of the 2-methylhexyl ion was measured in the reaction system consisting of 2-methylpentane and 2-methylhexane and also in a three-component equilibrium system where, in addition, 2-methylbutane was also present. The results obtained in the two-component system were in satisfactory agreement with those obtained in the three-component system.

Values (averages of replicate measurements) of heats of formation, relative entropies, and hydride ion affinities for four tertiary C_7^+ alkyl carbonium ions are given in Table I. Two sets of values are given for 2-methylhexyl ion, where each set is obtained using a different reactant ion. The heats of formation of the reactant ions, i.e., 2-methylbutane and 2-methylpentane, had in turn previously been measured[2] in their reaction with isobutane. The agreement of the values for the 2-methylhexyl ions thus provides a measure of the internal consistency in a cycle involving four different equilibrium studies. The average of the two values of hydride affinity for this ion is virtually identical with the value obtained previously[2] for 2-methylpentyl ion (232.1 kcal/mol). Thus the additional methylene group does not affect the intrinsic stability of the ion. The hydride affinity of 2,4-dimethylpentyl ion is lower than that of 2-methylhexyl ion by an amount which is only marginally significant. The values for 3-ethylpentyl ion and 2,2,3-trimethylbutyl ion are somewhat lower. The results can be rationalized by the idea that the intrinsic ion energy is affected by the number of alkyl groups attached to carbon atoms α to the nominal charge center.

In evaluating the results as presented in Table I it must be remembered that the structures of ions in our reaction systems cannot be demonstrated. If rearrangements occur, our observed equilibrium constants are actually steady-state constants for reactions involving different isomers, and the thermodynamic values are incorrect to an unknown extent. This question requires further studies of ion structures by independent techniques.

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Catalyzed Oxidation Reactions. I. Picolinic Acid Catalysis of the Chromic Acid Oxidation of Isopropyl Alcohol[1]

Sir:

We have reported earlier that the oxidation of alcohols by chromic acid is accelerated by several orders of magnitude if it is carried out in the presence of oxalic acid[2] or α-hydroxy acids.[3,4] In these cases the fast reaction resulted not only in the oxidation of the alcohol but also of the added acid; these reactions thus represented examples of cooxidations.

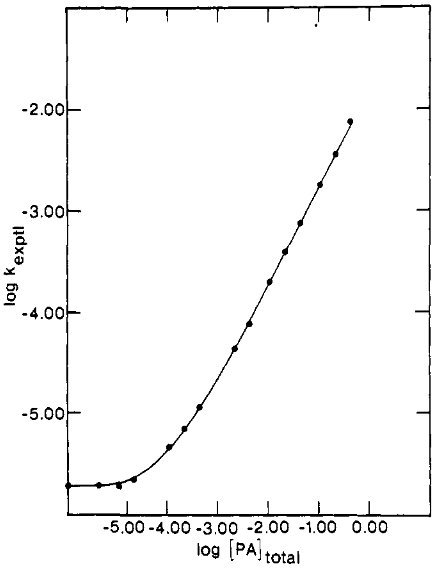


Figure 1. Picolinic acid catalysis: initial chromium(VI) = 4.50×10^{-4} M; isopropyl alcohol = 0.0186 M; H^+ = 0.1 M; ionic strength = 0.596 M; 25°.

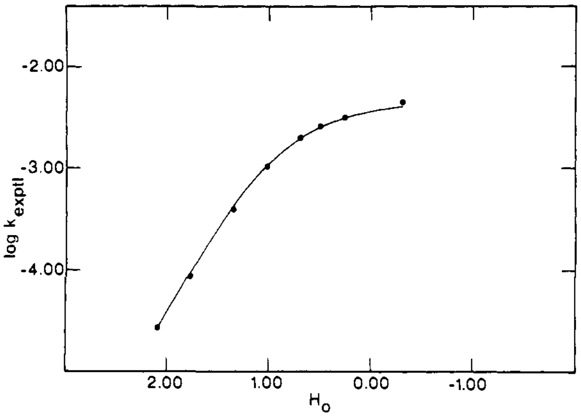


Figure 2. Acidity Dependence: initial chromium(VI) = 4.50×10^{-4} M; isopropyl alcohol = 0.0261 M; picolinic acid = 0.0472 M; ionic strength = 1.18 M; 25°. (Curve calculated from eq 1.)

