deuterium, the activities are correct. If the reaction is first order, the activities should be increased by about 10%. Such a change would be within the reproducibilities of these experiments.

The relative rate of the hydrogenation or dehydrogenation which accompanies the hydrogen–deuterium exchange reaction was determined roughly in a few experiments. Thus, with acetone, (% hydrogenation)/(% HD) was about 0.2. The same value was found with butanone. With 2-butanol, (% dehydrogenation)/(% HD) was 0.2 and with 2-propanol, 0.1.

As shown in Table II, the effect of feeding a mixture of butanone (65 mol %) and 2-propanol (35 mol %) was determined. Catalyst deactivation was observed as with butanone, but it seemed to be somewhat less extensive. Deactivation was much less extreme when chromatographed butanone was employed. The hydrogen–deuterium exchange reaction was accompanied

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(8) G. F. Shipman, *Anal. Chem.*, 34, 877 (1962).

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 187–193.

Table III. Interaction of Deuterium with Ethanol and *tert*-Butyl Alcohol

	tert-BuOH		Ethanol		
Run no.	L_{57}	H_{31}	H_{35}	H_{34}	H_{36}
Temp, °C	132	125.5	124	124	153
D_2 flow[a]	4630	109	333	87	87
P_{alc}, mm	46	71	69	69	69
OD, %	Negligible[c]	74	Negligible[c]	10	16
D_0, %[b]	100	100	*d*	90.6	60.3
D_1, %	0.0	0.0	*d*	5.9	21.7
D_2, %	0.0	0.0	*d*	3.4	17.9
D_3, %	0.0	0.0	*d*	0.2	0.2
Aldehyde, %			*d*	0.3	1.0

[a] Flow rate of deuterium as in Table II. [b] From mass spectroscopy after converting all OD to OH. [c] Less than 2–3%. [d] Not determined.

Table IV. Interaction between Deuterium and 2-Butanol

Run no.	L_{55}		E_{25}	H_{13}			
Temp, °C	132		151	124			
D_2 flow	4800		206	95			
P_{alc}, mm	62		73	60			
OD, %	Negligible		6	22			
D_0, %[f]	96.7[a]	96.2[b]	74.1[b]	8.1[a]	10.0[b]	84.1[d]	91.9[e]
D_1, %	3.3	3.8	24.6	85.6	88.1	14.1	7.4
D_2, %	0.0	0.0	1.1	5.9	1.6	1.6	0.7
D_3, %	0.0	0.0	0.7	0.5	0.3	0.3	0.03
Ketone, %	1.7		12.1	8.4			
Ketone,[c] %, at "equil"	8.4		15.9	5.9			

[a] Analyzed from the CH_3CHOH^+ fragment. [b] Analyzed from $C_2H_5CHOH^+$. [c] Computed for presence of hydrogen rather than deuterium. [d] 2-Butanone isolated by gas chromatography from reaction mixture. [e] Computed for butanone made by mere dehydrogenation of 2-butanol in the sample. In the butanone, we assume $CH_3CO–$ to be $D_0 = (8.1 + 85.6)$, $D_1 = 5.9$, $D_2 = 0.5$; and $C_2H_5CO–$ to be $D_0 = (10.0 + 88.1)$, $D_1 = 1.6$, $D_2 = 0.3$. Butanone-D_0 is then $0.01(8.1 + 85.6)(10.0 + 88.1)$, -$D_1$ is $(0.01)(8.1 + 85.6)(1.6) + 0.01(10.0 + 88.1)(5.9)$, etc. [f] From mass spectroscopy after converting all OD to OH.

by the formation of acetone and 2-butanol. The ratio, (% butanone converted to 2-butanol)/(% HD), was about 0.7. However, our data were subject to considerable scatter, at least in part, because the catalyst was undergoing deactivation and the gas sample analyzed for hydrogen deuteride did not exactly match in time the sample analyzed for alcohols and ketones. The sample for HD was removed with a gas syringe at one moment; the sample for alcohols and ketones represented a 15-min accumulation. Experiments with butanone were subject to the same difficulty.

