KETONE SOLVATION

AND

CYANOHYDRIN EQUILIBRIA

Thesis by

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Abstract

The measured heats of solution of methyl alkyl ketones do not correlate with their relative dissociation constants. The heats of solution are explicable if hydrogen bonding is considered.

Discussion

The dissociation constants of a number of methyl alkyl ketone cyanohydrins have been measured relative to acetone-acetone cyanohydrin by K.L. Servis[1]. He proposes that the determining factor in the magnitude of these constants is solvation of the ketone.

The heats of solution of the ketones (Table 1) do not substantiate this. In the series of straight-chain alkyl ketones, the heats of solution do not correlate at all with the dissociation constants (Figure 1). For the branched-chain ketones, the lack of correlation is just as pronounced (Figure 2). The heats of solution of the cyanohydrins are being measured now to determine the magnitude of their contribution to the dissociation constants, but no definite conclusions can be reached yet. The series of ketones is also being extended to include methyl s-butyl ketone and methyl neopentyl ketone.

Attempts to explain the relative sizes of the heats of solution on the basis of steric effects alone are quite satisfactory except in the case of methyl t-butyl ketone. One would expect the heat of solution of the s-butyl ketone to be greater than that of the t-butyl ketone, but this is not the case. If hydrogen bonding

is considered absent, since nuclear magnetic resonance and infra-red studies have shown that in general, methyl groups do not hydrogen bond[2], then I am unable to give a completely reasonable explanation for this.

If, however, we do consider the possibility of hydrogen bonding between a hydrogen attached to a carbon γ to the carbonyl carbon, then the entire series is explicable. The series of alkyl groups with increasing α substitution: methyl, ethyl, isopropyl, t-butyl, have heats of solution in the same order as would be expected on consideration of steric effects alone. By Newman's Rule of Six[3] we see that these ketones are not of sufficient length to effectively hydrogen bond.

For the other two straight-chain alkyl ketones, hydrogen bonding is possible, but very likely to be small, since the chain is flexible and the solvation of the methanol around the carbonyl is a stronger effect than hydrogen bonding between the methyl and the carbonyl.

With the isobutyl ketone, being di-β-substituted, there are now two methyl groups that can be hydrogen bonded to the carbonyl, which in addition to steric effects, may cause it to be less solvated than t-butyl. The tri-β-substituted ketone, methyl neopentyl ketone has a correspondingly lower value, meaning less solvation than the others. This, too, is reasonable if hydrogen bonding is allowed.

The low value for methyl s-butyl ketone is expected since it is both α and β substituted, with increases then in steric hindrance to solvation and hydrogen bonding.

Experimental

The ketones studied were used as they are commercially available, reagent grade, without further purification. The methanol used in the determination of the relative dissociation constants of methyl s-butyl ketone and methyl neopentyl ketone was reagent grade, dried by distillation from magnesium methoxide. The dried methanol was stabilized with a trace of triethyl amine. The methanol used in the determination of the heats of solution was reagent grade, no further purification.

Relative dissociation constants were measured by the method of K.L. Servis[1]. Hydrogen cyanide, prepared by adding sulfuric acid to a solution of potassium cyanide, and passing the vapors through a drying tube into a gas-storage vessel, was distilled into a solution of acetone and the desired ketone in methanol. The samples were prepared in 4.94-mm O.D. pyrex tubing. The nuclear magnetic resonance spectra were taken on the Varian A-60.

Heats of solution were measured for a mixture of 10 ml. of the ketone in 200 ml. (approx. 5 moles) of methanol. The calorimeter employed was a one-pint dewar with a cap made of polyurethane foam, resistant to ketones. Through the cap a heating coil, Beckman thermometer, and container for the ketone were inserted into the solution. The mixture was stirred magnetically. The ketone was introduced into solution by puncturing with a slender glass rod an aluminum foil cap on the glass tubing holding the ketone. Heat capacities were measured by heating with the resistance heater and measuring the current and potential applied across it by the circuitry shown in Figure 3.

