Acknowledgment

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Nomenclature

T = temperature, K
VP = vapor pressure, mm Hg
X = liquid mole fraction
Y = vapor mole fraction
α, β, δ = constants in vapor-pressure equations
γ = activity coefficient
π = total pressure, mm Hg

Subscripts

i = indefinite component number
j = indefinite component number
1 = acetone
2 = isopropenyl acetate
3 = acetic anhydride

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Dissociation Constants of 1(2-Pyridyl)-2-alkanones

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The acid dissociation constants of a homologous series of nine 1(2-pyridyl)-2-alkanones were determined by potentiometric titration. These pK_a's correlated with the Taft polar constituent constants (σ^*) for the ketones.

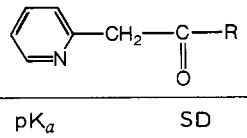
Previous studies have shown a strong correlation between Taft steric substituent constants and the equilibrium values for the enol-keto tautomerism of a series of 1(2-pyridyl)-2-alkanones (*6*). Since the acid dissociation constants for this series of ketones had not been determined, we felt it would be of value to measure these constants as well as to investigate any relationships they might have with Taft steric substituent constants, E_s, and/or Taft polar substituent constants, σ^*.

Experimental

The 1(2-pyridyl)-2-alkanones were prepared by the method of Goldberg et al. (*2*), and the synthesis as well as the physical properties and derivatives of these ketones has been reported previously (*3*). The ketones were purified on a Nester Faust annular teflon spinning band column, and the purity was checked by gas chromatography using a 5-ft × ¼-in., 3% S.E. 30 column in a Varian 90-P aerograph instrument. The pK_a's were determined by potentiometric titrations using conventional calculations (*1*). A Leeds and Northrup Model 7415 research pH meter, Beckman 39099 glass electrodes, and Beckman 39170 calomel reference electrodes were employed to monitor pH. The titrations were performed in a flow-through thermostated titration vessel. The temperature was controlled at 20.0° ± 0.1°C in all titrations with a Haake Model KT-41 constant temperature bath. This titration vessel was fitted with a teflon sealer cap containing the electrodes, nitrogen purge tube, and a 5-ml microburet readable to ±0.001 ml.

All solutions were prepared from distilled and demineralized water having a conductivity of less than 10^{-5} mho. Aqueous solutions (0.01*M*) of the ketones were placed in the titration vessel and purged for 10 min prior to titration with purified nitrogen gas. A slow stream of nitrogen was thereafter maintained for stirring and only discontinued during readings. The

Table I. pK_a's of 1(2-Pyridyl)-2-alkanones



R	pK_a	SD	σ^* (*5*)
CH_3	4.587	0.037	0.000
C_2H_5	4.677	0.013	−0.100
n-C_3H_7	4.634	0.003	−0.115
iso-C_3H_7	4.671	0.006	−0.190
n-C_4H_9	4.647	0.005	−0.130
iso-C_4H_9	4.595	0.004	−0.125
sec-C_4H_9	4.594	0.017	−0.210
tert-C_4H_9	4.743	0.019	−0.300
n-C_5H_{11}	4.670	0.011	−0.162 (*4*)

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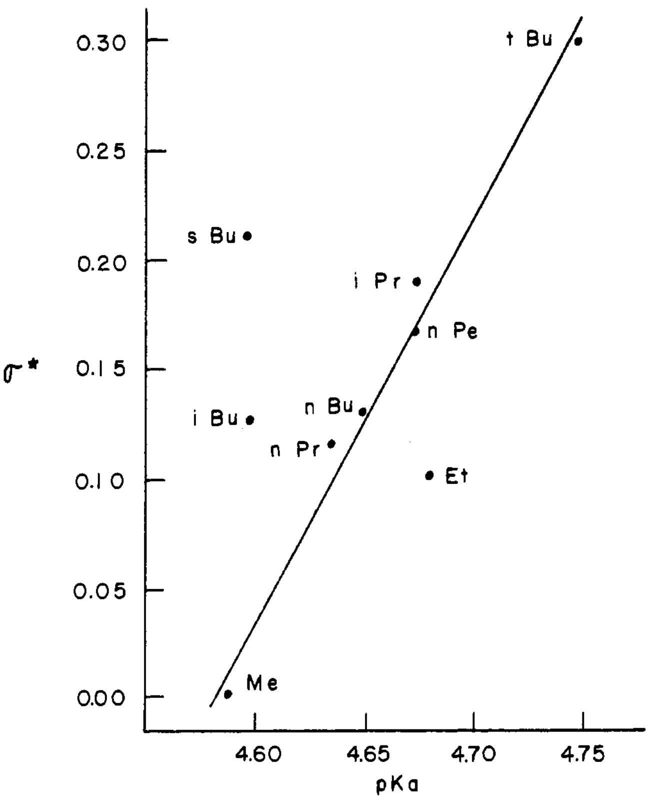

Figure 1. Correlation of pK_a's with Taft polar substituent constants

titrant was a 0.01*M* hydrochloric acid solution that was standardized against a standard carbonate free sodium hydroxide solution in the normal way using phenolpthalien indicator. the pH meter and electrdes were standardized and checked for drift with commericial buffers of pH = 4.01 and 7.00.

Results

Each pK_a listed in Table I is the average of a minimum of at least 16 individual determinations. A graph of pK_a vs. Taft steric substituent constants contained too much scatter to indicate any significant relationships. The Taft polar substituent constant (*5*) did show an unambiguous correlation with the pK_a's of the ketones as shown in Figure 1.

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Liquid-Liquid Equilibria for System Methanol–2-Propanol–*n*-Hexane

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Ternary liquid-liquid equilibrium data are reported at −17.8°, 5°, and 25°C for the system methanol-2-propanol-*n*-hexane. The tie lines and solubility curves for these Type 1 ternary systems are obtained by gas chromatographic analysis.

Liquid-liquid equilibrium data for a Type 1 ternary system were needed at three different temperatures to establish the temperature dependence of parameters to be used in the prediction of multicomponent equilibria. The system methanol-2-propanol-*n*-hexane was chosen to augment literature data for ternary systems that fit the criteria just established. No tie line data for this system were found in the literature.

Experimental

Materials. Reagent grades of methanol and 2-propanol and pure grade *n*-hexane obtained from Phillips Petroleum Co. were used in this study. An analysis of these solvents is presented in Table I. The manufacturer's stated purity for the solvents was verified by use of gas chromatographic analysis.

Procedure. Clean equilibrium cells were charged with about a 15-ml mixture of approximately 30 wt % methanol and 70 wt % *n*-hexane. To these cells was added a quantity of 2-propanol so that the overall 2-propanol composition of the ternary mixture in the cells would be 0–12 wt % in 1 or

Table I. Analysis of Solvents

Solvent	Purity minimum, %
Methanol	99.5
n-Hexane	99.0
2-Propanol	99.5

Table II. Gas Chromatograph Conditions

Injection port temp	250°C
Detector	TC
Detector temp	250°C
Detector power	165 mA
Oven conditions	140–220°C at 8°C/min
Carrier gas	He
Gas flow rate	30 ml/min

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