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Studies of Acid Catalyzed Reactions

XII. Alcohol Decomposition over Hydroxyapatite Catalysts

C. L. KIBBY AND W. KEITH HALL

Gulf Research and Development Company, P. O. Drawer 2038,
Pittsburgh, Pennsylvania 15230

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Structure-reactivity relationships for alcohol elimination reactions were studied over two well-characterized hydroxyapatite catalysts. A "stoichiometric" preparation (HA), with the composition $Ca_{10}(PO_4)_6(OH)_2$, catalyzed both dehydration and dehydrogenation. A "non-stoichiometric" catalyst (NHA) with Ca/P = 1.58 was active only for dehydration. The dehydration rate constants for fifteen acyclic alcohols over the NHA catalyst correlated with Taft σ_α^* constants for substitution at the alpha carbon atom yielding $\rho_\alpha^* = -5$ at 230°C. The dehydration rates were much slower over the less acidic HA catalyst, and a temperature of 400°C was needed for a linear relation between σ_α^* values and the logarithms of the rate constants. At that temperature $\rho_\alpha^* = -2$ for alpha substitution. The structure-reactivity relationships were remarkably similar to those for gas phase reactions such as HBr-catalyzed alcohol dehydration and the pyrolysis of esters. Like the latter, the eliminations over hydroxyapatite were mainly *syn*-eliminations. The necessary requirement is apparently the presence of a sufficiently acidic hydroxyl group at the surface. Beta elimination predominated in the alcohol dehydrations, but, over the NHA catalyst, both primary and secondary alcohols yielded products attributable to gamma elimination, and some of the primary alcohols gave cyclopropanes.

Dehydrogenation of secondary alcohols over the HA catalyst could be correlated with σ^* values at 400°C but in the opposite direction to dehydration; $\rho_\alpha^* = +1.5$ for alpha substitution, suggesting that the transition state is negatively charged. An alkoxide ion is a likely precursor, with hydride transfer as the rate-limiting step.

INTRODUCTION

Metal oxides are effective catalysts for the decomposition of alcohols, either by dehydration or dehydrogenation (*1*). The selectivity for one of these two types of elimination from simple, acyclic primary and secondary alcohols is largely governed by properties of the catalyst, but the rates are also affected by changes in the alcohol structure (*1, 2*). Dehydration is favored over oxides with small, highly-charged cations, while dehydrogenation has been associated with larger more polarizable cations such as the alkaline earth ions (*1, 3–5*). It has been postulated (*3–9*) that acidic hydroxyl groups are required for dehydration. Exposed cations may be needed for dehydrogenation (*3–6*) and in some cases also for dehydration (*2*). Thus, studies of alcohol decomposition may be used to define some of the properties of certain surfaces and to elucidate the nature of the catalytic sites which are present.

Most often, the products of alcohol dehydration are an olefin and water, but ethers may be formed (*9, 10*). The hydrogen eliminated with the hydroxyl group is usually derived from the β-carbon atom, although, in the formation of certain products, it may come from elsewhere in the molecule. When there are two or more different β-eliminations possible, the selectivity towards each may be governed by either Saytzeff or Hofmann orientation rules, depending upon the reaction mechanism (*11–14*). The direction of elimination of the

β-hydrogen atom, relative to the hydroxyl group, may be either *syn* or *anti* in a concerted reaction, or nonspecific (as in a stepwise ionic process). The arrangements of substituents in the olefins formed may be either *cis* or *trans*. All of these selectivities may be determined by use of suitable alcohols. Some of them are sensitive to very small changes in relative rates, and almost any combination of the various results is possible. Taken together, they provide a "fingerprint" of a catalyst which, if properly related to its structure and chemistry, can provide much useful information concerning the way in which it functions.

The literature (*13*, *14*) contains a large amount of information relating reactivity and selectivity data for olefin-forming reactions in solution to their reaction mechanisms. This knowledge has been used judiciously to make inferences concerning mechanisms of certain gas phase eliminations (*15*) and all this background is now available for comparison with data for heterogeneously-catalyzed eliminations. This comparison must be made cautiously, however, because steric effects may be much more important in the heterogeneous case.

Dehydration rates of alcohols are strongly dependent upon the alcohol structure (*16*), especially on increasing α-substitution which tends to shift the mechanism towards E1 (*14*). The response of dehydration rates to changes in alcohol structure may be used as a test of the uniformity of a catalytic reaction mechanism and correlations with polar and/or steric substituent parameters can indicate their importance.

In the present paper an extensive study of the effects of alkyl substituents on the dehydration and dehydrogenation of acyclic aliphatic alcohols over two well-characterized hydroxyapatite catalysts (*17*) is reported. One of these crystalline catalysts favored dehydration, and the other dehydrogenation (*18*). The relative rates and selectivities were determined at several temperatures for each alcohol, so that activation energy differences could be obtained. Correlations, using the Taft σ^* parameters (*16*), were made using both dehydration and dehydrogenation rate constants. Hydroxyapatites vary from the "stoichiometric composition," $Ca_{10}(PO_4)_6(OH)_2$ (HA), to nearly that of a tricalcium phosphate, $Ca_9(HPO_4)(PO_4)_5OH$ (NHA), without any fundamental change in the crystal lattice (*17*). For moderate changes in the Ca/P ratio, calcium deficiencies are compensated by protons. Thus, the composition of hydroxyapatite may be varied from calcium rich suitable for alcohol dehydrogenation, to phosphate-rich, suitable for dehydration of alcohols. It was the purpose of the present work to add information concerning the effects of changes in alcohol structure to the existing knowledge concerning this model catalyst system.

EXPERIMENTAL

Materials

Ethanol was obtained from Commercial Solvents Corporation (Rossville "Gold Shield"); propanol, isopropanol, and 2-butanol were Fisher Certified reagents, and *tert*-pentanol was Fisher Reagent Grade; 3-pentanol, 3-methyl-2-butanol, and 2-methyl-1-butanol were Eastman White Label reagents; 2-pentanol and neopentanol were obtained from Chemicals Procurement Company; butanol, *tert*-butanol, pentanol, isopentanol, and isobutanol were all 99+% "chromatoquality" reagents from Matheson, Coleman, and Bell. None of the alcohols was further purified, but all were checked by gas chromatography and only the *tert*-pentanol was found to be less than 98% pure (excluding water). A second lot of *tert*-pentanol was about 99% pure. Common impurities in the secondary alcohols were the corresponding ketones, and all of the alcohols contained traces of water.

Catalysts

The preparation of the hydroxyapatite catalysts has been described (*17*) previously. A 150-mg sample of each catalyst was used for the full set of experiments. One was a "stoichiometric" hydroxyapatite with a Ca/P ratio of 1.67 and a specific surface area of 75 m^2/g. The other was a calcium-deficient or "non-stoichiometric" hydroxyapatite with a Ca/P ratio of 1.58 and a specific surface area of 46 m^2/g. These will be referred to as the HA and NHA catalysts, respectively. Both could be regenerated in a flow of dry helium at 500°C for 15–20 hr (the trace oxygen impurity was sufficient to remove hydrocarbon residues). This was adopted as a standard pretreatment for the HA catalyst. It was also used for the NHA catalyst, but, in addition, a one-hour treatment with water (ca. 300 Torr in helium carrier) at 350°C was necessary to restore its maximum activity for dehydration. The NHA catalyst became dehydroxylated below 500°C with formation of pyrophosphate groups; this decreased the dehydration activity by a factor of two or three.

