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Heats of Solution and Neutralization of Protonic Acids and Bases in Ethanol

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Heats of solution of several protonic acids and bases in ethanol have been measured and the following order of their relative strengths is inferred: $HSO_3F > H_2S_2O_7 > H_2SO_4 > HCOOH$ and sodium ethoxide > potassium ethoxide > piperidine > *n*-butylamine > benzylamine > morpholine > α-picoline > pyridine > quinoline. Major enthalpy change in the neutralization reactions is attributed to the combination of ethoxonium and ethoxy ions resulting in the formation of ethanol.

(Keywords: Calorimetry; Thermodynamics)

Lösungs- und Neutralisationswärmen von Protonsäuren und Basen in Ethanol

Lösungswärmen einiger Protonensäuren und Basen wurden gemessen, wobei sich folgende Reihungen der relativen Stärken ergaben: $HSO_3F > H_2S_2O_7 > H_2SO_4 > HCOOH$ und Natriumethoxid > Kaliumethoxid > Piperidin > *n*-Butylamin > Benzylamin > Morpholin > α-Picolin > Pyridin > Chinolin. Der Hauptanteil bezüglich der Enthalpie-Änderung bei der Neutralisation wird der Reaktion von Ethoxonium- und Ethoxy-Ionen zu Ethanol zugeschrieben.

In continuation of the thermochemical studies in methanol and *n*-butanol[2], heats of solution and neutralization of certain protonic acids and bases in ethanol are reported with a view to understanding the nature of their solutions and the solvent.

Experimental Procedure

Ethanol was dried successively over lime and anhydrous copper sulphate, and distilled over sodium. The distillate was treated with pure magnesium

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turnings and a little iodine, warmed under reflux to start the reaction and then allowed to stand till the reaction subsided. The contents were finally distilled at 78 °C at a take-off ratio of 1 : 5. Tertiary nitrogen bases were kept over potassium hydroxide beads over night and distilled in dry nitrogen atmosphere. Acids[3] and bases[1, 2] used were purified as described earlier.

Thermochemical measurements were carried out in an isothermal phase-change calorimeter, using diphenyl ether as the dilatometric fluid, designed after *Dainton* et al.[4]. Details to the calorimeter and the method of determinating heats of solution and neutralization have already been reported[1].

Results and Discussion

Heats of Solution of Protonic Acids

The heat of solution of fluorosulphuric acid in ethanol is of the order of 29.66–31.26 $\mathrm{kcal\,mol^{-1}}$ with a slight concentration effect (more exothermic at greater dilutions). The resultant heat effect is mainly due to the formation of an adduct between the acid and the solvent and its subsequent ionization. Heat of solution thus pertains to the following reaction:

$$C_2H_5OH + HSO_3F \rightarrow (C_2H_5OH \cdot HSO_3F) \rightleftharpoons C_2H_5OH_2^+ + SO_3F^- \qquad (1)$$

The solvation of ions formed may further affect the heat of solution but this effect is usually small in the present case.

The interaction between formic acid and ethanol is very weak and results in the evolution of — 1.34 to — 1.37 $\mathrm{kcal\,mol^{-1}}$ only. Formic acid is a weakly ionized acid in this solvent and the reaction may be represented as

$$HCOOH + C_2H_5OH \rightarrow (C_2H_5OH \cdot HCOOH) \rightleftharpoons C_2H_5OH_2^+ + HCOO^- \qquad (2)$$

Since the reaction does not proceed to completion, a low heat of solution is expected.

The heat of solution of pyrosulphuric and sulphuric acids (H_2A) in ethanol is found to be —50.03 to —52.64 and —16.33 to —18.37 $\mathrm{kcal\,mol^{-1}}$, respectively. The enthalpy change exhibits a small decrease in the value with an increase in concentration of these acids. The values suggest that the reaction is uniform with very low chances of esterification; particularly when the reaction period is small and it proceeds at room temperature (27 °C). If the reaction would follow the course suggested by *Kremann*[5], more water would have been formed at higher concentrations of the solute causing an appreciable error in the enthalpy values since the heat of solution of water in ethanol is found to be —0.29 $\mathrm{kcal\,mol^{-1}}$ (exothermic). The chemical change may rather be represented as

$$C_2H_5OH + H_2A \rightleftharpoons C_2H_5OH_2^+ + HA^- \qquad (3)$$

$$C_2H_5OH + HA^- \rightleftharpoons C_2H_5OH_2^+ + A^{2-} \qquad (4)$$

Table 1. *Heat of solution of protonic acids in ethanol (amount of solvent 0.4290 mol)*

