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Dehydrogenation of Alcohols and Hydrogen Transfer from Alcohols to Ketones Over Hydroxyapatite Catalysts

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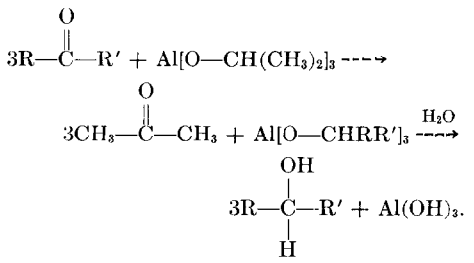
Kinetic data are reported for the dehydrogenation of 2-butanol and hydrogen transfer from this alcohol to 3-pentanone over the same catalysts. Both reactions were zero order in reactant pressures and were poisoned by a side reaction product of the ketone. Both reactions were much faster over the stoichiometric hydroxyapatite than over preparations having calcium deficiencies or containing fluoride ions. The activation energies for dehydrogenation (22 kcal/mol) and hydrogen transfer (12 kcal/mol) were both about 10 kcal/mol greater than the corresponding reaction enthalpies and the difference in rate could be traced mainly to this factor. The data suggest that both reactions occur on the same sites and involve the same intermediate species. Tracer experiments revealed a very specific transfer of D from 2-butanol-2d_1 to the product 3-pentanol-3d_1. In dehydrogenation, the labeled butanol produced HD exclusively along with butanone. Similar kinetic isotope effects were found for the two reactions using the labeled butanol, viz., k_H/k_D values of 1.8 and 1.9 for dehydrogenation and transfer, respectively. Fairly detailed mechanisms can be inferred from these findings coupled with earlier work.

INTRODUCTION

The Meerwein-Ponndorf-Verley (MPV) reduction of ketones with aluminum isopropoxide is a well-known hydrogen transfer reaction (*1*) whose mechanism probably involves a hydride transfer from the alkoxide to the carbonyl carbon of the ketone (*2*), i.e.,



A similar step is also postulated for some oxidations of alcohols in solution (*3*).

When alcohols are chemisorbed on oxides, surface alkoxide species are often formed (*4*). Therefore, it might be suspected that some of these would be capable of hydrogen transfer to adsorbed ketone (or aldehyde) molecules with chemistry analogous to the MPV reaction. This is indeed the case; alumina (*5*, *6*), MgO (*7–9*), CaO (*10*), ZnO and CdO (*8*), MgO–SiO_2 (*11*), H,Na–Y zeolite (*5*), aluminum, calcium, and zirconium phosphates (*12*), ThO_2, CeO_2, and ZrO_2 (*12*) have all been reported as active hydrogen transfer catalysts. The oxides with large (soft) cations are also selective catalysts for alcohol dehydrogenation (as opposed to dehydration) (*13*). The relative accessibility of the surface cations has been considered to be an important factor in determining the dehydrogenation selectivity (*13–15*). Since the above-mentioned cations may be hydride (soft ion) acceptors, alcohol dehydrogenation and hydrogen transfer to ketones may be related reactions on metal oxides.

In the course of a study of the factors controlling the selectivity of hydroxyapatite catalysts for alcohol dehydrogenation and dehydration (*16*), it was found that

the hydroxyapatite catalysts with the highest selectivity for dehydrogenation were also the most active for hydrogen transfer to ketones. The results of some tracer and kinetic experiments are given herein on a representative hydrogen transfer reaction, Eq. (2), over a stoichiometric,

$$\text{2-butanol} + \text{3-pentanone} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{2-butanone} + \text{3-pentanol}, \quad (2)$$

hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. Data for comparable studies of alcohol dehydrogenation over the same catalyst are also presented.

Experimental Methods

Materials. Reagent grade 2-butanol and 3-pentanone were used without further purification after gas chromatographic analysis revealed no major impurities. Analysis of 2-butanol-2-d_1 from Merck, Sharp, and Dohme of Canada, Ltd by mass spectrometry indicated an isotopic purity of 96%, with all of the label in the 2-position.