Apparatus

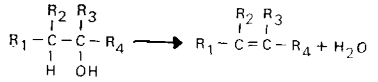
The microreactor has been described previously *(18)*; it was used in the continuous flow mode. Alcohols were separated from ketones and olefins on a 10 ft, ¼ in. column of 10% polypropylene glycol on 60/80 mesh Chromosorb P at 85–100°C. The olefin products were further separated on a 30 ft, ⅜ in. column of 15% dimethylsulfolane on 60/80 mesh Chromosorb P operated at 0°C. Identifications were made from the retention times and by analysis with a Nuclide 6 in.-60° magnetic sector mass spectrometer.

Procedures

The dehydration and dehydrogenation rates of all of the alcohols were zero order in alcohol pressure between 5 and 100 Torr. Rates were taken as the limiting slopes of the conversion vs reciprocal flow rate curves, as the abscissa approached zero. The linear region extended to about 20% conversion for secondary and tertiary alcohols over the NHA catalyst, and to 50% conversion for primary alcohols. Over the HA catalyst, however, inhibition by product ketone was very strong so that conversions had to be kept below 5%. Even so, the dehydrogenation rates decreased rapidly with throughput so that it was necessary to extrapolate the rate data back to zero time and to make a separate run for each temperature. Consequently, the Arrhenius parameters for dehydrogenation were less precise than those for dehydration where data at several temperatures could be determined during a single experiment. For primary alcohols, polymerization of the product aldehydes was so extensive on the HA catalyst that the rate data for dehydrogenation were not reliable, and side reactions also interfered with the dehydration reaction. Data for dehydration of *n*-propanol reported for the HA catalyst are probably reliable at the high temperature extreme, but the low temperature data and the corresponding Arrhenius parameters may have been altered by the dehydrogenation reaction. Olefin product distributions were reasonably independent of flow rate for the linear alcohols, but branched olefins such as 2-methyl-1-butene and 2-methyl-2-butene were easily equilibrated. Initial distributions were obtained by extrapolation of the olefin ratios to zero reciprocal flow rate.

RESULTS

Over the calcium-deficient hydroxyapatite catalyst, dehydration was the only reaction observed. Both dehydration and dehydrogenation occurred over stoichiometric hydroxyapatite, with dehydrogenation favored at lower temperatures. On both catalysts, the major dehydration products from alcohols having a β-hydrogen were those attributable to β-elimination, i.e.,



$$R_1-\underset{H}{\overset{R_2}{C}}-\underset{OH}{\overset{R_3}{C}}-R_4 \longrightarrow R_1-\overset{R_2}{C}=\overset{R_3}{C}-R_4+H_2O \quad (1)$$

No other products were formed by tertiary alcohols. As shown in Table 1, primary and secondary alcohols also yielded olefins which required hydrogen or alkyl group migration when passed over the NHA catalyst, and ring closure to cyclopropanes was found in dehydrations involving primary alcohols. The temperatures required for dehydration increased in the order tertiary < secondary < primary; tertiary alcohols were dehydrated at 150–250°C, secondary alcohols at 250–350°C, and primary alcohols at 300–400°C. No ethers were formed from any of the alcohols. Since the dehydrations were

TABLE 1

PRODUCT DISTRIBUTIONS IN ALCOHOL DEHYDRATION OVER A CALCIUM-DEFICIENT HYDROXYAPATITE CATALYST (Ca/P = 1.58)[a]

Alcohol[b]	β-Elimination products[c]		Other products[d]
t-Butyl	*i*B	100%	
t-Pentyl	2MB	100%	
2-Propyl	*n*-C_3H_6	100%	
2-Butyl	*n*B	100%	
2-Pentyl	*n*P	100%	
3-Pentyl	2P	98%	2% 1P
(3-Methyl-2-Butyl)	(3M1B + 2M2B)	80%	20% 2M1B[c]
Ethyl	C_2H_4	100%	
1-Propyl	*n*-C_3H_6	98%	2% cyclo-C_3H_6
1-Butyl	1B	80%	20% 2B, *c*/*t* = 1.2
1-Pentyl	1P	80%	20%, 2P, *c*/*t* = 0.9
Isobutyl	*i*B	90%	10% *n*B, 3:3:4 = 1B:*t*2B:*c*2B
Isopentyl	3M1B	85%	11% 2M2B, 4% 2M1B
(2-Methyl-1-Butyl)	2M1B	70%	(15% 2M2B,[c] 1% 3M1B, 10% *n*P, 2% *t*DMC, 2% C_3H_6 + C_4H_8)
Neopentyl	No β-hydrogen		(70% 2M1B, 28% 2M2B, 1.5% *i*B, 0.5% 3M1B and/or *g*DMC)

[a] Results for secondary and tertiary alcohols were much the same over the stoichiometric catalyst (Ca/P = 1.67), except that somewhat smaller amounts of "other products" were produced. Primary alcohols were not studied extensively because the aldehydes produced by dehydrogenation underwent secondary reactions which complicated separation and produced catalyst poisons.

[b] Tertiary alcohols at 181°C, secondary alcohols at 282°C, and primary alcohols at 352°C.

[c] *n* = normal, *i* = iso, M = methyl, DM = dimethyl, B = butene, P = pentene, C = cyclopropane, *t* = trans, *c* = cis, *g* = geminal.

[d] Some of this product may be formed by isomerization.

zero order in alcohol pressure, the rate constants have the units of the rates themselves.

In Table 2 zero order rate constants are presented for dehydration of fifteen alcohols over the NHA catalyst. The rate constants are given relative to those for 2-propanol, as log (k/k_0) at three temperatures characteristic of the three ranges for the different alcohol types. Arrhenius constants are given for the variation of rate constant with temperature for each alcohol, as obtained from least squares fits of the relation:

$$\log k = \log A - E(1/2.3\,RT) \tag{2}$$

Rate constants for temperatures not covered by experimental data were calculated using Eq. 2. Thus, columns 3, 4, and 5 include some data obtained by extrapolation. The sum of the Taft σ^* values for the alkyl groups at the α-carbon, relative to $\Sigma\sigma_\alpha^* = 0.49$ for the three groups (two methyl, one hydrogen) of 2-propanol, are listed in column 2 as $(\sigma^* - \sigma_0^*)_\alpha$. The relative rate constants for dehydration followed the Taft equation (*19*) in the form:

$$\log(k/k_0) = \rho^*(\sigma^* - \sigma_0^*) \tag{3}$$

This is illustrated in Fig. 1 for the data at 230°C ($10^3/T = R$). The ρ_α^* value was −5 at that temperature and it decreased to −4 at 350°C. As shown in Fig. 2, the activation energies themselves were correlated with the σ_α^* parameter, although three secondary alcohols had relatively low activation energies and appeared to define a separate line (in compensation for their low activation energies, each had a low *A* factor as well).

