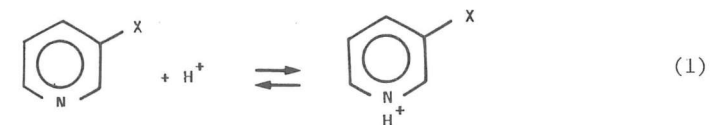


ENTHALPY-ENTROPY RELATIONSHIP FOR THE PROTONATION OF SOME  
 META-PYRIDINE DERIVATIVES IN WATER

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Enthalpy-Entropy compensation effect has been studied for the protonation equilibria of 3-x-pyridines (where x = H, NH<sub>2</sub>, CH<sub>3</sub> and Br).

The protonation equilibria can be represented as follows:



Thermodynamic equilibrium constants of pyridinium dissociation have been obtained at 20,30,40 and 50°C. The determination of the equilibrium constants was made by potentiometric titration of *meta*-pyridine derivative solutions with hydrochloric acid using a glass electrode.

The experimental equilibrium constants (table 1) are in good agreement with literature values for 25°C [1].

TABLE 1. Experimental equilibrium constants (pK) corrected for ionic strength

SUBSTITUENT (X) 3-X-py	TEMPERATURE (K)			
	293	303	313	323
Br	3.03	2.97	2.92	2.85
H	5.29	5.23	5.15	5.02
CH <sub>3</sub>	5.74	5.65	5.50	5.39
NH <sub>2</sub>	6.12	5.98	5.82	5.69

The data obtained for each reaction show a good correlation with the van't Hoff equation (fig. 1).

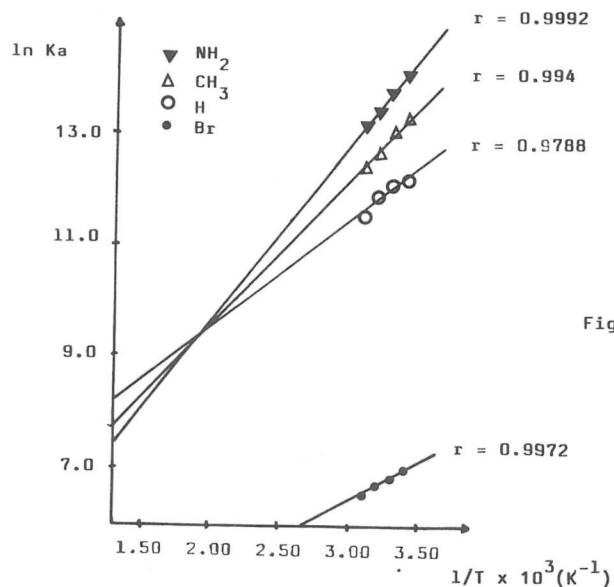


Fig. 1. Van't Hoff plots of 3-X-pyridinium dissociation

If a linear Enthalpy-Entropy relationship existed, van't Hoff plot should display a single point of concurrence at the isoequilibrium temperature. From figure 1 we cannot conclude about the existence of a single concurrence point.

An analysis of variance (ANOVA) was made in order to calculate the probability of detection of concurrence.

TABLE 2. ANOVA Table for detection of an Enthalpy-Entropy linear relationship

SOURCE OF VARIATION	DF	SS	MS
TOTAL	15	144.9	7.661
SUBSTITUENTS	3	113.7	37.89
TEMPERATURES	3	1.141	0.3803
INTERACTIONS	9	0.1170	0.01309
SLOPES (van't Hoff reln.)	3	0.1094	0.03648
CONCURRENCE (linear comp. effect.)	1	0.08970	0.08970
NONCONCURRENCE	2	0.01973	0.009864
RESIDUALS	6	0.008425	0.001404

DF - degree of freedom  
 SS - sum of squares  
 MS - mean sum of squares

The estimated variances of experimental results were calculated for the different sources of variation and are presented in table 2. From those values, probabilities can be assigned for different effects by evaluation of F-statistic.

The mean sum of squares of the residuals (which is an estimate of the square of the standard deviation of the measurement errors) is very small relatively to the other mean sum of squares. Thus the data fit well the van't Hoff equation displaying both substituent and temperatures effects.