The reactions of the mixture in the presence of hydrogen were examined in a series of runs at 136° with reactivation following each run and with analysis of only the first sample. The catalyst was derived from a copper oxide prepared by Newham.[6] The activity fell by a factor of about 10 during the first 7 runs and then remained reasonably constant for 18 runs. During this latter period, flow rates were varied from 60 to 284 mmol of hydrogen per gram of copper oxide per hour. The ratio, (mol of acetone formed)/(mol of 2-butanol formed), was 0.36 ± 0.05 up to a conversion of about 21% of the 2-propanol to acetone when it began to decrease. At 136°, only 10% of the 2-propanol would be dehydrogenated at equilibrium in the reaction

$$\text{2-propanol} = \text{acetone} + H_2$$

Since conversions of 2-propanol to acetone considerably exceeded this in a number of experiments, the alcohol–ketone interchange reaction

$$\text{2-propanol} + \text{butanone} = \text{acetone} + \text{2-butanol}$$

must accompany hydrogenation of butanone and dehydrogenation of 2-propanol. However, in our previous work on the same catalyst,[6] we found a ratio, acetone/2-butanol, about twice as large as in the current measurements. We do not understand the origin of the discrepancy.

Reactions between Deuterium and Alcohols. Tables III–V present some results of passage of mixtures of deuterium and several alcohols over copper catalysts. The weights of initial copper oxide were: H series, 0.426 g; E series, 0.392 g; and L_5 series, 0.054 g. Catalysts were regenerated after each experiment. Three processes were observed: isotopic exchange of the OH group, skeletal exchange, and dehydrogenation. The sensitivity for exchange of the OH group was only 2–3 percentage units. Conditions which permitted measurement of the OH exchange of ethanol and 2-butanol gave extensive conversions for the other two processes. *tert*-Butyl alcohol exhibited only OH exchange.

Before analysis of 2-butanol by mass spectroscopy, the H in the OH group was converted to protium.[7] D_0 (% d_0) was always nearly the same in the fragment ions CH_3CHOH^+ and $C_2H_5CHOH^+$. Either –CDOH– was always present in molecules of 2-butanol which had undergone any exchange, or the fraction of CH_3 and C_2H_5 groups exchanged was always identical in those molecules containing –CHOH–. If we reject the latter as too improbable, then d_1 is always $CH_3CDOHC_2H_5$ and d_2, d_3, ... result from exchange of CH_3 and C_2H_5.

From Table IV, the great majority of exchanged 2-butanol is $CH_3CDOHC_2H_5$. In runs at lower conversions of series L and H, about 4.5% of the molecules which exchanged to –CDOH– were also exchanged in

Table V. Interaction between Deuterium and 2-Butanol at Very Extensive Conversion.[a] Run H_{17}

	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8
CH_3CHOH^+ [b]	1.0	2.3	13.2	34.2	49.4				
$C_2H_5CHOH^+$ [b]	0.0	8.2	33.2	51.2	4.9	1.6	0.8		
$C_2H_5COCH_3$ calcd	0.3	2.2	8.9	22.3	34.6	27.2	3.1	1.1	0.4
$C_2H_5COCH_3$ obsd	1.7	6.4	9.6	18.9	32.2	27.9	1.9	1.0	0.3

[a] 151°, 14 mmol of deuterium per gram of catalyst per hour, P_{alc} = 60 mm. The first two rows give the analysis of 2-butanol derived for the CH_3CHOH^+ and $C_2H_5CHOH^+$ fragments. The third row gives the analysis assuming this alcohol to be dehydrogenated without isotopic exchange. The last row is observed butanone. [b] From mass spectroscopy after converting all OD to OH.

Table VI. Reaction between Deuterium and Butanone at 160°

Run no.	D_2 flow[a]	OD, %[b]	Alcohol, %	MEK-D_0	Alcohol-D_1[c]
H_{51}	104	13	23.5	*d*	*d*
H_{52}	207	*d*	2.3	98.0	97
H_{53}	62	27	4.3	96.1	96[e]
H_{54}	21	26	13.0	89.0	90

[a] Flow rate of deuterium in millimoles per gram of copper oxide per hour. P_{ket} = 120 mm. [b] Per cent of alcohol formed which is OD. [c] After exchange of OD to OH. [d] Not determined. [e] The CH_3CHOH^+ ion was not analyzed. This number was computed assuming that the relative degrees of exchange of CH_3CHOH^+ and $C_2H_5CHOH^+$ were the same in all cases.