The preparation and characterization of the hydroxyapatite catalyst has been described previously (*17*). Its specific surface area was 75 m^2/g. The same 150 mg sample was used in all of the experiments; treatment at 500°C in a flow of dry helium for 15–20 hr provided reproducible catalyst activities except when the catalyst had been exposed to a ketone for an extended period. In the latter case, the catalyst was treated for 1 hr with oxygen at 500°C to restore its activity.

Apparatus. The continuous flow microreactor has been described (*18*). Isotopic compositions of alcohols, ketones, and olefin products were determined with a Nuclide 6-in., 60° magnetic sector mass spectrometer after rigorous separation by gas chromatography.

Treatment of kinetic data. The rates of 2-butanol dehydrogenation and hydrogen transfer from 2-butanol to 3-pentanone decreased steadily with throughput at a given temperature. The reaction orders were estimated by taking data under a standard set of conditions to establish a curve for the change in activity, then comparing data for other partial pressures to the standard. Dehydrogenation of 2-butanol was zero order at low conversions, but strongly inhibited by product ketone; it was estimated that the adsorption equilibrium constant for the ketone at dehydrogenation sites was an order of magnitude greater than that of the alcohol. The hydrogen transfer also was zero order in each reactant if a constant alcohol/ketone ratio was maintained. Thus, changing the (alcohol + ketone) partial pressure at a constant (alcohol + ketone) flow rate, by dilution with helium carrier gas, had no effect on the conversion. The rates were highest when the alcohol/ketone ratio was slightly higher than unity, suggesting that the adsorption equilibrium constant for the ketone was only a little greater than that for the alcohol. However, for the analysis of the kinetic data for hydrogen transfer, it was assumed that all of the adsorption constants of the reacting species were equal. The absolute values of the calculated rate constants are therefore approximate, but since low conversions and the same alcohol-to-ketone ratio were used in all of the runs, the relative values of the rate constants (and the activation energy derived from them) should be fairly accurate. Starting with 2-butanol and 3-pentanone as the only reactants, the rate of 3-pentanone reduction is given by Eq. (3).

$$-dA/dt = \frac{k_1(A)(B) - k_{-1}(C)(D)}{(A_0 + B_0)^2}, \quad (3)$$

where A 3-pentanone concentration (moles/m^2)
B 2-butanol concentration (moles/m^2)
C 3-pentanol concentration (moles/m^2)
D 2-butanone concentration (moles/m^2)
A_0 initial value of A
B_0 initial value of B
k_1 zero order rate constant for transfer from 2-butanol to 3-pentanone (moles/m^2/sec)
k_{-1} zero order rate constant for transfer from 3-pentanol to 2-butanone (moles/m^2/sec)

The equilibrium value of the 3-pentanone concentration is given by Eq. (4).

$$A_e = \frac{Q}{2} - \frac{K_1(B_0 - A_0) + 2A_0}{2(K_1 - 1)}, \quad (4)$$

where $K_1 = k_1/k_{-1}$,

and $$Q = (K_1^2(B_0 - A_0)^2 + 4K_1B_0A_0)^{1/2}/(K_1 - 1).$$

The integrated form of Eq. (3) is then given by Eq. (5).

$$\ln \frac{(A_0 - A_e)(A - A_e + Q)}{(A - A_e)(A_0 - A_e + Q)} = \frac{Q(k_1 - k_{-1})t}{(A_0 + B_0)^2}. \quad (5)$$

Defining $a = A/A_0$, $a_e = A_e/A_0$, $q = Q/A_0$, then

$$\ln \frac{(1 - a_e)(a - a_e + q)}{(a - a_e)(1 - a_e + q)} = \frac{qA_0(k_1 - k_{-1})t}{(A_0 + B_0)^2}. \quad (6)$$

The flow rate of reactants, normalized to constant catalyst area, is given by Eq. (7).