Over the stoichiometric hydroxyapatite, 3-pentanol yielded traces (<0.5%) of 1-pentene, and 3-methyl-2-butanol produced about 10% 2-methyl-1-butene. These were the only products found which could not

TABLE 2

EFFECTS OF α-SUBSTITUTION ON DEHYDRATION OF ALCOHOLS OVER A CALCIUM-DEFICIENT HYDROXYAPATITE (Ca/P = 1.58)

Alcohol	$(\sigma^* - \sigma_0^*)_\alpha$[a]	log (k/k_0)[b]			E[c]	log A[c]
		$10^3/T = R$[d]	$10^3/T = 1.8$	$10^3/T = 1.6$		
Ethyl	0.49	−2.79	−2.35	−1.89	41.7	5.9
Propyl	0.39	−2.16	−1.79	−1.39	40.1	5.8
Butyl	0.375	−1.83	−1.51	−1.15	39.0	5.7
Isopentyl	0.365	−1.98	−1.63	−1.26	39.4	6.1
Pentyl	0.36	−1.81	−1.47	−1.12	39.0	5.7
Isobutyl	0.30	−1.62	−1.28	−0.91	39.4	5.7
2-Methyl-1-Butyl	0.28	−1.16	−0.86	−0.53	38.5	6.1
Neopentyl	0.19	−1.35	−1.07	−0.78	37.8	5.6
2-Propyl	0	0	0	0	31.0	4.0
(k_0, mole/m^2/sec)		(3.7×10^{-10})	(6.8×10^{-9})	(1.6×10^{-7})		
2-Butyl	−0.10	0.48	0.39	0.29	28.9	3.6
2-Pentyl	−0.115	0.15	0.19	0.23	32.0	4.6
3-Methyl-2-Butyl	−0.19	0.91	0.76	0.60	27.4	3.4
3-Pentyl	−0.20	0.92	0.92	0.93	31.2	5.0
t-Butyl	−0.49	2.36	2.21	2.06	27.5	4.9
t-Pentyl	−0.59	3.14	3.00	2.85	27.5	5.6
$(\rho_\alpha^*)_T$[e]		−5.1	−4.5	−3.9		
$(r_\alpha^*)_T$[f]		0.994	0.992	0.985		

[a] Taft σ_α^* values (*19*) for substitution at the α-carbon atom (additivity of σ^* assumed for multiple substitution), relative to 2-propanol.

[b] Rate constant ratio for *total* dehydration, at specified temperature. k_0 is for propylene from 2-propanol.

[c] Arrhenius constants from least squares fits of $\log k = \log A - [(E/2.3R)\ (10^3/T)]$. E is in kcal/mole, with standard deviation ± 1 kcal/mole for most alcohols. Both k and A are in units of mole/m^2/sec, with standard deviation of log A ± 1.5 or less.

[d] $R = 1.987$.

[e] Constants from least squares fits of $\log(k/k_0)_T = (\rho_\alpha^*)_T(\sigma^* - \sigma_0^*)_\alpha$. Standard deviations of $(\rho_\alpha^*)_T$ were ± 0.2.

[f] Correlation coefficients for least squares fits made in *e*.

be attributed to β-elimination. Rate constant data for dehydrations over the HA catalyst are given in Table 3. A linear plot of log (k/k_0) vs $(\sigma^* - \sigma_0^*)$ for α-substitution was found (Fig. 3) at 395°C ($10^3/T = 1.5$), from which a value of $\rho_\alpha^* = -2.3$ was derived. Only the data for the primary alcohols were obtained experimentally at that temperature, however, and at 282°C ($10^3/T = 1.8$) the LFER plots had considerable curvature as both primary and tertiary alcohols had lower activation energies than the secondary alcohols and their rate constants increased relative to those of the standard 2-propanol. Thus, for the range between primary and secondary alcohols, $\rho_\alpha^* = 1.5$, while for that between the tertiary and secondary alcohols $\rho_\alpha^* = -3$. The overall value calculated for all of the data was −2.5, i.e., just a little higher than the value obtained at the higher temperature. Secondary and tertiary alcohol dehydrations at 282°C were 10–100 times faster on NHA than on HA.

One method of determining the effects of β-substitution is to compare the appropriate dehydration rates for a series of different alcohols. Since the σ^* values for β-substitution are strongly correlated with the values for α-substitution (with $\sigma_\beta^* \approx 5\ \sigma_\alpha^*$ as can be seen in Table 4), the relative rate constants will necessarily give a linear relation with σ_β^* if they do with σ_α^*. The variation of log (k/k_0) vs $(\sigma^* - \sigma_0^*)_\beta$ for 1-olefin formation (β-elimination) from primary alcohols over the NHA catalyst is given in Table 4 and is shown in Fig. 4. At 282°C, values of $\rho_\beta^* = -1.2$ and $\rho_\alpha^* = -6.0$ were derived; the latter is about 30% larger than the ρ_α^* value for total dehydration at this temperature given in Table 2. Variations of β-elimination rate constants for secondary alcohols are compared for the two catalysts in Fig. 5. At 282°C, the value of $\rho_\beta^* = -1.0$ for the NHA catalyst is in good agreement with that for the primary alcohols. For the HA catalyst, $\rho_\beta^* =$

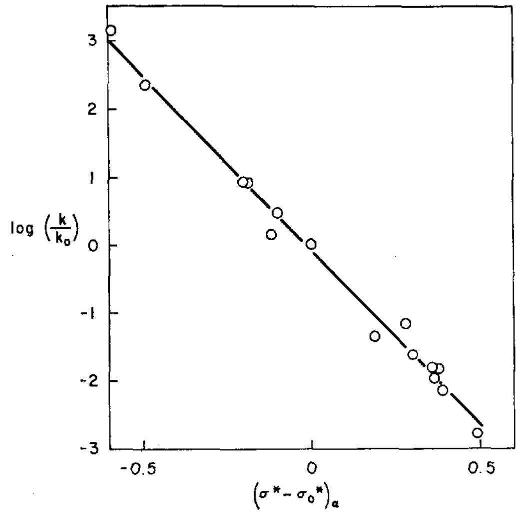


FIG. 1. Variation of alcohol dehydration rate constants with Taft σ* (Ref. *19*) for reactions over calcium-deficient hydroxyapatite at 230°C. The reference compound is isopropanol and the data (Table 2) are for α-substitution.