Table VII. Reaction between Deuterium and Butanone at 160°

Run		D_0, %	D_1, %	D_2, %	D_3, %	D_4, %	D_5, %
H_{52}	EtCHOH$^+$ [a]	0.7	98.4	0.9	0.0		
	MeCHOH$^+$ [a]	0.3	97.8	1.6	0.3	0.0	
	Ketone, calcd[b]	97.2	2.5	0.3	0.0		
	Ketone, obsd	98.0	1.6	0.4	0.0		
H_{54}	EtCHOH$^+$ [a]	1.0	95.6	2.9	0.5	0.0	
	MeCHOH$^+$ [a]	0.4	92.9	6.3	0.4	0.05	
	Ketone, calcd[b]	90.1	8.8	1.0	0.1	0.0	
	Ketone, obsd	89.0	10.0	0.9	0.2	0.0	
L_{111}[c]	EtCHOH$^+$ [a]	5.1	72.5	18.0	2.7	1.1	0.5
	MeCHOH$^+$ [a]	6.1	57.8	29.9	5.7	0.5	
	Ketone, calcd[b]	49.6	34.7	11.6	2.9	0.9	0.2
	Ketone, obsd	52.1	33.3	11.1	2.6	0.7	0.2

[a] After exchange of OD to OH. [b] Computed from butanol by assuming simple dehydrogenation. [c] At 165°, 136 mmol of deuterium per gram of copper oxide per hour, P_{ket} = 128 mm, 47.8% hydrogenation, 12.2% OD. The catalyst was 0.352 g of freshly reduced CuO.

CH_3 and C_2H_5 (about 3.0 and 1.5%, respectively). In these experiments, a number of which are not presented here, the ratio, (exchanged CH_3)/(exchanged C_2H_5), lay between 1.7 and 2.5. In our earlier work,[6] the fraction of exchanged molecules which were also exchanged in CH_3 or C_2H_5 was about 3%, and there was also some variation in this ratio from run to run.

In a number of runs, we separated the butanone formed during reaction and determined its isotopic distribution. Assuming that all 2-butanol which has undergone any reaction has exchanged at carbon atom 2, one may compute the isotopic distribution of the butanone which would be formed from the butanol by mere dehydrogenation, as shown in footnote *e* of Table IV. Table V shows a similar calculation for run H_{17}. These runs are at conversions which are too high to reveal initial behavior, but at low conversions, the small yields at d_2^+ in the butanol make the comparisons not very accurate. However, it is clear that the observed and computed distributions are of the same type and not far apart quantitatively. From runs at low conversions not shown in the tables and from previous work[6] the observed degree of side-chain exchange in alcohol seems usually to exceed that in ketone by a factor of about 1.5. As D_0 in the alcohol becomes small, the ratio declines. The distribution of side-chain exchange in alcohols is subject to substantial errors by the nature of its determination.

From similar runs in hydrogen which preceded run L_{55} of Table IV, the rate of dehydrogenation in the presence of hydrogen was between 80 and 100% of that in the presence of deuterium; that is, they are the same to within our limit of reproducibility.

The ratio of rates of formation of >CO/DCOH = 0.4 in runs at 132° (Table IV). The same value was measured previously[6] at 153°. Accuracy is low since the fraction of dehydrogenation at equilibrium is small and even a few per cent ketone represents a substantial degree of approach to equilibrium.

Butanone + Deuterium. Two series of runs, H_5 and L_1, involved passage of butanone and deuterium over a copper catalyst. The runs were continuous and without intermediate regenerations. Because of the deactivation which always accompanied the use of butanone, rather high temperatures were used, 160 and 165°. Considerable deactivation was observed in the first two or three runs following which deactivation was slow. Data for the H_5 series are given in Table VI.

Table VII presents the results of mass spectrographic analysis of the butanol and butanone in the product after separation by gas chromatography. In all cases, the isotopic distributions closely resembled those found in reaction between alcohol and deuterium including the relative degrees of exchange of methyl and ethyl side chains in the 2-butanol. Further, the isotopic distribution of the ketone and that computed from the alcohol assuming simple dehydrogenation were nearly the same. Other results in the H_5 and the L_1 series correlate well with the examples presented here. The initial ratio of the rate of the formation of ketone which had suffered exchange to that of hydrogenation was near 0.9.

