## Base Strength of Urea and Thiourea in Methanol

By Ralph G. Pearson and James Tucker

In some work with solutions containing thiourea and strong acids dissolved in methanol it became apparent that salt formation was appreciable even though thiourea is generally considered too weak a base to form salts stable in solution. The explanation lies in the inherent weak basicity of methanol which causes other bases to appear abnormally strong in this solvent.[1]

The hydrolysis constants for thiourea and urea in dry methanol were determined by a conductimetric method essentially the same as that used by Goldschmidt and Dahlls[1a] to find the base strength of water in methanol. β-Naphthalenesulfonic acid was recrystallized from water and dried to the composition of the monohydrate in a vacuum oven at 60°. Methanol was dried by the use of magnesium turnings.[2] C. P. thiourea and urea were used.

Resistances were measured at 25.0 ± 0.03° on a Jones bridge of solutions containing a fixed amount of acid and varying amounts of base. If $R_0$ is the resistance of the solution containing only acid and $R$ the resistance of a solution with added base, then $R/(R - R_0)$ plotted against the reciprocal of the base concentration[3] gave straight lines which could be extrapolated to infinite base concentration. From this a value of $R_\infty$ could be found corresponding to the resistance of a solution completely converted to the salt of the base. From $R_0$, $R_\infty$ and $R$ the fraction of acid converted to salt could be found for each solution and the concentration equilibrium constant, $K_h$, for the reaction could be determined.

$$BH^+ + CH_3OH \rightleftharpoons B + CH_3OH_2^+ \qquad (1)$$
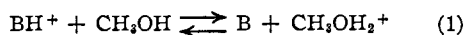
Table I shows the experimental results, the calculated values of $R_\infty$ and the average value of $K_h$ for each base. The effect of urea and thiourea on the resistances of methanolic solutions of lithium acetate and potassium chloride was checked and found to be negligible except for the more concen-

### TABLE I
#### THIOUREA

| Thiourea, molar | Resistance, ohms |
|---|---|
| 0.00556 M β-Naphthalene Sulfonic Acid | |
| 0.0000 | 3111[a] |
| .0314 | 3709 |
| .0628 | 4164 |
| .1257 | 4643 |
| .2514 | 5103 |
| ∞ | 5942 |

$$K_h = 5.46 \pm 0.1 \times 10^{-2}$$

(1) (a) Goldschmidt and Dahlls, Z. physik. Chem., **108**, 121 (1924); (b) Unmack, ibid., **133**, 45 (1928).

(2) Lund and Bjerrum, Ber., **64B**, 210 (1931).

(3) The concentration of free base must be used, correcting for that used up in salt formation. Successive approximations as to the magnitude of $K_h$ are needed to bring the solutions of low base concentration into line.

#### Urea, 0.00525 M Acid

| Urea, molar | Resistance, ohms |
|---|---|
| 0.00000 | 2764[a] |
| .00271 | 3552 |
| .00525 | 4370 |
| .01080 | 5108 |
| .0314 | 5331[b] |
| .0627 | 5447[b] |
| ∞ | 5447 |

$$K_h = 4.37 \pm 0.2 \times 10^{-4}$$

#### 0.00592 M Potassium Chloride

| | |
|---|---|
| 0.0000 | 3974 |
| .0314 | 3986 |
| .0627 | 4002 |

[a] Different conductivity cells were used. [b] Not corrected for viscosity.

trated urea solutions. Assuming the effect here to be due to viscosity, an equivalent correction was made on the measured conductances of the acid solutions before any calculations were made.

The basic ionization constant can be obtained by dividing the hydrolysis constant into the ion product for methanol, $2.0 \times 10^{-17}$ at 25°.[1b] The corresponding hydrolysis constants in water are 9.0 for thiourea and 0.67 for urea.[4] The stability of the salts is thus increased several hundred-fold in methanol.

(4) Walker, J. Chem. Soc., **67**, 576 (1895).

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## Isomerization of Saturated Hydrocarbons. VI.[1] Effect of Benzene upon the Isomerization of Methylcyclopentane

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The study of the isomerization of n-butane[3] and cyclohexane and methylcyclopentane[1] in the presence of aluminum bromide–hydrogen bromide catalyst using a high vacuum technique and highly purified materials has been reported recently. This work has shown that under certain carefully controlled conditions the isomerization of saturated hydrocarbons does not proceed unless a small amount of an olefin or an alkyl or cycloalkyl halide is present.

In the study of isomerization of methylcyclopentane it was found that small amounts of impurities which are present commonly in this hydrocarbon, such as benzene, have a profound effect upon the rate of isomerization. By fractional distillation it is difficult to eliminate the last traces of benzene; this can, however, be accom-

(1) For paper V of this series see H. Pines, B. M. Abraham and V. N. Ipatieff, This Journal, **70**, 1742 (1948).

(2) Universal Oil Products Company Research Fellow 1947-1948.

(3) H. Pines and R. C. Wackher, This Journal, **68**, 585 (1946), **68**, 2518 (1946).