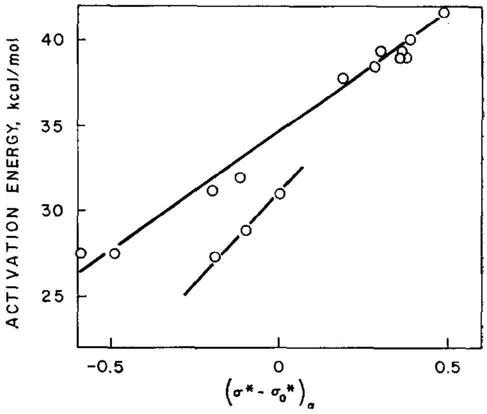


FIG. 2. Variation of activation energy with Taft σ* (Ref. *19*) for alcohol dehydration over calcium-deficient hydroxyapatite. The reference compound is isopropanol and the data (Table 2) are for α-substitution.

TABLE 3

EFFECTS OF α-SUBSTITUTION ON DEHYDRATION OF ALCOHOLS OVER STOICHIOMETRIC HYDROXYAPATITE (Ca/P = 1.67)

Alcohol	$(\sigma^* - \sigma_0^*)_\alpha$[a]	$\log(k/k_0)$[b] $10^3/T = 1.8$	$10^3/T = 1.5$	E[c]	$\log A$[c]
Propyl	0.39	−0.50	−0.85	29.0	1.8
2-Propyl	0	0	0	34.2	4.4
(k_0, mole/m²/sec)		(7.9×10^{-10})	(1.4×10^{-7})		
2-Butyl	−0.10	0.11	−0.02	32.0	3.6
2-Pentyl	−0.115	0.32	0.27	33.5	4.4
3-Methyl-2-Butyl	−0.19	0.35	0.11	30.4	3.2
3-Pentyl	−0.20	0.27	0.05	30.8	3.2
t-Butyl	−0.49	1.64	1.23	28.6	3.8
t-Pentyl	−0.59	1.80	1.38	27.7	3.6
$(\rho_\alpha^*)_r$[d]		−2.5 ± 0.3	−2.3 ± 0.2		
$(r_\alpha^*)_r$[e]		0.94	0.96		

[a] As defined in Table 2.

[b] As defined in Table 2.

[c] As defined in Table 2. Standard deviations of ±2 kcal/mole for E and ±2 for $\log A$ are higher than those for Table 2.

[d] As defined in Table 2; standard deviations are shown.

[e] As defined in Table 2.

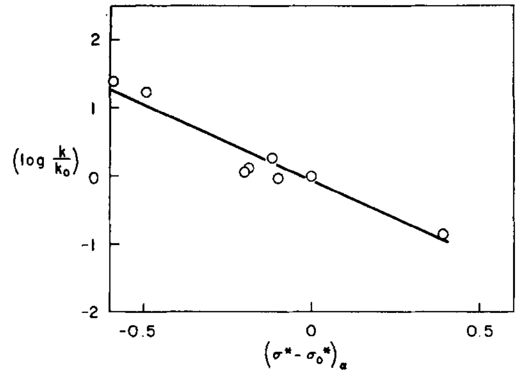


FIG. 3. Variation of alcohol dehydration rate constants with Taft σ^* (Ref. *19*) for reactions over stoichiometric hydroxyapatite at 395°C. The reference compound is isopropanol and the data (Table 3) are for α-substitution.

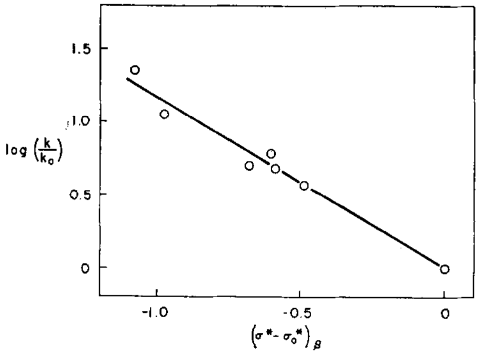


FIG. 4. Variation of β-elimination rate constants with β-substitution. Intermolecular comparisons of primary alcohol dehydration over calcium-deficient hydroxyapatite at 282°C. The reference compound is ethanol and the data (Table 4) are for β-substitution.

TABLE 4

EFFECTS OF β-SUBSTITUTION ON ALCOHOL DEHYDRATION OVER HYDROXYAPATITE. INTERMOLECULAR COMPARISONS OF β-ELIMINATIONS

A. Primary alcohols:

	$(\sigma^* - \sigma_0^*)_\beta$[a]	$(\sigma^* - \sigma_0^*)_\alpha$[b]	$\log(k/k_0)$[c], NHA catalyst			
			$10^3/T = 1.8$		$10^3/T = 1.6$	
Ethyl	0	0	0		0	
Propyl	−0.49	−0.10	0.57		0.50	
Butyl	−0.59	−0.115	0.68		0.65	
Pentyl	−0.605	−0.13	0.78		0.69	
Isopentyl	−0.68	−0.125	0.70		0.56	
Isobutyl	−0.98	−0.19	1.05		0.96	
2-Methyl-1-Butyl	−1.08	−0.21	1.35		1.21	
				r^*[f]		r^*[f]
$(\rho_\beta^*)_r$[d]			(−1.2)	0.98	(−1.1)	0.98
$(\rho_\alpha^*)_r$[e]			(−6.1)	0.99	(−5.5)	0.99

B. Secondary alcohols:

	$(\sigma^* - \sigma_0^*)_\beta$[a]	$(\sigma^* - \sigma_0^*)_\alpha$[b]	$\log(k/k_0)$[c] at $10^3/T = 1.8$			
			NHA catalyst		HA catalyst	
2-Propyl	0	0	0		0	
2-Butyl	−0.49	−0.10	0.49		0.21	
3-Methyl-2-Butyl	−0.98	−0.19	1.01		0.40	
				r^*[f]		r^*[f]
$(\rho_\beta^*)_r$[d]			(−1.03)	0.99	(−0.41)	0.99
$(\rho_\alpha^*)_r$[e]			(−5.3)	0.99	(−2.1)	0.99

[a] Taft σ_β^* values (*19*) for substitution at β-carbon.

[b] Taft σ_α^* values (*19*) for substitution at α-carbon.

[c] Rate constant ratio for β-elimination from substituted carbon.

[d] Constant from least squares fit of $\log(k/k_0) = \rho_\beta^*(\sigma^* - \sigma_0^*)_\beta$.

[e] Constant from least squares fit of $\log(k/k_0) = \rho_\alpha^*(\sigma^* - \sigma_0^*)_\alpha$.

[f] Correlation coefficients for fits made in *d* and *e*.

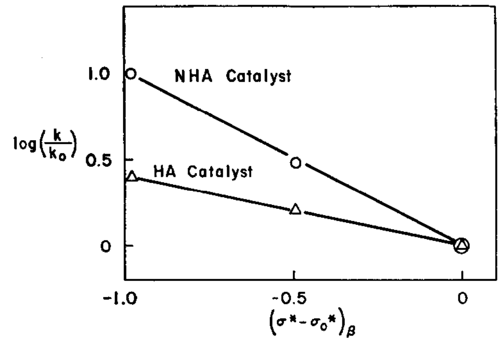


FIG. 5. Variation of β-elimination rate constants with β-substitution. Intermolecular comparisons of secondary alcohol dehydration at 282°C. The reference compound is isopropanol and the data (Table 4) are for β-substitution.