$$F_1 = (A_0 + B_0)/t, \quad (7)$$

where F_1 = flow rate of (A + B) (moles/m^2/sec). Defining $f = A_0/(A_0 + B_0)$, then the zero order rate constant for hydrogen transfer is

$$k_1 = \frac{K_1F_1}{(K_1 - 1)fq} \ln \frac{(1 - a_e)(a - a_e + q)}{(a - a_e)(1 - a_e + q)}. \quad (8)$$

Defining x as the fractional conversion of the alcohol, and F_0 as the flow rate of the alcohol (moles/m^2/sec), then the zero order rate constant for dehydrogenation is

$$k_0 = xF_0. \quad (9)$$

Results

Over a stoichiometric hydroxyapatite the hydrogen transfer reaction of Eq. (2) proceeded readily above 150°C. No other products were observed up to 250°C if contact times were kept below 1 sec. At about 250°C, dehydrogenation of the alcohols started, and at 300°C, dehydration also occurred. The hydrogen transfer kinetics were measured between 160°C and 280°C; conversions were kept low at the higher temperatures to avoid interference from the competitive dehydrogenation.

Since the hydrogen transfer reaction was reversible a determination of the equilibrium constant was necessary for analysis of the kinetic data [Eq. (8)]. Two determinations were made, at 260°C and 279°C; the result at each temperature was $K_1 = 0.80$. Yager and Hancock (*19*) measured the equilibrium constants for the reduction of a number of ketones with 9-fluorenol and aluminum *t*-butoxide. They found $K_B = 1.64$ for 2-butanone and $K_p = 1.29$ for 3-pentanone at 45°C. Since $K_1 = K_p/K_B$, their results yielded a value of 0.79 for K_1 at that temperature. An alternative value of $K_B = 1.60$, which they calculated from the data of Adkins *et al.* (*20*) (obtained from oxidation potentials of 2-butanone and 9-fluorenol) yielded $K_1 = 0.81$. These values bracket the high temperature value found in the present study. Apparently, the equilibrium constant is insensitive to changes in temperature, indicating, as expected, a very small enthalpy change for the reaction [Eq. (2)]. Hence, the value 0.80 was used for K_1 over the entire temperature range for which kinetic data were available.

An approximately equimolar mixture of 2-butanol and 3-pentanone was passed over the hydroxyapatite catalyst at several temperatures and flow rates. The product balances required by Eq. (2) were found for each component within the experimental error (about ± 1% for each). The zero order rate constant, k_1, was calculated using Eq. (8). Values of k_1 are given in Table 1. At each temperature they decreased steadily with throughput. The decrease in activity could also be produced by passing the ketone over the catalyst alone, and it is probably due to minor side reactions of the ketone (*vide infra*). The decrease was nearly exponential at first, yielding linear plots of $\ln k_1$ versus time. The initial rate constants at each temperature were found by extrapolation back to zero throughput. These are given in Table 2. The corresponding Arrhenius plot of the data is shown in Fig. 1. An activation energy of 12 ± 2 kcal/mole was derived for the hydrogen transfer.

TABLE 1
HYDROGEN TRANSFER FROM 2-BUTANOL TO 3-PENTANONE OVER HYDROXYAPATITE[a]

Temp (°C)	Time over catalyst (min)	Rate constant, k_1 (moles/m²/sec × 10^8)
162	15	8.9
	37	6.9
	57	5.6
	80	4.8
	102	4.6
	121	4.6
	141	4.5
176	10	10.1
	33	6.2
210	166	9.5
	185	7.7
	238	5.0
231	42	32.2
	63	26.9
	84	22.9
	103	19.4
260	180	35.1
	201	29.6
	221	26.0
279	83	86
	125	63

[a] Variation of rate constant with temperature and throughput.