Amount of acid mol	$-\Delta H$ kcal mol^{-1}	Amount of acid mol	$-\Delta H$ kcal mol^{-1}
HSO_3F		$HCOOH$	
0.00064	31.26	0.00468	1.37
0.00138	30.54	0.00910	1.36
0.00183	29.82	0.01435	1.34
0.00203	29.70	0.01806	1.36
0.00273	29.66	0.02413	1.35
H_2SO_4		$H_2S_2O_7$	
0.00086	18.37	0.00068	52.64
0.00128	17.20	0.00110	51.46
0.00176	17.10	0.00133	51.28
0.00218	16.33	0.00198	50.03

High heat of solution of pyrosulphuric acid is indicative of the fact that both the protons may be solvated by the solvent, either in steps (3) and (4) or directly as

$$2\,C_2H_5OH + H_2A \rightleftharpoons 2\,C_2H_5OH_2^+ + A^{2-} \tag{5}$$

The heat of solution in the case of sulphuric acid is much lower than those of pyrosulphuric and fluorosulphuric acids. It is possible that only one of its protons is available for solvation in this medium.

On the basis of heat of solution values (Table 1), these acids may be arranged in the following order of decreasing strength taking into account their basicity:

$$HSO_3F > H_2S_2O_7 > H_2SO_4 > HCOOH$$

Heats of Solution of Bases

Heat of solution of sodium and potassium ethoxides in ethanol is —6.41 and —4.96 kcal mol^{-1}, respectively. An almost constant value of the heat of solution indicates complete reaction with the solvent in the concentration range studied. The lower heat of solution of potassium ethoxide as compared to that of sodium ethoxide may be due to the greater ionization of potassium ethoxide which has higher lattice energy. But for the heat absorbed in breaking the lattice bonds on dissolution of the solid ethoxides, the heat of their solution would have been higher than that obtained because ethoxides in ethanol give ions characteristic

Table 2. *Heat of solution of various bases in ethanol (amount of solvent 0.4290 mol)*

Amount of base mol	$-\Delta H$ kcal mol^{-1}	Amount of base mol	$-\Delta H$ kcal mol^{-1}
Sodium ethoxide		Morpholine	
0.00116	6.32	0.00216	1.71
0.00215	6.35	0.00320	1.48
0.00320	6.54	0.00374	1.55
0.00426	6.44	0.00496	1.39
Potassium ethoxide		α-Picoline	
0.00175	4.88	0.00319	1.05
0.00197	4.98	0.00540	1.12
0.00330	5.02	0.00726	1.04
Piperidine		Pyridine	
0.00173	3.51	0.00129	0.77
0.00232	3.27	0.00196	0.77
0.00374	3.18	0.00197	0.78
n-Butylamine		0.00263	0.77
0.00500	2.75	Quinoline	
0.00848	2.76	0.00014	0.47
0.00871	2.76	0.00123	0.49
Benzylamine		0.00333	0.49
0.00421	1.53	0.00497	0.48
0.00442	1.59		
0.00755	1.86		

of the solvent. Alkali metal ethoxides (C_2H_5OM) are ionic solids and the strongly polar alkali metal ions polarize the solvent inducing ionization:

$$C_2H_5OH + C_2H_5O^- + M^+ \rightleftharpoons C_2H_5OHM^+ + C_2H_5O^- \qquad (6)$$

Organic tertiary bases (B) are strong proton acceptors and act as solvo-bases in ethanol:

$$C_2H_5OH + B \rightarrow (CH_{25}OH \cdot B) \rightleftharpoons C_2H_5O^- + BH^+ \qquad (7)$$

The heat evolved on dissolution of piperidine, *n*-butylamine, benzylamine, morpholine, α-picoline, pyridine and quinoline in ethanol is —3.32, —2.76, —1.66, —1.53, —1.07, —0.77 and 0.48 kcal mol^{-1}, respectively. The protonation of the bases in ethanol is almost complete as nearly constant values are obtained at varying concentrations (Table 2). Heat evolved on dissolution of organic tertiary bases is much less than that on the dissolution of ethoxides as expected. The bases studied may be arranged in the following order of relative strength: sodium ethoxide > potassium ethoxide > piperidine > *n*-butylamine > benzylamine > morpholine > α-picoline > pyridine > quinoline. This agrees with the results obtained from conductometric studies on a few of these bases in methanol[1].