-0.4 and $\rho_\alpha{}^* = -2.1$ at the same temperature. The effects of β-substitution on (total) β-elimination rates are therefore predictable from the effects of α-substitution.

A more subtle effect of β-substitution is on the selectivity between alternate modes of β-elimination from secondary and tertiary alcohols. A negative value of $\rho_\beta{}^*$ for alkyl group substitution would be associated with Saytzeff (*12*) and a positive value with Hofmann (*11*) orientation when comparing elimination from two branches of an alcohol. Data concerning this type of selectivity are given in Table 5 and are plotted in Fig. 6 for both catalysts. The less substituted group in each case studied was methyl, so all of the alcohols had the same reference group. Over the NHA catalyst at 282°C, the $\rho_\beta{}^*$ value for this intramolecular β-substitution was -0.6, while it was -0.3 over the HA catalyst. Saytzeff (*12*) orientation was therefore favored over both catalysts and a LFER relation was obeyed for each. Comparison of the data in Figs. 5 and 6 shows that β-substitution also accelerated elimination from the unsubstituted β-carbon over the NSA catalyst, and that the $\rho_\beta{}^*$ values were much larger for an intermolecular comparison than for an intramolecular comparison. Over the HA catalyst the effect was mainly localized in the substituted branch and the $\rho_\beta{}^*$ values were more nearly equal for the two types of comparison.

Another type of product selectivity in dehydrations of secondary alcohols is *cis/trans* selectivity in 2-olefin formation. Data for this are presented in Table 6. Comparisons of *cis/trans* ratios among the three alcohols studied, as well as activation energy differences between *cis*-2-olefin and *trans*-2-olefin formation were fairly precise. The

TABLE 5

EFFECTS OF β-SUBSTITUTION ON ALCOHOL DEHYDRATION OVER HYDROXYAPATITE. INTRAMOLECULAR COMPARISON OF β-ELIMINATIONS

Alcohol	$(\sigma^* - \sigma_0{}^*)_\beta{}^a$	$\log(k/k_0)^b$ at $10^3/T = 1.8$ NHA catalyst	 HA catalyst
2-Butyl	−0.49	0.33	0.27
2-Pentyl	−0.59	0.27	0.21
3-Methyl-2-Butyl	−0.98	0.62	0.33
t-Pentyl	−0.49	0.32	0.17
$\rho_\beta{}^{*\,c}$		−0.61	−0.36
$r_\beta{}^{*\,d}$		0.99	0.97

[a] Taft $\sigma_\beta{}^*$ values (*19*) for group on substituted carbon, relative to hydrogen (on methyl carbon).

[b] Ratio of rate constant for elimination from the substituted group to that for elimination from the methyl group. Values for *t*-pentanol corrected by multiplying k/k_0 by two.

[c] Constant for least squares fit of $\log k/k_0 = \rho_\beta{}^*(\sigma^* - \sigma_0{}^*)_\beta$.

[d] Correlation coefficient for fit made in *c*.

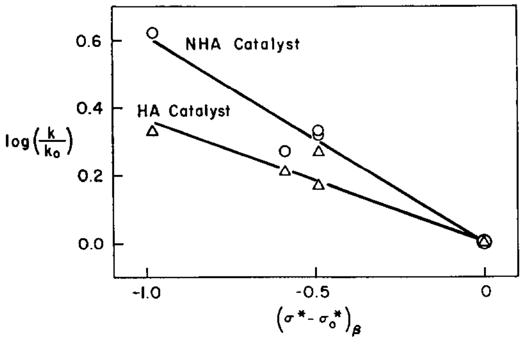


FIG. 6. Variation of β-elimination rate constants with β-substitution. Intramolecular comparison of secondary alcohols at 282°C. The reference compound was isopropanol and the data (Table 5) are for β-substitution.

TABLE 6

cis/trans RATIOS IN DEHYDRATIONS OF SECONDARY ALCOHOLS OVER HYDROXYAPATITE

Alcohol	Catalyst[a]	Ratio[b]	Value at 282°C	$(E_t - E_c)$[c]	(A_c/A_t)[d]
2-Butyl	NHA	c2B/t2B	1.46	2.6	0.14
	HA		1.43	2.3	0.18
2-Pentyl	NHA	c2P/t2P	1.12	2.2	0.15
	HA		1.08	2.4	0.13
3-Pentyl	NHA	c2P/t2P	0.91	2.0	0.15
	HA		0.93	2.3	0.11

[a] NHA = hydroxyapatite with Ca/P = 1.58.
HA = hydroxyapatite with Ca/P = 1.67.

[b] c = cis, t = trans, B = butene, P = pentene.

[c] Activation energy difference, kcal/mole.

[d] Ratio of preexponential factors, from $(cis/trans) = (A_c/A_t) \exp (E_t - E_c)/RT$.

absolute values of the ratios varied by as much as 50% from those given in the table, depending upon the state of the catalyst. Comparisons between catalysts were therefore difficult, but the data in Table 6, which are averages of many runs, indicate that there was no significant difference between the NHA and HA catalyst with respect to *cis/trans* ratios. For both catalysts, introduction of larger alkyl groups decreased the *cis/trans* ratio. This is apparently due to a lower activation energy *difference* favoring the *cis*-2-olefin over the NHA catalyst, whereas it seems to be related to a lower frequency factor ratio with the HA catalyst. The data were not sufficiently precise, however, for such distinctions to be considered established.

Dehydrogenation

The stoichiometric hydroxyapatite dehydrogenated primary alcohols to aldehydes and secondary alcohols to ketones. Under most of the conditions investigated, these reactions were faster than dehydration over a fresh catalyst. Condensation reactions were even faster for the aldehydes formed from primary alcohols so that the major

TABLE 7

EFFECTS OF α-SUBSTITUTION ON DEHYDROGENATION OF ALCOHOLS OVER STOICHIOMETRIC HYDROXYAPATITE (Ca/P = 1.67)

		$\log(k/k_0)$[b]			
Alcohol	$(\sigma^* - \sigma^*_0)_\alpha$[a]	$10^3/T = 1.8$	$10^3/T = 1.5$	E[c]	$\log A$[c]
2-Propyl	0	0	0	24.0	1.2
(k_0, mole/ml/sec)		(4.9×10^{-9})	(1.7×10^{-7})		
2-Butyl	−0.10	−0.03	−0.18	21.7	0.2
2-Pentyl	−0.115	−0.12	−0.15	23.4	0.8
3-Methyl-2-Butyl	−0.19	−0.29	−0.37	23.3	0.6
3-Pentyl	−0.20	−0.13	−0.24	22.3	0.3
$(\rho_\alpha^*)_T$[d]		+1.11 (±0.08)	+1.52 (±0.06)		
$(r_\alpha^*)_T$[e]		0.79	0.91		

[a] As defined in Table 2.