TABLE 2
HYDROGEN TRANSFER FROM 2-BUTANOL TO 3-PENTANONE OVER HYDROXYAPATITE[a]

Temp (°C)	Rate constant, k_1[b] (moles/m²/sec × 10^8)	$\log_e(k_1)$	$10^3/T$ (°K^{-1})
162	10.6	2.36	2.298
176	13.0	2.56	2.226
210	30.6	3.56	2.070
231	45	3.81	1.983
260	123	4.81	1.876
279	165	5.10	1.811

[a] Variation of initial rate constant with temperature.

[b] $k_1 = 0.1 \exp(-12{,}000/RT)$ moles/m²/sec.

TABLE 3
DEHYDROGENATION OF 2-BUTANOL OVER HYDROXYAPATITE[a]

Temp (°C)	Rate constant, k_0[b] (moles/m²/sec × 10^8)	$\log_e(k_0)$	$10^3/T$ (°K^{-1})
248	0.12	−2.15	1.919
254	0.15	−1.86	1.897
280	0.37	−1.00	1.808
294	0.79	−0.24	1.763
301	0.91	−0.09	1.742
323	1.37	0.32	1.677
332	2.49	0.87	1.652

[a] Variation of initial rate constant with temperature.

[b] $k_0 = 1.8 \exp(-22{,}000/RT)$ moles/m²/sec.

Dehydrogenation of 2-butanol over the same catalyst was observed in the temperature range 248–332°C. It was zero order with respect to the alcohol but inhibited at high conversions by the 2-butanone product. Plots of fractional conversion vs reciprocal flow rate were linear only below 5% conversion. Again the rates decreased with throughput and the decrease was faster at higher conversions to 2-butanone. Zero order rate constants, k_0, were found again by extrapolation to zero time. These are given in Table 3, and the corresponding Arrhenius plot is presented in Fig. 2. The activation energy for 2-butanol dehydrogenation was found to be 22 ± 2 kcal/mole.

A mixture of 2-butanol-2-d_1 and 3-pentanone, when passed over hydroxyapatite at 300°C gave a nearly equilibrated product mixture of 2-butanol, 3-pentanol, 2-butanone, and 3-pentanone. Neither of the ketones contained any deuterium. The deuterium contents of the 2-butanol and 3-pentanol were both 0.96 D/molecule, the same as the starting 2-butanol-2-d_1. Moreover, the fragmentation patterns revealed that the deuterium was located exclusively at the carbinol carbon in both of the alcohols. Similarly, dehydrogenation of 2-butanol-2-d_1 at 300°C gave 2-butanone free of deuterium, and there was no change in the isotopic composition of the alcohol. The

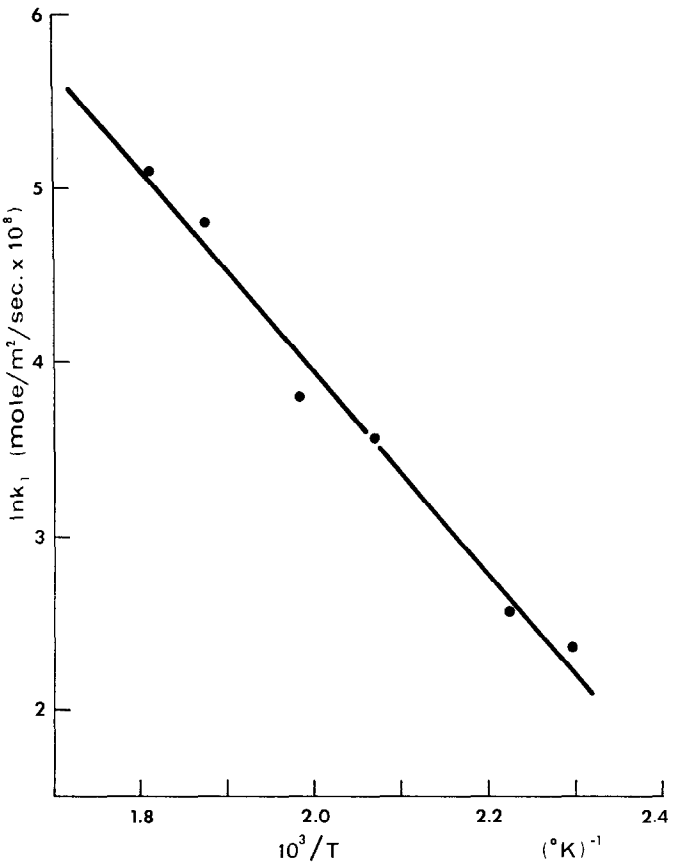


FIG. 1. Variation of hydrogen transfer rate constant with temperature; 2-butanol + 3-pentanone over hydroxyapatite.