2-Propanol-*O*-d_1 + Butanone + Hydrogen. Four runs were carried out in which the azeotrope of 2-propanol (70.7 or 63.8% deuterated at the hydroxyl) and butanone was carried over copper catalyst at 126 and 147° in hydrogen carrier. The partial pressure of alcohol plus ketone was 112 mm. Under the conditions chosen, the per cent loss of deuterium from the hydroxyl ranged from 15 to 47, and at lower conversions, it was about ten times the per cent of ketone converted to 2-butanol. Acetone was also formed, about 0.4 as much as 2-butanol in absolute amount. The deuterium lost went entirely to gas-phase HD, since no skeletal deuterium could be detected in butanone or 2-butanol. Presumably, deuterium was equilibrated between the hydroxyl groups of 2-propanol and 2-butanol, but this could not be examined.

Discussion

The Effect of Alcohols and Ketones upon the Hydrogen–Deuterium Exchange Reaction. At 135°, the hydrogen–deuterium exchange reaction is fast on the copper catalyst of this research. The addition of 2-propanol, 2-butanol, *tert*-butyl alcohol, or acetone to a pressure of about 0.1 atm depresses the exchange rate to about one-fifth of its initial value (Table II). 2-Butanone gives about the same rate depression initially, but the activity continues to fall. Removal of the organic compounds from the vapor phase causes the exchange reaction rapidly to return about to its original rate. With 2-butanone, however, the recovery is only partial.

In our mixtures of hydrogen, deuterium, and 2-butanol, the *rate* of formation of HD is about 50 times that of the *rate* of dehydrogenation. Since initially, $D_2/H_2 \simeq 1$, $H_2 + 2HD + D_2$ desorbs. Thus, the rates of adsorption and desorption of deuterium (hydrogen) are about 100 times the rate of dehydrogenation.

Results with *tert*-butyl alcohol establish that inhibition of the exchange reaction by alcohols does not depend upon availability of an α-hydrogen atom nor formation thence of $RR'(OH)* + H*$. However, the several-fold greater exchange rate of the hydroxyl hydrogen atoms of *tert*-butyl alcohol *vs.* those of ethanol and 2-butanol (Tables III and IV) does suggest that ethanol and 2-butanol occupy the surface partly in forms other than $RHO*$ and $RO*$, the only species which appear to be formed from *tert*-butyl alcohol.

Exchange between Deuterium and Alcohols. Figure 1 summarizes the rates of the reactions which occur when deuterium and 2-butanol are passed over copper: the rates of exchange of the five types of hydrogen atoms, the rate of dehydrogenation to butanone, and the rate of racemization[6] when optically active 2-butanol is used. All rates are relative to the fastest rate of exchange, that of the α-H atom. $D*/H*$ is always large because of the large rate of desorption of D_2 (or HD). This large value is in accord with the identity between rate of racemization and rate of exchange of α-H.

That the rate of exchange of RO–H is only one-fifth that of α-H is unusual. The rate ratio on palladium is 100 rather than one-fifth.[7] The ratio is also large on platinum and nickel.[10]

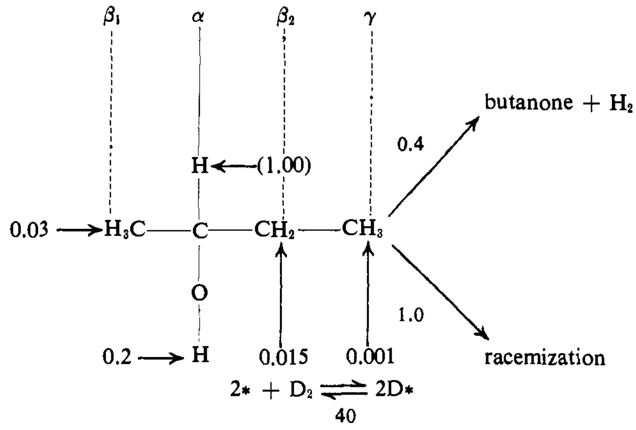
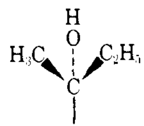


Figure 1. Rates of various processes in reaction between 2-butanol and deuterium at 125–150°, $P = 1$ atm, $P_{D_2}/P_{alc} \simeq 10$. The numbers with arrows leading to hydrogen atoms show the relative rates of exchange of the five types of hydrogen atoms. The rate of exchange of the hydrogen atom at carbon 2 is taken as unity. The value for exchange of the γ-hydrogen atoms is an approximate one derived from runs like H_{17} (Table V) with the assumption that D_4, D_5, and D_6 in $C_2H_5CHOH^+$ correspond to exchange of γ-hydrogen atoms. The sharp break which follows D_3 accords with this assumption.