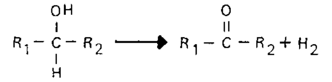
[b] Ratio of dehydrogenation rate constants at specified temperature. k_0 is for acetone from 2-propanol.

[c] As defined in Table 2. Standard deviations of E were ±2 kcal/mole, standard deviations of $\log A$ were ±2.

[d] As defined in Table 2. Standard deviations are shown.

[e] As defined in Table 2.

products were often neither aldehyde nor olefin. Hence, the rate data for these dehydrogenations were not very reproducible. Secondary reactions of ketones were much slower and the data more reliable. Some zero order rate constants for secondary alcohol dehydrogenation are reported in Table 7. The activation energies were lower than those for dehydration by 7–10 kcal $mole^{-1}$, and the *A* factors lower by a factor of about 10^3. Only one ketone product was formed from each alcohol, according to Eq. 4:



$$R_1-\overset{OH}{\underset{H}{C}}-R_2 \longrightarrow R_1-\overset{O}{\overset{\|}{C}}-R_2+H_2 \qquad (4)$$

Molecular hydrogen, not water, was formed as expected since no reduction of hydroxyapatite is possible. The relative rate constants at 395°C ($10^3/T = 1.5$) varied in accord with σ_α^* for α-substitution as shown in Fig. 7. The positive value of ρ_α^* obtained, 1.5, suggests that a negative charge is developed at the α-carbon in the transition state for dehydrogenation. It may be compared with the value of $\rho_\alpha^* = -2.3$ at the same temperature for dehydration. At 282°C, the corresponding values were $\rho_\alpha^* = -2.5$ for dehydration (of secondary alcohols). The range in σ_α^* values (0.2) was quite small for dehydrogenation, and the correlation coefficients were not as high as those for dehydration.

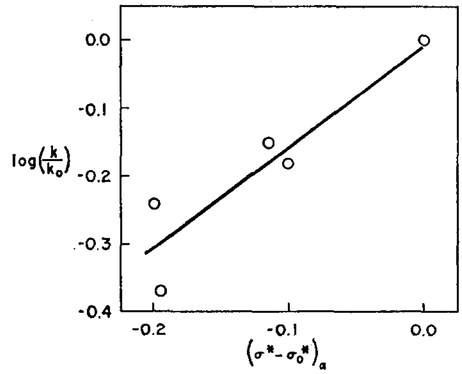


FIG. 7. Variation of alcohol dehydrogenation rate constants with Taft σ^* (Ref. *19*) for reactions over stoichiometric hydroxyapatite at 395°C. The reference compound was isopropanol and the data are for α-substitution.

DISCUSSION

The relative rate constants for most olefin-forming eliminations from α-methyl substituted compounds fall in the order (*15*, *20*):

t-butyl ≫ isopropyl ≫ ethyl.

The induction of an α-methyl group has an adverse effect on the acidity of β-hydrogens (*13*) but helps stabilize a positive charge at the α-carbon; through hyperconjugation, an α-methyl group will also help stabilize the double bond as it is formed. The increasing positive charge on the α-carbon tends to shift the mechanism towards the E1 extreme (*14*). As shown in Table 8, not only the order but the magnitudes of the relative rate constants for reactions of a variety of α-methyl substituted compounds are nearly the same for several quite different conditions. These data may be correlated by the Taft equation (*16*, *19*), leading to negative values of ρ_α^* (-2 to -3). Hence, these reactions may all be classed as concerted, but with an appreciable amount of charge separation in their transition states. After Maccoll (*15*), we would refer to them as "quasiheterolytic." The data for alcohol dehydration over the calcium-deficient hydroxyapatite are in remarkable agreement with those for both gas-phase and solution reactions (Table 8).

The effects of β-substitution depend much more upon the reaction mechanism than do those of α-substitution. A β-methyl group will tend to stabilize a partially-formed α–β double bond in an E2 transition state, just as will an α-methyl group. Its stabilizing influence on a positive charge at the α-carbon will be much weaker, however, while its adverse effect on β-hydrogen acidity will be much stronger (*13*). Thus, β-methyl substitution should cause a smaller rate increase than an α-methyl substitution. In fact, for transition states on the E1cB side, for which C–H bond breaking is further advanced than the C–X bond breaking at the α-carbon (*14*), β-methyl substitution will retard the rate of elimination. Thus,

TABLE 8

EFFECTS OF ALKYL SUBSTITUENTS ON ELIMINATION RATE CONSTANTS

	Relative rate constants						
	Catalyzed alcohol dehydration		Gas phase pyrolysis			Solution reactions (E2, by OEt-)	
Alkyl group	HBr[a]	NHA catalyst[b]	Acetate[c]	Formate[c]	Bromide[d]	Sulfonium[e] ion	Bromide[e]
Ethyl	1	1	1	1	1	1	1
2-Propyl	25	26	26 (24)	20	140	23	10
t-Butyl	1600	2000	1000 (2000)	720	10,000	590	120
[Temp, °C]	440	440	400	400	440	45	25
2-Propyl	1	1	1	—	1	1	1
2-Butyl	2.0	1.5	0.96 (1.6)	—	1.7	0.7, (2.0)[f]	1.5
[Temp, °C]	446	440	308 (411)	—	440	64	2.5
t-Butyl	1	1	1	—	1	1	1
t-Pentyl	1.7	6.0	1.5 (2.5)	—	2.4	0.7, (4.6)[f]	4.2
[Temp, °C]	361	361	237 (311)	—	361	25	25
Orientation[g]	[S]	S	H	—	[S]	H [S]	S

[a] Homogeneous, bimolecular gas phase reaction. From data of Stimson (*21–26*).

[b] Reaction over calcium-deficient (Ca/P = 1.58) hydroxyapatite.

[c] Unimolecular gas phase reactions. Data of Maccoll (*27*) and Scheer *et al.* (*28*) (in parentheses), taken from Ref. *15*.

[d] Data of Thomas (*29*), Maccoll and Thomas (*30*), and Sergeev (*31*), taken from Ref. *15*.

[e] In dry ethanol. Data of Hughes *et al.* (*13*).

[f] For unimolecular E1 reaction in same solvent. Data of Hughes *et al.* (*13*).

[g] S = Saytzeff orientation, H = Hofmann orientation. Brackets indicate products may have isomerized.

positive ρ_β^* values result in correlations of ethyl, propyl, and isobutyl elimination rates from positive ions such as alkylammonium and alkylsulfonium ions (*13*). In these cases, steric effects have also been proposed (*32*, *33*) to account for Hofmann elimination. While Hofmann elimination is characteristic of E1cB-like states, those on the E1-side, as evidenced by a negative ρ_α^* value for overall rates, may *also* follow the "generalized" Hofmann rule. For instance, *t*-pentyl acetate undergoes elimination considerably faster than *t*-butyl acetate (Table 8), but the product from *t*-pentyl acetate pyrolysis is mainly 2-methyl-1-butene (*15*). The necessity, in acetate pyrolysis, that the leaving group also be the base which abstracts the β-proton evidently introduces steric factors which lead to the Hofmann-rule product.