Table I. Chromic Acid Oxidation Rates[a] with Pyridine Carboxylic Acids in 0.185 M Perchloric Acid at 25° [b]

Pyridinecarboxylic acid (concn, M)	$10^4 k_{exptl}$, s^{-1}
None	4.25
Picolinic acid (1.54×10^{-2})	306
2,4-Pyridinedicarboxylic acid (1.54×10^{-2})	1210
2,6-Pyridinedicarboxylic acid (1.32×10^{-2})	24.2
Nicotinic acid (1.47×10^{-2})	3.06
Isonicotinic acid (1.46×10^{-2})	3.43
2-Pyridylacetic acid (1.54×10^{-2})	3.79

[a] Rates were determined spectrophotometrically at the absorption maximum for chromium acid (350 nm) under pseudo-first-order conditioning. [b] Isopropyl alcohol = 0.928 M.

We now wish to report the first example of a specifically catalyzed oxidation of an organic substrate by chromic acid. While picolinic acid alone reacts with chromic acid only very slowly, it exhibits a very strong rate accelerating effect on the reaction between chromic acid and isopropyl alcohol (Figure 1). Nevertheless, practically quantitative yields of acetone are obtained.

The picolinic acid catalysis is highly specific and is related to the proximity of the nitrogen atom and the carboxylic group: 2,6- and 2,4-pyridinedicarboxylic acids also catalyze

Table II. Effect of the Concentration of Isopropyl Alcohol on Oxidation Rates at 25° [a]

$[HClO_4]$, M	[ROH], M	$[PA_T]$, M	k_{exptl}, s^{-1}	$k_{exptl}/[ROH]$ $(M^{-1}\,s^{-1})$
1.85	0.117	0.0220	0.0162	0.14
1.85	0.0466	0.0220	0.0062	0.13
1.85	0.0230	0.0220	0.0033	0.14
1.85	0.00930	0.0220	0.0013	0.13
1.85	0.00465	0.0220	0.00058	0.12
0.102	0.371	0.0712	0.055	0.15
0.102	0.148	0.0712	0.0187	0.13
0.102	0.0742	0.0712	0.0101	0.14
0.102	0.0371	0.0712	0.0042	0.11
0.102	0.00371	0.0712	0.00043	0.11
0.102	0.00182	0.0712	0.000196	0.11
0.102	0.000910	0.0712	0.000121	0.13
0.102	0.000456	0.0712	0.000057	0.12
0.0118	0.131	0.118	0.0034	0.026
0.0118	0.0131	0.118	0.00033	0.025
0.0118	0.00652	0.118	0.000156	0.024

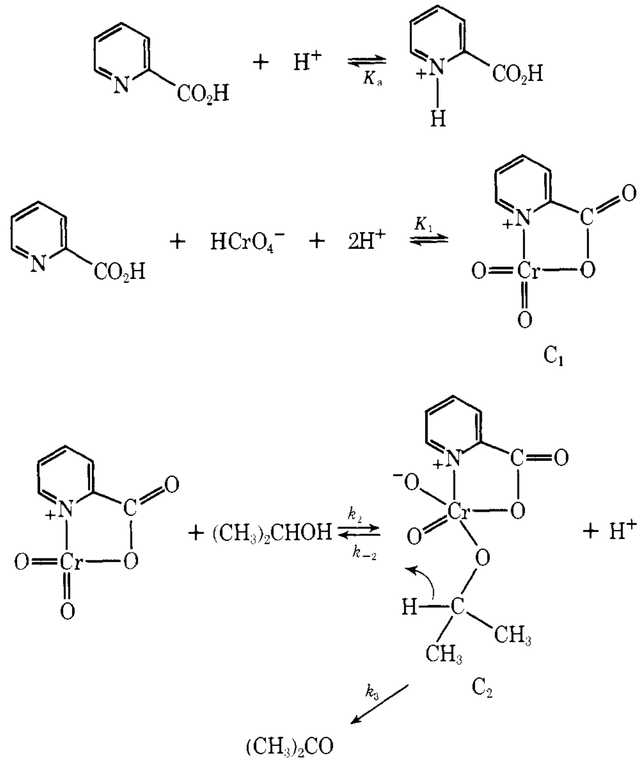
[a] Initial chromium(VI) = 6.24×10^{-4} M.