hydrogen formed was 7% H_2 and 93% HD. Allowing for an isotope effect, k_H/k_D = 1.8, all of the H_2 could be accounted for by the unlabeled 2-butanol impurity. Thus, essentially all of the hydrogen from dehydrogenation of 2-butanol-2-d_1 over hydroxyapatite was HD.

The kinetic isotope effect on dehydrogenation caused by deuterium substitution was determined in separate runs using 2-butanol and 2-butanol-2-d_1 at 300°C. At that temperature, k_H/k_D = 1.8 for dehydrogenation. The kinetic isotope effect on the hydrogen transfer reaction was determined by a competitive method. An equimolar mixture of 2-butanol and 2-butanol-2-d_1 was passed over the catalyst at 160 and 184°C together with 3-pentanone. The isotopic composition of the 3-pentanol in the product mixture was determined at low conversions. The relative hydrogen transfer rate constants were then obtained by extrapolation back to zero conversion. At both temperatures, k_H/k_D = 1.9 for the hydrogen transfer from 2-butanol to 3-pentanone over hydroxyapatite.

Adsorption of 2-butanol on hydroxyapatite yielded a surface carboxylate species observable by its infrared absorption spectrum (*4c*) which was similar to those formed by primary alcohols on alumina (*4a*). Its origin was uncertain, since the loss of an alkyl group was implied, and this was not accounted for in other products.

In the present work an extra olefin was found in the decomposition products of those secondary alcohols which could also

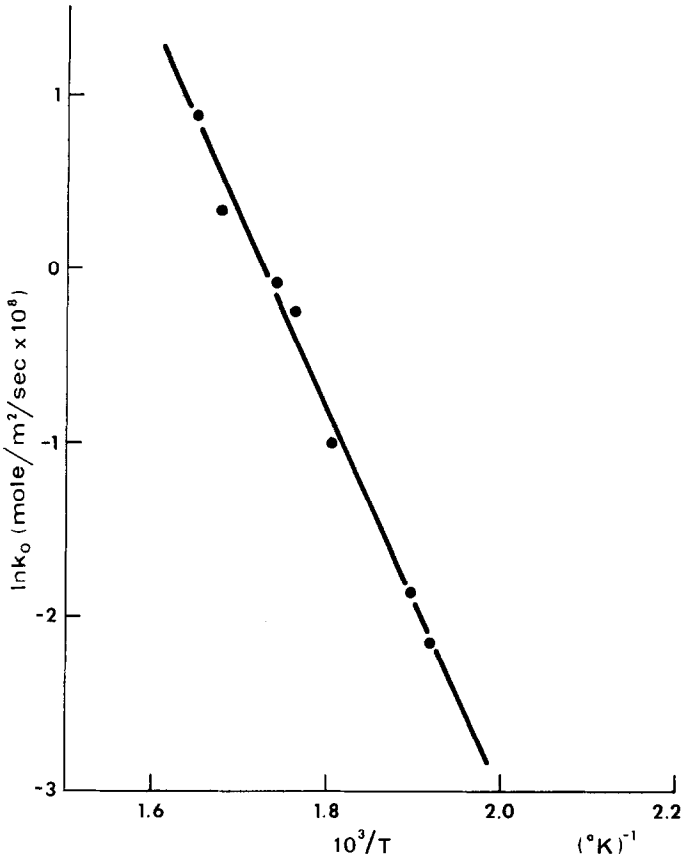


FIG. 2. Variation of dehydrogenation rate constant with temperature; 2-butanol over hydroxyapatite.