Exchange between ethanol and deuterium is similar. However, there are two α-H's in ethanol and both can exchange in one period of adsorption, as may be seen from run H_{34}, Table III. The β-H atoms exchange distinctly more slowly than the β_1-H atoms of 2-butanol. From the data of Pitzer and Weltner,[11] one estimates that dehydrogenation would proceed only to the extent of a few tenths of a per cent at equilibrium under our conditions. Measurement of the ratio of dehydrogenation to exchange would be difficult.

We shall consider that exchange at α-H identifies those molecules of 2-butanol which have reacted. On this basis, at lower conversions,[6] the degree of exchange of β-H in the 2-butanol which has reacted is about 1.5 times that of skeletal exchange in the butanone formed by dehydrogenation. The figure is of low precision.

Mechanism. Let us consider these results in terms of Figure 2. We have entered no process which requires two bonds to be broken in one elementary step, for example, A → E, and we have omitted some like $ROH(g) \rightleftharpoons B + H*$, which are equivalent to others in Figure 2, here, reactions 2 + 3. We also omit 2-monoadsorbed 2-butanol (D), which, if present, is assumed to be in equilibrium with C. In any case, species D is not likely to be formed directly from ROH(g) because of the observation that both α-H atoms in ethanol can exchange in one period of adsorption.



D

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[10] Some discussion of this with references to previous literature appears in ref 7.

[11] K. S. Pitzer and W. Weltner, Jr., *J. Amer. Chem. Soc.*, **71**, 2842 (1949).

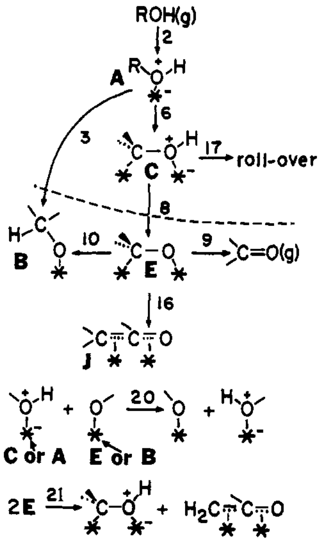


Figure 2. Mechanism.

To accommodate the model of Figure 2 to the data of Figure 1, one must assume that the slow steps in forming ketone from alcohol are reactions 8 and 3. Thus, species A, C, and D are adsorbed alcohol, B, E, and J are adsorbed ketone, and the slow step in forming ketone is the cleavage of the O–H bond. However, the reactions on copper under our conditions are near a region in which one cannot properly speak of a rate-limiting step; *i.e.*, reaction −6 is not much faster than 8 + 3.

The mechanistic conclusions with regard to the dehydrogenation of alcohols on *group VII metals* of Kemball and Stoddart,[2] Mears and Boudart,[4] and Cornet and Gault[3] are different. The proposed mechanism is essentially[4]

$$\text{ROH(ads)} = \text{D} + \text{H}* \qquad (5)$$

$$\text{D} + 2* = \text{E} + \text{H}* \qquad (12)$$

$$\text{E} = \text{ketone(g)} + 2* \qquad (9)$$

$$2\text{H}* = \text{H}_2\text{(g)} + 2* \qquad (-1)$$

ROH(ads) in reaction 5 is assumed to be physically adsorbed.[4] The slow step is the cleavage of the α-C–H bond in reaction 5 and D is "adsorbed ketone" rather than "adsorbed alcohol."

In Figure 2, ROH is adsorbed initially as A, $\text{RHO}^+\text{–}*^-$, which should be a rather weakly adsorbed species. In the classification of Pearson,[12] the surface of copper is a soft acid, whereas ROH is hard. Experimentally, the effect of alcohols, and particularly of *tert*-butyl alcohol, upon the rate of the hydrogen–deuterium exchange reaction indicates that the adsorption of alcohols is rather weak. It might be difficult to distinguish between A and the strong physical adsorption of Mears and Boudart[4] in reaction 5.

Which bond in A should break more easily, O–H or α-C–H? It is by no means to be expected that the former bond will always cleave more easily. The bond dissociation energies, 102 and 90 kcal/mol,[13] favor cleavage of α-C–H, but one must also consider the energetics of binding RR′HCO– and RR′(OH)C– to the surface.