Table III. Isotope Effect in the Oxidation of 2-Deuterio-2-propanol with Different Acidities[a]

10^3H^+, M	k_H/k_D	10^3H^+, M	k_H/k_D
8.22	1.5	204	4.3
16.8	1.9	318	5.1
44.5	2.9	550	5.5
95.0	3.6		

[a] Picolinic acid (total) = 0.0472 M; isopropyl alcohol = 0.0261 M.

Scheme I



the oxidation, but nicotinic acid, isonicotinic acid, or 2-pyridylacetic acid are ineffective (Table I).

At constant acidity, the reaction is first order in chromium(VI), isopropyl alcohol, and in picolinic acid (Figure 1). It is also first order in isopropyl alcohol throughout the entire range of acidities (Table II). The acidity dependence is second order in hydrogen ions at low acidities and approaches a zero-order acidity dependency at high acid concentrations (Figure 2).

The deuterium isotope effect is also acidity dependent (Table III), indicating that the rate limiting step of the reaction involves the breaking of the carbon-hydrogen bond in the alcohol at high but not at low acidities.

These observations are consistent with the reaction mechanism shown in Scheme I, which involves the formation of a negatively charged termolecular complex (C_2) and its oxidative decomposition to reaction products. The carbon-hydrogen bond of the alcohol is broken in the latter step. The hydrolysis of the complex C_2 requires a proton and will therefore be acid catalyzed, while rate of the oxidative decomposition of C_2 is not. Consequently, the formation of C_2 will be reversible at high acidities but rate limiting at low acid concentrations.

The mechanism given in Scheme I leads to the rate law (eq 1)

$$k_{cat} = \frac{K_aK_1k_2k_3[PA_T][ROH][H^+]^2}{k_3K_a + (k_{-2}K_a + k_3)[H^+] + k_{-2}[H^+]^2} \qquad (1)$$

for the catalyzed reaction; the rate law can be derived from eq 2-6:

$$-\frac{d[HCrO_4^-]}{dt} = k_{cat}[HCrO_4^-] = k_3[C_2] \qquad (2)$$

$$[C_2] = \frac{k_2[C_1][ROH]}{k_{-2}[H^+] + k_3} \qquad (3)$$

$$[C_1] = K_1[PA][HCrO_4^-][H^+]^2 \qquad (4)$$

$$[PA] = \frac{[PA_T]K_a}{K_a + [H^+]} \qquad (5)$$

$$[PA_T] = [PA] + [PAH^+] \qquad (6)$$

where PA and PAH^+ represent picolinic acid and its protonated form; $K_a = 0.098$ is the acid dissociation constant of picolinic acid.[5] Equation 3 is obtained from applying the steady-state approximation to C_2. Figure 2 shows an excellent agreement between experimental points and the calculated curve.

We believe that the reason for the catalytic activity of picolinic acid depends on its ability to stabilize intermediate chromium valence states, probably chromium(IV), through complex formation.

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Singlet Molecular Oxygen from Hydrogen Peroxide Disproportionation[1]

Sir:

Despite the long recognized association of "active oxygen" with aqueous H_2O_2 solutions, the electronic excitation state of molecular oxygen evolved in base catalyzed (eq 1 and 2) or spontaneous (eq 3) disproportionation of H_2O_2