form methylketones. The same olefin could also be formed from the methylketones themselves. In each case the structure of the extra olefin product was isoelectronic with that of the methylketone, with CH_2 replacing the carbonyl oxygen (Table 4). Its formation may be explained by a disproportionation reaction of the ketone.

$$2CH_3\overset{O}{\overset{\|}{C}}—R \rightarrow CH_3\overset{CH_2}{\overset{\|}{C}}—R + R—\overset{O}{\overset{\|}{C}}—OH. \quad (10)$$

The carboxylic acid which is formed concomitantly (also isoelectronic with the ketone) is undoubtedly the source of the carboxylate species seen in the ir spectra in the earlier work (*4c*). The carboxylate is held very strongly and is an effective poison for alcohol dehydrogenation and hydrogen transfer to ketones.

TABLE 4
EXTRA OLEFIN PRODUCTS IN THE DECOMPOSITION OF SECONDARY ALCOHOLS OVER STOICHIOMETRIC HYDROXYAPATITE

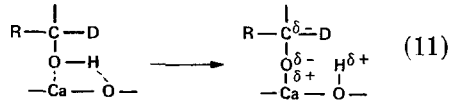
Alcohol	Ketone product	Extra olefin product
2-Propanol	Acetone	Isobutene
2-Butanol	2-Butanone	2-Methyl-1-butene
2-Pentanol	2-Pentanone	2-Methyl-1-pentene
(3-Methyl-2-butanol)	(3-Methyl-2-butanone)	(2,3-Dimethyl-1-butene)

DISCUSSION

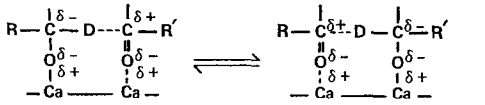
Alcohol dehydrogenation and hydrogen transfer to ketones exhibited many similarities over hydroxyapatite. Both were much faster on the stoichiometric preparation

(Ca/P = 1.67) than on fluorided or calcium-deficient preparations. Both were poisoned by long exposure to methylketones, presumably by a carboxylic acid formed in a disproportionation reaction [Eq. (10)] in which an olefin is also formed. The olefin was readily desorbed, but the carboxylic acid was held so strongly that it could not be removed by prolonged evacuation at 240°C (*4c*). The apparent activation energies found for dehydrogenation and hydrogen transfer were both about 10 kcal/mole greater than the corresponding enthalpies of reaction, and the rate differences between the reactions were mainly due to the difference in activation energies. Similar kinetic isotope effects for substitution of deuterium on the α-carbon indicate a rate-limiting transfer of the α-hydrogen in both reactions. The absence of any isotopic mixing of the hydrogen at the α-position is consistent with a hydride transfer mechanism for both.

A plausible mechanism for the hydrogen transfer reaction is represented in Eqs. (11) and (12). The cleavage of the alcohol to form the alkoxide (Eq. 11) is probably heterolytic; if so, this would leave a net negative charge on the α-carbon as indicated.



(11)

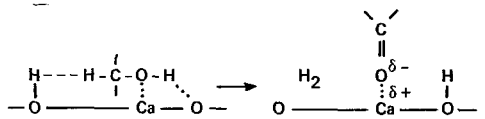


(12)

The alkoxide can then transfer its α-hydrogen (as H^-) directly to an adsorbed ketone molecule [Eq. (12)] just as in the MPV reaction (*1, 2*). Similar mechanisms have been proposed by Bullard, Finch and Winkler (*7*) and by Okamoto, Imanaka and Teranishi (*9*) for hydrogen transfers on magnesium oxide. As argued by Bullard, Finch and Winkler (*7*) it is likely that the ketone is adsorbed on an adjacent calcium ion rather than on that to which the alkoxide is bound. This is geometrically reasonable in terms of the catalyst structure (*17, 21*).