Copper as a soft acid would bond better to the soft base H^- than to H^+. Thus, a surface hydride on copper probably has some contribution from $*^+\text{H}^-$, and we shall refer to this hydrogen atom as *hydride-like*. The hydrogen atom in α-C–H is also hydride-like, as may be seen in the Meerwein–Ponndorf reaction.[14] On the other hand, the hydrogen atoms adjacent to the carbonyl and the hydrogen atom of ROH are "proton-like" in the sense that they have some, if weak, acidic character. The β-hydrogen atoms of 2-butanol may be classified among the proton-like hydrogen atoms because they may acquire this character *via* conversion of the alcohol to ketone. Thus, in

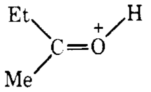
$$2* + \text{H}_2 \rightleftharpoons 2*\text{H}$$

$$\text{CH}_3\text{—}\mathit{CH}_2\text{—}\overset{\text{H}}{\underset{\underset{\mathit{H}}{\text{O}}}{\text{C}}}\text{—}\mathit{CH}_3 \qquad \text{CH}_3\text{—}\mathit{CH}_2\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\mathit{CH}_3$$

H is hydride-like and *H* is proton-like. These groups might be expected to exchange preferentially among themselves.

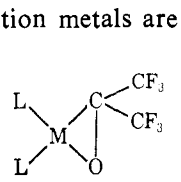
Reaction 3 is required by the formation of ROD from *tert*-butyl alcohol and some reaction like 6 is required by formation of D–COH from 2-butanol. Species B cannot be a required intermediate in the exchange of α-CH since formation of α-CD is five times faster than that of ROD with 2-butanol.

The identity in rates of formation of α-CD and of racemization when (+)2-butanol is employed requires some other reaction. An equivalent problem appears in exchange between deuterium and alkanes[15] and roll-over of 1,2-diadsorbed alkanes has been suggested to be the reaction providing racemization. We suggest that racemization is provided by a similar roll-over reaction of species C, reaction 17. This reaction must be fast relative to reaction 6. The transition state (or, perhaps, intermediate) in roll-over of C can be considered to be



so bonded that its plane is perpendicular to the surface.[15] Butanone(g) would be an extreme form of a roll-over intermediate but it is formed much too slowly (Figure 1) to function as such in the present work.

We have shown C as a diadsorbed species but it might be supposed a π complex. Few molecular analogies exist, and it is clear that complexes of ketones and atoms of transition metals are weak. Complexes represented as



have been reported with M = Ni(0) and Pt(0).[16,17]

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(12) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 23, 113; R. G. Pearson, *Science*, **151**, 172 (1966).

(13) R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3480 (1966).

(14) O. W. Wheeler, "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, p 532.

(15) R. L. Burwell, Jr., *Accounts Chem. Res.*, **2**, 289 (1969).

(16) J. Browning, D. J. Cook, C. S. Cundy, M. Green, and F. G. A. Stone, *Chem. Commun.*, 929 (1968).

(17) M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *ibid.*, 502 (1966).

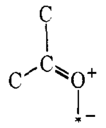
CF_3 *vs.* CH_3 would stabilize π complexes with atoms of transition metals.

Side-chain exchange is provided as usual by the enolic form, J, formed by reaction 16. The binding is shown as analogous to a π-allyl complex but it might be a σ complex, for example, 1-monoadsorbed butanone.

Reaction 20 is a proton-transfer reaction in the adsorbed layer. Interconverting A and B and also C and E provides that the degree of exchange in the side chains is approximately the same in desorbed alcohol and in desorbed ketone. It also provides for the alcohol–ketone interchange reaction

$$\text{butanone} + \text{2-propanol} = \text{2-butanol} + \text{acetone}$$

When interchange is run in the presence of deuterium, butanone as E reacts to C which must react with *D to generate 2-butanol. Thus, all butanol formed should have α-D, as is observed.[6] This mechanism is much simpler than the one which we proposed (and now abandon) when we erroneously thought that *D/*H was small rather than large. Our former mechanism involved



F

We do not now think F an important reaction intermediate, although some ketone should certainly adsorb as F even if weakly (ketone is a hard base, the surface is a weak acid).