Comparing the mean sum of squares due to concurrence and nonconcurrence by F-statistic,

$$\frac{MS_{con}}{MS_{ncon}} = 9.09 > F(1,2,1-\alpha = 0.90)$$

We conclude that the probability of concurrence, in the van't Hoff plot, is greater than that of nonconcurrence at 10% level of significance.

The probability of detection of concurrence will be given by the ratio  $MS_{con}/MS_{ncon}$  if the mean sum of squares due to nonconcurrent is comparable to the mean sum of squares of the residuals. However, the variation due to concurrence is greater than that due to measurement errors at the 5% level of significance

$$\frac{MS_{ncon}}{MS_{\epsilon}} = 7.03 > F(2,6,1-\alpha = 0.95)$$

Thus, within the precision of the data, no concurrence is detected in the van't Hoff plot i.e., the reported data do not support the existence of a well defined isoequilibrium temperature. The reactions represented by (1) will never occur in the same extension whatever the temperature is. However, there is a temperature at which the differences between the equilibrium constants are minimized. The determination of the minimal difference temperature,  $T_{c,m}$  was made following the Krug's method for the determination of the isoequilibrium temperature [2,3].

$T_{c,m}$  was calculated from the slope ( $\gamma$ ) of the line in the plot of  $\Delta_R H^{\circ}$  vs  $\Delta_R G^{\circ}_{T_{hm}}$  (fig. 2).

$$T_{c,m} = T_{hm} / (1 - 1/\gamma)$$

where  $T_{hm} = n / \sum 1/T_i$ ,  $T_i$  - experimental temperatures and the obtained value was -1046K.

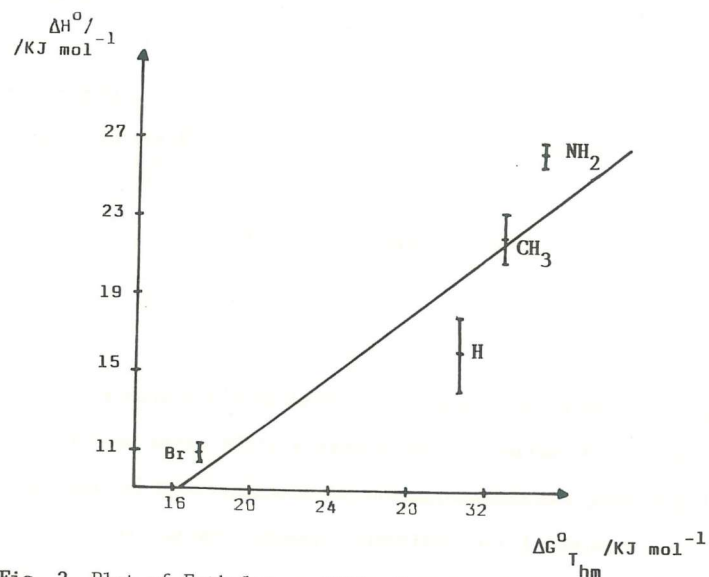


Fig. 2. Plot of Enthalpy vs Gibbs Energy estimates with 50% joint confidence regions.

The line in figure 2 cannot be used to represent the observed relation between  $\Delta_R H^{\circ}$  and  $\Delta_R G^{\circ}_{T_{hm}}$  because data do not display a linear compensation effect but do display a nonlinear pattern. We don't present a nonlinear relationship owing to the few number of elements of the studied series.

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#### A MICROELECTRODE STUDY OF THE METHOXYLATION OF FURAN

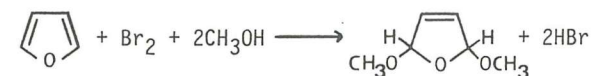
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In the conventional synthesis of 2,5-dimethoxy-2,5-dihydrofuran, furan is treated with bromine in a solution of methanol according to the following reaction<sup>(1)</sup>:



The main disadvantage of this method, however, is the formation of halogen by-products. To overcome this problem a method for methoxylation of furan was developed using electrochemical indirect oxidation, in a methanol solution of potassium bromide<sup>(2)</sup>.

Here, we present a study of the catalytic oxidation of furan at finite platinum microdisc electrodes, using conditions very close to industrial practice.

For the determination of the kinetics of the pseudo-first order homogeneous chemical reaction coupled to the heterogeneous electron transfer reaction, a technique involving the recording of steady state current-voltage curves at microelectrodes was used with the assumption that the limiting current can be analysed in terms