In a correlation of alcohol dehydrogenation rates with alkyl group substitution on the α-carbon (*16*), a positive ρ^* was found for reactions over hydroxyapatite using the Taft equation (*22*). To the extent that steric effects are not involved, this implies that in a rate-determining step of the reaction, the electron density at the α-carbon increases in passing through the transition state. Consequently, a step such as that shown in Eq. (11) is likely to be a slow step in both dehydrogenation and hydrogen transfer.

At higher temperatures where dehydrogenation is favorable, the alkoxide species of Eq. (11) may transfer its α-hydrogen to a less suitable acceptor than a ketone molecule. One possibility is a direct transfer to the proton of an adjacent hydroxyl group. If this were concerted with loss of the hydroxyl hydrogen of the alcohol [Eq. (11)], the chemistry of dehydrogenation would be quite similar to that visualized by Eucken (*14*) and Wicke (*15*) for dehydration. This is shown in Eq. (13).

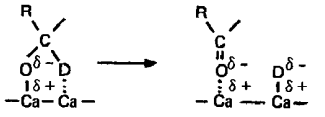


(13)

The only role provided for calcium ions by this mechanism is coordination with the alcohol oxygen to facilitate the loss of its hydrogen. This appears unlikely. It affords no explanation for the large change in selectivity favoring dehydrogenation when small amounts of Cu^{2+} or Ni^{2+} is substituted for Ca^{2+} (*21*). Futhermore, the much stronger effect of added ketone in inhibiting dehydrogenation, as opposed to hydrogen transfer, is evidence that a site which adsorbs ketones strongly is active in abstracting the α-hydrogen during dehydrogenation. This is most likely an adjacent Ca^{2+} (or Cu^{2+} or Ni^{2+}), acting as a hydride acceptor, as indicated in Eq. (14).

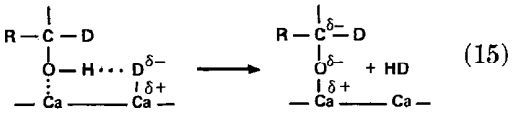
A subsequent reaction of the hydride

species of Eq. (14) with any suitable proton would complete the sequence to form



(14)

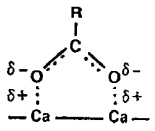
hydrogen. If the reaction were with another alcohol molecule, as shown in Eq. (15), the alkoxide would be regenerated.



(15)

A mechanism very similar to this has been proposed by Noto *et al.* (*23*) for the dehydrogenation of formic acid on ZnO. Recently Misono and Hall (*24*) studied H_2–D_2 exchange over hydroxyapatites containing small amounts of Cu^{2+} or Cu^{+}. In this reaction the recombination and desorption steps may be the same as in the dehydrogenation reaction. It was observed that the reaction was much faster and had a lower activation energy when the copper was present as Cu^{2+} or Cu^{+} than when it had been reduced to Cu^{0} clusters. (Under the reaction conditions Cu^{2+} was unstable with respect to Cu^{+}.) The data were consistent with the view that H_2 (and D_2) are cleaved heterolytically to form CuH from Cu^{+} with the corresponding proton reacting with PO_4^{3-} to form HPO_4^{2-}. Isotopic mixing may have resulted from the proton mobility among the phosphate groups. Thus, dehydrogenation could result from the reaction of Eq. (14) followed by reaction of the H^{-} with a proton held on a phosphate group.

Poisoning of the catalytic sites for dehydrogenation and hydrogen transfer by carboxylic acids can be easily rationalized by assuming that the mechanisms require adjacent exposed calcium ions on the surface of hydroxyapatite. Thus, the carboxylate anion can bond to both calcium ions, as shown in Eq. (16). Such sites should be common at the surface of stoichiometric hydroxyapatite, where calcium ion triangles exist on both *ab* and *ac* faces (*21*). These are thought to be the



(16)

basis for the use of hydroxyapatite as a chromatographic adsorbent for the separation of proteins (*25*). The sites may also be blocked by fluoride ions or by phosphate ions (in calcium-deficient hydroxyapatite).

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