Deuterium Plus Butanone. Butanone leads to deactivation of the copper catalyst much more rapidly than alcohols or acetone (see Table VI). Kawamoto[18] reported that 2-propanol passed over copper catalysts prepared from material precipitated by sodium or potassium hydroxides gave considerable isobutyl methyl ketone as well as acetone. Precipitation by potassium carbonate gave a little condensation, sodium or potassium bicarbonate, none. Since our precipitant was ammonium bicarbonate, condensation should not have been favored. However, even a very small amount of condensation might lead to substantial deactivation. Somewhat similar deactivation was reported by Cornet and Gault on platinum and nickel catalysts.[3] Whatever its origin, the deactivation required experiments with butanone to be at temperatures about 30° higher than those of our other experiments.

Results of reaction between deuterium and butanone are given in Tables VI and VII and Figure 3. The H series of runs gave a ratio of side-chain exchange to hydrogenation about twice that for the L series. The origin of such variation is unknown. It might be thought to result from traces of impurities, perhaps base. However, the demonstrated capacity of evaporated metal films of group VIII metals to give ketone exchange[2] suggests that pure copper should have at least some capacity for ketone exchange. We cannot rigorously eliminate the possibility that varying distributions of the 1% nickel in our catalysts plays some role in these variations. However, if one may intercompare results with butanone and with 2-methylpentanone, pure nickel gives results substantially different from those on our catalysts: nickel gives a much larger ratio of exchange to hydrogenation, much readier exchange of the γ positions (nomenclature of Figure 1), and an alcohol in which all hydroxyl is OD.[3]

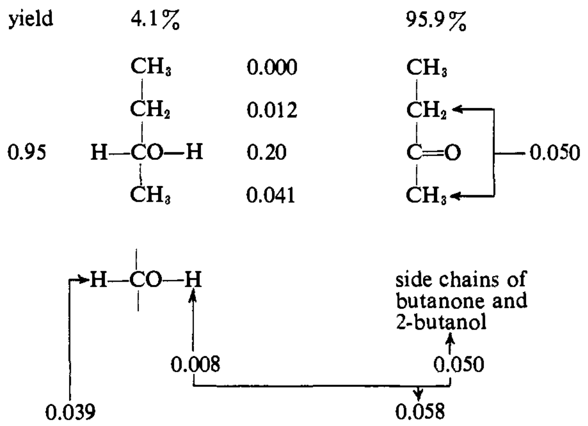


Figure 3. Results of reaction between deuterium and butanone at 165°, run L_{113}, second run after L_{111} of Table VI, at a flow rate 2.3 times larger. The upper portion gives the average number of deuterium atoms per molecule of each product. The lower portion gives summed amounts of deuterium *atoms* in moles per mole of initial butanone. In the hydride-like position, there is 0.039 mol of D and in the acid-like positions, 0.058.

Figure 3 summarizes a run at low conversion. The most striking item is the low % D in the hydroxyl group. We make 2-butanol by adding deuterium to butanone yet the product alcohol is largely CH_3CD-OHC_2H_5. However, there must be at least 2 mol of deuterium atoms in the product per mole of ketone hydrogenated. One of these moles of D appears as α-CD. The missing deuterium is in the side chains of alcohol and ketone, largely the latter since, although the side chains of alcohol and ketone are about equally exchanged, there is much more ketone. At 4.1% hydrogenation, 0.039 mol of D is in α-CD and 0.058 in the acid-like positions. Since the ratio, (0.039 + 0.058)/0.041, somewhat exceeds 2.0, some net isotopic exchange with deuterium occurred.

If D–CO–H is the major product, D* must react with >C=O to give α-CD but either (a) D* does not give deuterium addition to the oxygen atom or (b) D* does react to give OD but this rapidly exchanges with the side chains. The following experiment eliminates (b) as a possibility. Hydrogen, butanone, and 2-propanol-*O-d* were passed over the copper catalyst at several flow rates. Loss of deuterium from OD ranged from 15 to 47%, but no deuterium could be detected in the skeletal positions of the product. We suggest—rather speculatively—that (a) is reaction 21 of Figure 2 and that this is the major path of ketone hydrogenation at low degrees of hydrogenation; that is, the hydrogen atom which adds to the oxygen atom of the ketone comes mainly from the "acidic" hydrogen atoms of butanone to form species C and J. Species C itself is assumed to interchange rather rapidly with adsorbed ketone E and to proceed relatively rapidly to alcohol by reaction with D*. On this model, ketone hydrogenation on copper at low conversions proceeds mainly by a mechanism different from that of dehydrogena-

(18) K. Kawamoto, *Bull. Chem. Soc. Jap.*, 34, 161 (1961).

tion of alcohol at low conversions. Of course, at equilibrium, the principle of microscopic reversibility requires that both mechanisms contribute equally to the forward and reverse reactions.

