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Heats of Solution and Neutralization of *Lewis* Acids and Bases in Acetic Anhydride

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Heats solution of some *Lewis* acids and bases in acetic anhydride have been determined and the following order of their relative strengths is proposed: $SbCl_5 > SO_3 > SnCl_4 > TiCl_4 > AsCl_3$ and piperidine > *n*-butylamine > potassium acetate > sodium acetate ≈ α-picoline > quinoline. Heats neutralization of these *Lewis* acids and bases in acetic anhydride suggest that the major enthalpy change in these neutralization reactions is due to the combination of a proton and the $(CH_2COOCOCH_3)^-$ ion, resulting in the formation of acetic anhydride.

(Keywords: Calorimetry; Thermodynamics)

Lösungs- und Neutralisationswärmen von Lewis-Säuren und -Basen in Essigsäureanhydrid

Es wurden die Lösungswärmen einiger *Lewis*-Säuren in Essigsäureanhydrid bestimmt und folgende Reihung nach ihrer relativen Stärke vorgeschlagen: $SbCl_5 > SO_3 > SnCl_4 > TiCl_4 > AsCl_3$ und Piperidin > *n*-Butylamin > K*Ac* > > Na*Ac* ≈ α-Picolin > Chinolin. Die Neutralisationswärmen dieser *Lewis*-Säuren und -Basen legen nahe, daß der Hauptanteil daran auf die Reaktion eines Protons mit $(CH_2\text{—}COOCOCH_3)^-$ zurückzuführen ist.

In continuation of the studies carried out in acetic anhydride in these laboratories[1–3], heats of solution and neutralization of certain *Lewis* acids and bases were determined.

Experimental Procedure

Acetic anhydride (BDH, AnalaR), various *Lewis* acids and bases used were purified as reported earlier[1].

An isothermal phase-change calorimeter, using diphenyl ether as the dilatometric fluid, designed after *Dainton* et al.[4] was employed. The working of the calorimeter and the method of determining heats of solution and neutralization have already been reported[5].

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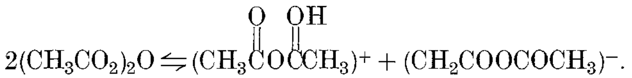
Results and Discussion

Heats of Solution of Bases

Heat of solution of bases (B) such as α-picoline, quinoline, n-butylamine, piperidine, sodium acetate and potassium acetate in acetic anhydride are presented in Table 1. Acetate should be the strongest base in this medium if the solvent ionizes as

$$(CH_3CO)_2O \rightleftharpoons CH_3CO^+ + CH_3COO^-. \qquad (1)$$

But the heat evolved on dissolution of the acetates in acetic anhydride is rather low although *Paul* and *Singh*[6] have reported that acetylium ions have strong solvation properties. Acetic anhydride may, therefore, behave as a protonic solvent and ionize as



$$2(CH_3CO_2)_2O \rightleftharpoons (CH_3\overset{O}{\overset{\|}{C}}O\overset{OH}{\overset{\|}{C}}CH_3)^+ + (CH_2COOCOCH_3)^-. \qquad (2)$$

This type of ionization is supported on the basis of infrared studies of tin(IV) chloride adduct with acetic anhydride where absence of acetylium ions has been shown[7]:

Heat of solution values may be explained on the basis of the following equation:

$$CH_3COOCOCH_3 + B \rightarrow (H_3CCO)_2O \cdot B \rightleftharpoons BH^+ + (CH_2COOCOCH_3)^-. \quad (3)$$

From the heats of solution, the relative order of strength of these bases is as follows:

$$\text{piperidine} > n\text{-butylamine} > \text{potassium acetate} >$$
$$> \text{sodium acetate} \approx \alpha\text{-picoline} > \text{quinoline}.$$

Heats of Solution of Lewis Acids

Heats of solution of antimony(V) chloride, tin(IV) chloride, titanium(IV) chloride, sulphur trioxide and arsenic(III) chloride in acetic anhydride (Ac_2O) are 45.40-48.36, 22.20-22.72, 13.42-14.00, 34.80-36.10 and 8.06-8.67 kcal mol^{-1} respectively. Heat of solution of antimony(V) chloride in acetic anhydride is comparable to that in dimethylformamide[5] and acetyl chloride[6]. The values for tin(IV) and titanium(IV) chlorides are lower than those in dimethylformamide[5] and are quite different from those in acetyl chloride[6] and benzoyl chloride[8]. Heats of solution of tin(IV) chloride, titanium(IV) chloride and sulphur trioxide are closer to those in acetic acid[9] indicating that here the initial bonding may also be akin to that in acetic acid. *Hunt* and *Satchell*[7] have reported that the complexes of *Lewis* acids with acetic anhydride involve coordination through carbonyl oxygen.

Table 1. *Heat of solution of various Lewis acids and bases in acetic anhydride (amount of solvent taken, 0.2647 mol)*

Amount of acid taken, mol	—ΔH kcal mol^{-1}	Amount of base taken, mol	—ΔH kcal mol^{-1}
Antimony(V) chloride		α-Picoline	
0.000237	45.44	0.00548	5.05
0.000666	47.80	0.00571	4.58
0.001066	45.40	0.00925	4.54
0.001139	48.36	0.01218	4.65
Tin(IV) chloride		*n*-Butylamine	
0.000854	22.20	0.00113	14.86
0.000935	22.38	0.00263	16.15
0.001060	22.72	0.00328	14.98
0.001437	22.48	0.00367	14.92
Titanium(IV) chloride		Quinoline	
0.000541	13.98	0.00131	2.61
0.000780	14.00	0.00179	2.61
0.001060	13.52	0.00222	2.73
0.001120	13.42	0.00234	2.71
Sulphur trioxide		Piperidine	
0.000648	34.80	0.00118	25.33
0.001280	35.36	0.00147	24.60
0.001860	36.10	0.00214	24.60
0.002560	35.00	0.00267	24.40
Arsenic(III) chloride		Sodium acetate	
0.00118	8.67	0.00156	5.16
0.00158	8.31	0.00255	4.94
0.00258	8.06	0.00299	5.28
0.00803	8.51	0.00313	5.06
		0.00335	4.76
		Potassium acetate	
		0.00168	7.01
		0.00179	7.16
		0.00300	7.21
		0.00355	7.16