The expectations for olefin-forming eliminations catalyzed by polar surfaces are that α-substitution should increase reaction rates of normal, "quasi-heterolytic" eliminations. This has indeed been found for many reactions on many surfaces (*2*, *9*, *34*). For most eliminations from neutral molecules such as esters, halides, and alcohols, the leaving group is sufficiently electronegative to expect that the reaction mechanism will be on the E1 side, and that Saytzeff orientation and increases in rate with β-substitution should be common. Hofmann orientation would not be expected unless the catalysts' basic centers were very strong and its acid centers weak (mechanism on the E1cB side), or unless steric requirements were very important. Both Hofmann and Saytzeff orientations have been observed (*2*, *34*, *35*).

Considering only an alcohol molecule, it is difficult to think of reasons why more *cis*-olefin might be produced than *trans*. Eclipsing of α- and β-alkyl groups, which is necessary when *cis*-olefins are formed via transition states with significant double bond character, or by *syn*-elimination, is not a factor in the formation of the *trans*-olefin. Special interactions which alter the picture may occur when a solid surface intervenes. Thus, high *cis/trans* ratios have been found (*42*) for *anti*-elimination from 2-butanol over alumina, because most of the molecular configurations which could produce *trans*-2-butene require a methyl group to be directed into the surface. *Cis*-selectivity should be traceable to a lower activation energy for this pathway.

The factors influencing *syn*- and *anti*-elimination are not fully understood, even for homogeneous reactions (*35*, *41*). The gauche configurations of the molecule are lower in energy than the eclipsed configurations which are necessary for *syn*-elimination. Thus, when the latter is obtained, particular interactions must be present which compensate for this energy cost, e.g., the formation of a closed ring involving charge-transfer interactions. In solution, *syn*-elimination has been ascribed to E1cB transition states (*43*) and to steric factors (*44*). Bulky groups, both in the substrate molecule and in the attacking base, can influence the direction of the elimination (*36*, *44*). In this connection, a solid surface should present very pronounced steric requirements so that *syn*-elimination might be expected to be common. Actually, the opposite is true (*2*, *9*, *34*) although complete stereospecificity has not been found for any surface-catalyzed reaction (*34*, *42*). A possible rationale is that *anti*-elimination occurs when a surface anion vacancy is filled by the hydroxyl group of the adsorbing alcohol, as with alumina (*42*), and that *syn*-eliminations will occur with a Bronsted acid when a cyclic transition state is formed involving the alcohol and the acidic surface OH.

Dehydration over hydroxyapatite was found to obey the Saytzeff rule. The effects of both α- and β-substitution were greater on the more acidic NHA than over the HA catalyst. β-substitution also accelerated elimination from unsubstituted branches of secondary and tertiary alcohols over NHA, while its effect was mainly localized in the substituted branch over HA. These findings were consistent with an "E1-like" transition state for both catalysts, with the mechanism over HA being more nearly synchronous, i.e., with a lower positive charge developed on the α-carbon.

Syn-elimination was shown to be the preferred mode over NHA, and a kinetic isotope effect, $k_H/k_D = 1.5$ at 300°C, was reported (*42*) for elimination of a β-hydrogen. The stereoselectivity was not complete; larger amounts of *anti*-elimination products were obtained than is usual for *syn*-eliminations in homogeneous systems. Lack of complete stereoselectivity in surface reactions has been suggested (*34*) to be caused by competition from a nonselective E1 mechanism. In our view, it is possible both for E1 surface reactions to be selective and E2 reactions, nonselective. Hence, a lack of stereoselectivity does not necessarily imply a transition state in which the identities of β-hydrogens are lost.

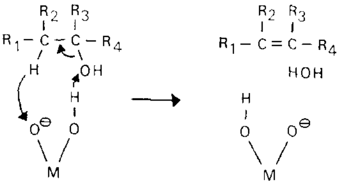
The *cis/trans* ratios in 2-olefin formation were nearly identical for both catalysts at a given temperature (Table 6). As in many surface-catalyzed dehydrations (*2*, *34*), the *cis*-2-olefins were formed as fast or faster than the corresponding *trans*-2-olefins. The data show that this was due to lower activation energies (2–3 kcal/mole) for the formation of the *cis*-2-olefins than for either *trans*-2-olefins or 1-olefins (matched by lower *A*-factors). As noted above, it is difficult to conceive of steric intramolecular interactions which would favor formation of the *cis*-2-olefins. Therefore, steric interactions with the surface probably play a controlling role. Such factors are known (*45*) to lead to *cis/trans* ratios near unity in the isomerization of 1-butene via an E1 mechanism.

The rate constant data in Tables 2 and 3 were for zero order kinetics (*18*) and thus represent the reactions of surface species. Changes in *A*-factor ratios due to surface coverages should not be important, nor should heats of adsorption be included in the activation energies. The *A*-factors for primary alcohol dehydration did not vary more than a factor of 2 from the mean value, and for all fifteen alcohols dehydrated over NHA, the average deviation from the mean value of log A was only 0.7 (a factor of 5). The major factor affecting the dehydration rates on both catalysts was the activation energy. The range of activation energies on NHA was 14.2 kcal/mol, corresponding to a rate difference of 4×10^5 at 282°C.

Comparing catalysts, it is seen that the activation energy differences for tertiary alcohols were very small, and that the differences in dehydration rates were mainly due to differences in the A-factors. The latter were 10–100 times greater on NHA than on HA, comparable to similar differences in the numbers of HPO_4^{2-} ions (*17, 18*) and in the number of carbonium ions which could be formed from indicators such as trianisylcarbinol (*17*). There was a definite trend in the differences in A-factors between the two catalysts depending upon alcohol structure, with smaller differences for lesser degrees of substitution. At the same time, activation energy differences increased, so that the activation energies for secondary alcohols were 2–3 kcal/mole lower on NHA than on HA. This suggests that the dehydrations became progressively more dependent upon the intensive properties of the catalyst (acidities) as the alcohol molecule itself became less able to ionize, but that for more readily ionized molecules such as t-butanol, the number of acid sites was more important. These findings suggest that a distribution of sites of varying acidity are present on the catalyst surface.

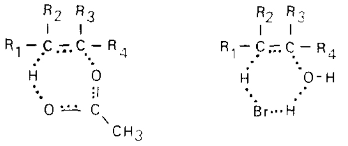
The differences between secondary and tertiary alcohol dehydration can be related to differences in the ease of forming secondary and tertiary carbonium ions. It was found, for example, that 2-methyl-1-butene and 2-methyl-2-butene were readily interconverted over both catalysts although at much slower rates over HA. Linear olefins and 3-methyl-1-butene were not isomerized at 300°C. Since the t-pentyl ion is 10–15 kcal/mole lower in energy than the 3-methyl-2-butyl ion (*46*) in acid solutions, a similar energy difference may be expected on hydroxyapatite. Consequently, tertiary alcohols may be dehydrated via carbonium ion formation (E1 mechanism), but this pathway is not possible for secondary or primary alcohols. The latter must be dehydrated in concerted reactions, although these may be on the E1 side (*14*).