Heat of solution of bases is uniformly lower in ethanol than in methanol[1] indicating thereby that the former is slightly more basic than the latter. Heat of solution of these bases in *n*-butanol is still lower[2]. This supports the observation of *Gerrard* and *Macklen*[6] regarding the basic strength of alcohols.

Heats of Neutralization

In order to study the nature of acid—base reactions in ethanol and to ascertain the mode of ionization of the solvent, neutralization reactions of certain protonic acids with bases have been studied. In all these cases, the acid has been used in excess.

Sodium and potassium ethoxides react with fluorosulphuric acid (both components in ethanol) with the evolution of —11.67 and —10.06 kcal mol^{-1} of the base neutralized, respectively. The heat effect may be ascribed to the following reaction:

$$C_2H_5OH_2^+ + SO_3F^- + C_2H_5OHM^+ + C_2H_5O^- \rightarrow 3\,C_2H_5OH + M^+SO_3F^- \quad (8)$$

The solutions of solvo-bases (*B*) such as quinoline, α-picoline, piperidine and *n*-butylamine in ethanol on neutralization with the solutions of fluorosulphuric acid in ethanol produce —2.64, —3.98, —11.80 and —14.10 kcal mol^{-1}, respectively. The enthalpy change may be attributed to the following reaction:

$$C_2H_5OH_2^+ + SO_3F^- + C_2H_5O^- + BH^+ \rightarrow 2\,C_2H_5OH + BH^+\cdot SO_3F^- \quad (9)$$

Table 3. *Heat of neutralization of protonic acids with certain bases in ethanol (average of 4–5 experiments)*

Acid	Base	Heat of reaction —Δ*H*, kcal mol^{-1}
HSO_3F	quinoline	2.64
	α-picoline	3.98
	potassium ethoxide	10.06
	sodium ethoxide	11.67
	piperidine	11.80
	n-butylamine	14.10
HCOOH	potassium ethoxide	7.29
	sodium ethoxide	7.81
	piperidine	11.32
	n-butylamine	11.71
CH_3COOH	sodium ethoxide	6.76
	piperidine	11.96
	n-butylamine	12.23

The heat of neutralization of alkali metal ethoxides is lower as compared to that of *n*-butylamine or piperidine. It may be due to higher absorption of heat of desolvation as the ions produced by these ansolvobases are highly solvated. The difference in the heats of neutralization of sodium and potassium ethoxides may be due to greater ionization of potassium ethoxides which has higher lattice energy.

The enthalpy values for the neutralization of formic and acetic acids (*R*COOH) with certain bases (both components in ethanol) are low compared to those of fluorosulphuric acid. It is possible that in view of the weak interaction between these acids and the solvent, heat of ionization is absorbed as the reaction proceeds towards completion.

$$C_2H_5OH_2^+ + RCOO^- + BH^+ + C_2H_5O^- \rightarrow 2\,C_2H_5OH + BH^+ \cdot RCOO^- \qquad (10)$$

As the reaction (10) proceeds to completion, some of the unionized acetic or formic acid will tend to ionize, thereby, contributing to heat of reaction.

In these neutralization reactions, the heat change due to the formation of salt makes relatively small contribution as it remains dissociated. Heat evolved is considered to be mainly due to the combination of ethoxonium ($C_2H_5OH_2^+$) and ethoxy ($C_2H_5O^-$) ions resulting in the formation of feebly ionized ethanol molecules. In these cases where neutralization product separates out, the enthalpy change also includes heat of precipitation of the salts. Thus the neutralization essentially involves the combination of solvo-acids and solvo-bases and not the original acid/base pairs. The solvent may undergo autoprotolysis (eq. 11).

$$2\,C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^- \qquad (11)$$

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