Table 1

Summary of Data

Ketone Alkyl Group	Heat Absorbed $\left(\frac{\text{kjoules}}{\text{mole}}\right)$	Relative Dissociation Constant
Methyl	0.0712	1.00
Ethyl	0.0519	0.82
n-Propyl	0.0513	1.17
n-Butyl	0.0509	1.1
Isopropyl	0.0485	0.34
Isobutyl	0.0420	2
s-Butyl	0.0376	0.3 (approx.)
t-Butyl	0.0445	0.95
Neopentyl	0.0404	0.3 (approx.)

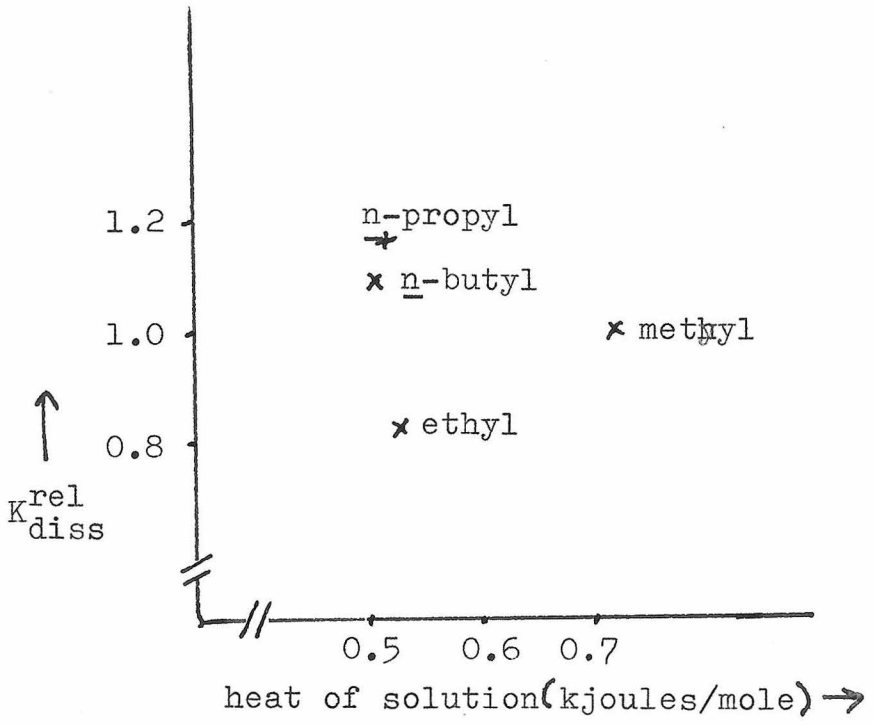


Figure 1