As with some other oxide systems, extensive dehydration of the NHA catalyst lowered its dehydration activity. Hence, the involvement of OH groups at the surface seems probable and the exchange mechanism of Eucken and Wicke (*3–6*) can be applied to the dehydration of alcohols over hydroxyapatite, i.e.,



(5)

It is possible that only one surface oxygen (the acidic hydroxyl group) is involved. The cyclic six-membered ring transition state which would be formed in the latter case has also been postulated for acetate pyrolysis (*47*) and HBr-catalyzed alcohol dehydrations (*15, 21–26*), i.e.,



(6)

A cyclic transition state is attractive in that it provides a ready explanation for *syn*-elimination.

A survey of the literature reveals that the substituent effects on rate constants of many surface-catalyzed olefin-forming reactions may be correlated by the Taft Eq. 3 (*48–63*). Most of these results yielded negative values of ρ_α^* (between -2 and -8); like the examples in Table 8, the reactions were "quasi-heterolytic." Alcohol dehydration over hydroxyapatite was typical of these contact eliminations in that Saytzeff orientation and high *cis/trans* ratios were obtained. It was atypical in that the direction of elimination was *syn*, which has usually been associated with Hofmann orientation.

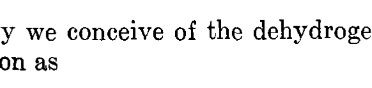
Since the Taft equation is believed to

account solely for the inductive effects of a substituent at a *saturated* carbon atom (*64*), it is surprising that it works so well for elimination reactions. In these, the hybridization at the α-carbon changes from sp^3 to sp^2 so that effects of resonance (hyperconjugation) might be expected. Also, steric effects must be important in surface reactions.

For α-methyl substitution, the effects of hyperconjugation should be in the same direction as inductive effects, and the same additive property seems to hold (*65, 66*). Likewise, steric effects are correlated with σ^* for small changes in the substituent. Thus, neither steric nor resonance interactions grossly change the relation with σ_α^* and they may reinforce it. As most surfaces cannot aid a heterolytic reaction to the extent that is possible by solvation in liquid media, the iductive effects of substituents in stabilizing or opposing a charge should be much more critical for the surface reactions. This will tend to overcome small perturbations by steric or resonance effects and results in good correlations of rate constants with σ_α^*.

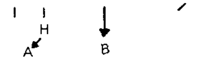
Alcohol dehydrogenation over hydroxyapatite yielded positive σ_α^* values, in accord with data from the literature (*48, 56, 57*). Thus, high electron density at the α-carbon is implied for the dehydrogenation transition state, whereas that for dehydration must have been electron deficient. This is in agreement with the expectation that heterolytic cleavage of the bond to oxygen is easiest in each case.

Just as the dehydration mechanism may be pictured as a nearly concerted elimination involving an acidic and a basic site, A and B respectively, i.e.,



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH \longrightarrow \;>C=C<\; + BH + AOH \qquad (7)$$

so may we conceive of the dehydrogenation reaction as



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O-H \longrightarrow \;-\overset{\diagdown}{C}-\overset{\diagdown}{C}=O + HA + HB \qquad (8)$$

In dehydration (Eq. 7), it is the C–O bond which is cleaved and the β-hydrogen which is discharged to the basic site; in dehydrogenation (Eq. 8), it is the alcoholic proton which is discharged to the basic site and the α-hydrogen to the acid. The identification of sites A and B for dehydrogenation is not as certain as for dehydration, but it is clear that they both cannot be the same for both reactions. This is because when the reactions are occurring simultaneously they have different poisoning characteristics. For dehydrogenation, possible choices for A include catalyst cations or the protons of HPO_4^{2-} groups; choices for B are OH^- and PO_4^{3-} groups.

In the apatite structure, monovalent anions (F^-, Cl^-, OH^-) occupy column positions at or near the centers of calcium ion triangles (*67, 68*). Anion adsorption from aqueous solutions is very strong, especially by "stoichiometric" hydroxyapatite (*69–74*). The sites responsible are probably the calcium ion triangles because the adsorption is decreased by fluoride ion substitution (*75*). It is also decreased where there is a calcium ion deficiency (*76*). The effects of fluoride substitution and calcium ion deficiency on the anion adsorption properties are exactly paralleled by their effects on alcohol dehydrogenation activity (*18, 77*). Dehydrogenation of primary and secondary alcohols was the predominant mode of decomposition over HA ($Ca/P = 1.67$), whereas NHA ($Ca/P = 1.58$) was inactive for this purpose. Similarly, fluoriding HA eliminated its dehydrogenation activity while increasing that for dehydration (*77*).

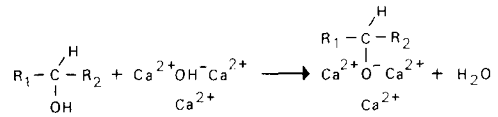
Alkoxide bands were found in the ir spectra (*78*) of 2-butanol adsorbed on hydroxyapatite; these disappeared on heating HA, and carboxylate and adsorbed ketone bands appeared concommitantly. The latter were not observed with NHA because desorption or dehydration of the alcohol occurred instead. Similarly, carbonate bands appeared on HA, but were very weak or absent with NHA when CO_2 was adsorbed (*78*). The CO_2 adsorption and reaction was probably with the hydroxyl ions at the calcium ion triangles (*79*), i.e.,

$$CO_2 + OH^- \longrightarrow HCO_3 \qquad (9)$$

and

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \qquad (10)$$

Catalytic dehydrogenation and carboxylate formation may have also occurred at the calcium ion triangle sites, and the carboxylate may have acted as a poison for dehydrogenation. Alkoxide formation may be visualized as



$$R_1-\overset{H}{\underset{OH}{C}}-R_2 + Ca^{2+}\underset{Ca^{2+}}{OH^-}Ca^{2+} \longrightarrow \overset{R_1-\overset{H}{C}-R_2}{Ca^{2+}\underset{Ca^{2+}}{O^-}Ca^{2+}} + H_2O \qquad (11)$$

In the catalytic reaction, the α-hydrogen (H^-) may combine with the proton of an adjacent HPO_4^{2-} group to yield H_2 and the adsorbed ketone. An anion vacancy is created on desorption of the ketone, which may be used to carry on the catalytic chain by the dissociative adsorption of an alcohol molecule to recreate the alkoxide species of Eq. 11 and the HPO_4^{2-} group. The salient feature of this mechanism is the rate-determining hydride transfer from an alkoxide at the calcium ion triangle. A fluoride or carboxylate ion at the triangle site would render it ineffective for the dehydrogenation reaction. Consistent with the view that the transition state is negatively charged, e.g., as an alkoxide ion, is the positive ρ_α^* value obtained when dehydrogenation rate constants are correlated with the σ_α^* parameter.

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