Though tin(IV) and titanium(IV) chlorides are known to form 1:2 complexes with acetic anhydride, in this case a 1:1 cyclic $O(COCH_3)_2MCl_4$ species seems more probable due to low heat values. It has already been reported that tin(IV) chloride reacts with acetic anhydride to form 1:1 *cis*-chelated adduct[7].

These *Lewis* acids thus react with the solvent forming adducts which subsequently ionize. The same amount of heat liberated with changing concentration indicates that these adducts are ionized to almost the same extent in the concentration range studied. On the basis of heat of solution aues, the following order of *Lewis* acid strength may be proposed:

$$SbCl_5 > SO_3 > SnCl_4 > TiCl_4 > AcCl_3.$$

The relative order of acceptor strengths remains the same as in some other solvents[5,6,8,9].

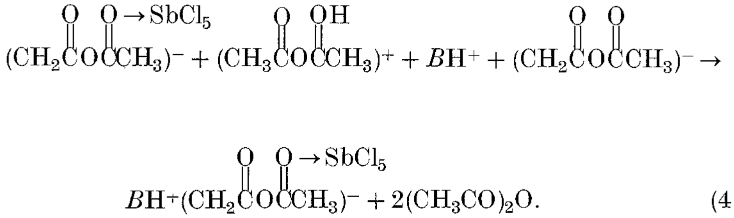
Heat of Neutralization

Heat of neutralization of *Lewis* acids with bases in acetic anhydride is measured to ascertain the mode of ionization of the solvent and to study the nature of acid—base reaction. These values (Table 2) are comparable with similar values in protonic solvents such as acetic acid[9] and dimethylformamide[5] and are lower than those in acetyl chloride[6] and benzoyl chloride[8]. Acetic anhydride, therefore, acts as a protonic solvent probably due to activation of methyl group. Since proton is too reactive to exist independently, it may get solvated (Eq. 2).

Table 2. *Heat of neutralization of various Lewis acids with bases in acetic anhydride (average of 4-5 experiments)*

Base	Heat of neutralization, kcal mol^{-1}			
	$SbCl_5$	$SnCl_4$	SO_3	$AsCl_3$
α-Picoline	15.15	15.22	14.67	10.45
Potassium acetate	13.77	13.44	11.68	6.25
Piperidine	10.75	10.83	7.72	0.31
n-Butylamine	9.18	10.80	8.42	0.26

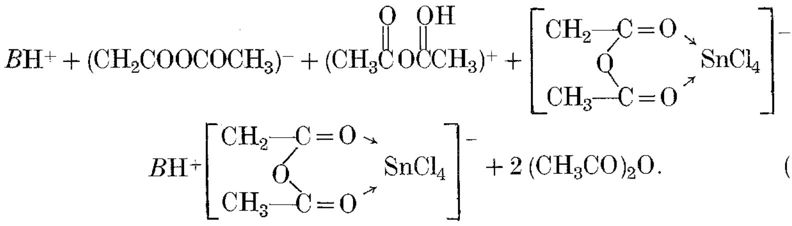
Antimony(V) chloride in acetic anhydride evolves 14.43-15.43, 13.24-14.10, 11.00-10.14 and 9.12-9.22 kcal mol^{-1} on reacting with α-picoline, potassium acetate, piperidine and *n*-butylamine respectively. The process of neutralization may thus be represented as



$$(CH_2\overset{O}{\overset{\|}{C}}O\overset{O\rightarrow SbCl_5}{\overset{\|}{C}}CH_3)^- + (CH_3\overset{O}{\overset{\|}{C}}O\overset{OH}{\overset{\|}{C}}CH_3)^+ + BH^+ + (CH_2\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3)^- \rightarrow BH^+(CH_2\overset{O}{\overset{\|}{C}}O\overset{O\rightarrow SbCl_5}{\overset{\|}{C}}CH_3)^- + 2(CH_3CO)_2O. \qquad (4)$$

Thus the neutralization essentially involves the combination of a proton and $(CH_2COOCOCH_3)^-$ ion so that heat effects may be the one corresponding to those in the protonic solvents.

Heat evolved per mole of tin(IV) chloride neutralized is 10.64-10.93, 14.69-16.02, 10.68-10.91 and 12.93-13.78 kcal mol^{-1} for piperidine, α-picoline, *n*-butylamine and potassium acetate respectively. The reaction may be written as



(5)

The value of heat of neutralization of piperidine, α-picoline, *n*-butylamine and potassium acetate are 7.58-7.83, 14.45-15.07, 8.33-8.58 and 11.59-11.75 kcal mol^{-1} with sulphur trioxide, and 0.29-0.32, 10.37-10.58, 0.26-0.27 and 6.10-6.35 kcal mol^{-1} with arsenic(III) chloride respectively. Arsenic(III) chloride which proved to be a weaker acid as compared to other acids in the heat of solution experiments has followed up the order in neutralization experiments also.

It is evident, therefore, that the solvent ionizes according to Eq. (2) and the heat of neutralization is essentially due to the combination of $(CH_3CO_2)_2OH^+$ and $(CH_3COOCOCH_2)^-$ ions although the ionization of the neutralization product and subsequent solvation of these ions influence the enthalpy values to some extent.

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