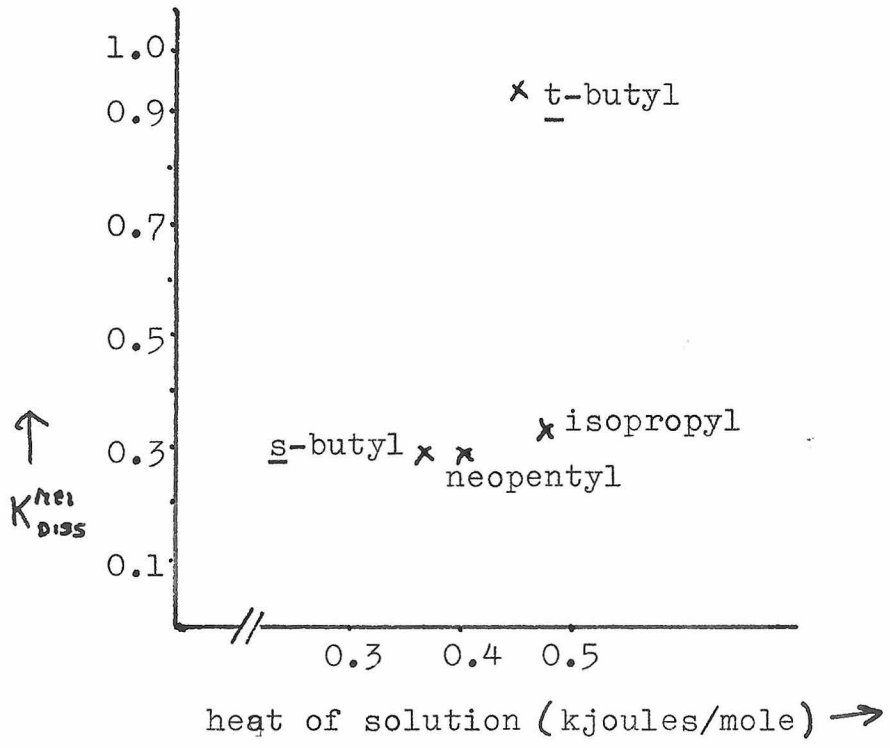
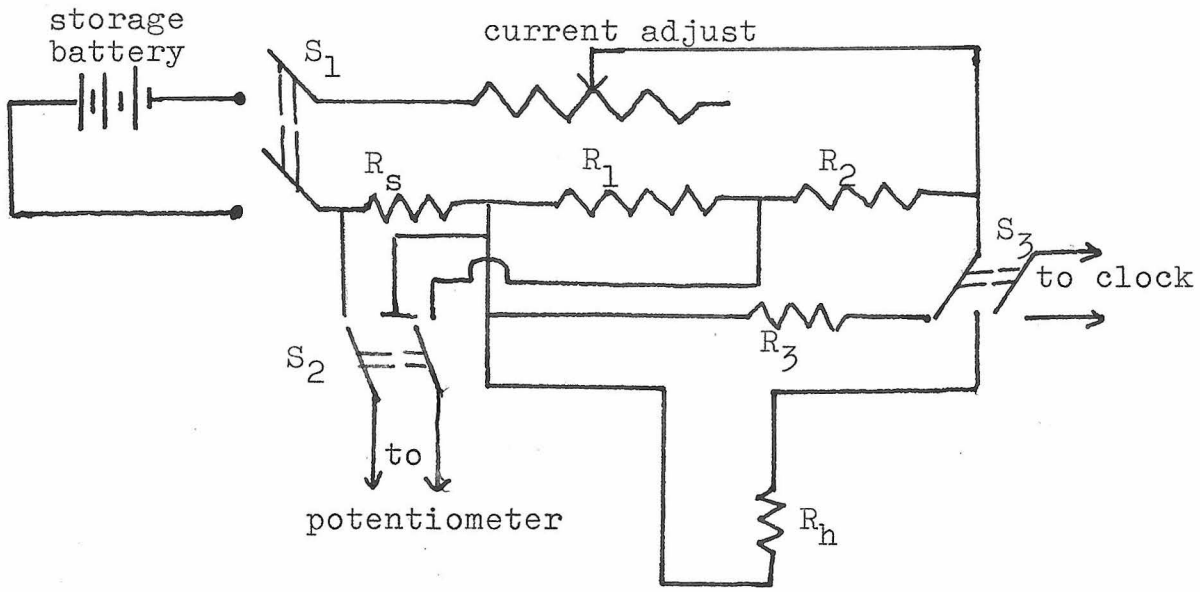


Figure 2



R_s = 0.2445 ohms
R_1 = 270.6 "
R_2 = 269,300 "
$R_3 \cong$ 18.9 " (Substitute for R_h in calibration)
R_h = 18.91 "

Figure 3

References

1) K.L. Servis, Research Report, pp. 13-21.

2) A. Allerhand and P. von Ragué Schelyer, J. Am. Chem. Soc., 85, 1715 (1963).

3) M.S. Newman, J. Am. Chem. Soc., 72, 4783 (1950).