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Conformational Effects of Sulfur, Silicon, Germanium, and Tin on Alkyl Radicals. An Electron Spin Resonance Study of the Barriers to Internal Rotation

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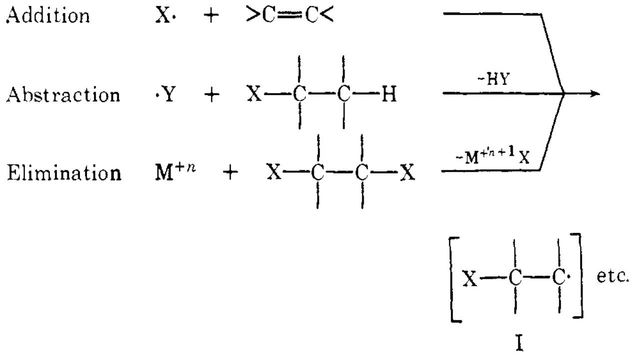
Received February 25, 1970

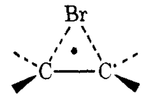
Abstract: The electron spin resonance spectra of a series of alkyl radicals substituted in the β position with sulfur, silicon, germanium, and tin groups are reported. The hyperfine isotropic coupling constants for the β protons are unusually small and show a marked temperature dependence. These results are interpreted in terms of hindered internal rotation about the C_α–C_β bond and a preferred conformational orientation in these radicals in which the sulfur, silicon, germanium, and tin atoms are eclipsed with the p orbital at the trigonal center. These conformational effects are attributed to incipient 1,3 bonding between the unfilled 3d orbitals of the heteroatom and the p orbital of the carbon radical center. A structure involving symmetrically bridged radicals is ruled out. A classical anisotropic averaging of the β hyperfine splitting is discussed and used to determine the heights of the potential barriers hindering rotation in these radicals. The classical treatment of hindered rotation is also applied to simple alkyl radicals. The barrier heights determined by this approach agree with those previously determined by a quantum mechanical treatment. The β hyperfine splittings in the mercaptoalkyl radicals are anomalously small and cannot be accounted for by the unmodified theory. A distorted structure for these radicals is considered in which the β hydrogens are displaced away from their tetrahedral positions. Concomitant with this distortion the sulfur atom is placed closer to the p orbital This model easily explains the anomalously low β-proton splittings. Similar distortions are suggested for simple alkyl radicals. Line-broadening effects in several alkyl and β-substituted alkyl radicals are reported and discussed in terms of the dynamic equilibrium conformations of the radical structures.

Stabilization of alkyl radicals and stereoselectivity in homolytic reactions is a subject which has been considered at length. The effects of a variety of substituents on the steric course of free-radical reactions occupies a prominent position in these investigations. Substituents located in the β position generally exert the strongest stereochemical effects and these have been observed in free-radical additions to alkenes, as well as elimination from and substitution in alkyl derivatives. The problem is largely associated with the β-substituted alkyl radical I formed as an intermediate in these reactions.

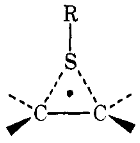


I

The β-bromo alkyl radical (I, X = Br) has been presented as a bridged species II and a similar delocalized structure has been attributed to the β-mercaptoalkyl radical III.[1]

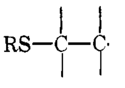


II



III

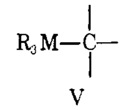
The electron spin resonance (esr) spectra of these radicals would provide the most direct approach to the study of their structure. In this paper we present an esr study of two groups of alkyl radicals substituted in the β position with an alkylmercapto group (IV) or a group IV metal (V). The esr spectra of these two



$$\mathrm{RS{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot}$$

IV

R = alkyl



$$\mathrm{R_3M{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot}$$

V

R = H, CH_3, CH_3CH_2, etc.
M = Si, Ge, Sn

classes of β-substituted alkyl radicals show remarkable similarities but they are unique compared to their hydrocarbon analogs. In the following presentation the esr spectra of a series of free radicals IV and V are

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(1) P. S. Skell, *Chem. Soc., Spec. Publ.*, No. 19, 131 (1965).