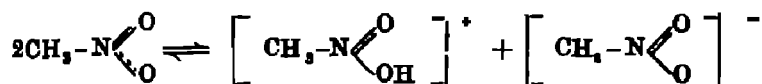


Nitromethane as Polar Solvent: Part V. Thermochemical studies in Nitromethane

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Thermochemical studies of the solution of various Lewis acids (SbCl_5 , SnCl_4 , AsCl_3) and protonic acids (HSO_3F , H_2SO_4 and HCOOH) in polar solvent nitromethane have been carried out using isothermal phase change calorimeter. From the heats of solution the order of relative strengths of the above acids comes out as $\text{SbCl}_5 > \text{SnCl}_4 > \text{AsCl}_3$ and $\text{HSO}_3\text{F} > \text{H}_2\text{SO}_4 > \text{HCOOH}$. Acid-base neutralisation reactions involving these acids and bases like α -picoline, dimethylaniline, pyridine and quinoline have been carried out, indicating that high heat effect is due to the combination of H^+ and CH_2NO_2^- resulting in the formation of nitromethane. Heats of neutralisation with protonic and Lewis acids in nitromethane are similar indicating their identical behaviour.

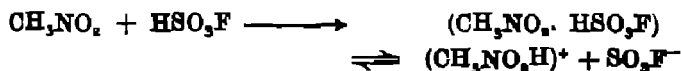
Based upon the conductance of the solutions of acids and bases¹ in nitromethane its autoionisation has been proposed as:



This has been further confirmed by carrying out acid-base neutralisation reactions conductometrically, by isolating the neutralization products², potentiometrically³ and on the basis of solvolytic reactions⁴.

In the present investigations, heats of solution of protonic and Lewis acids in nitromethane have been determined and attempts have been made to assign an order for their relative acid strengths. Heats of neutralisation of these acids with various bases have also been determined to understand the nature of the neutralisation reactions.

Heat of solution: Fluorosulphuric acid dissolves in nitromethane in an exothermic reaction. Heat of solution of fluorosulphuric acid in nitromethane ranges between 21.26—29.77 Kcal. mole in the concentration range studied. Solutions of fluorosulphuric acid in nitromethane are highly conducting and the nature of these solutions has already been proposed¹ as:



The enthalpy values are naturally due to this reaction and the subsequent ionisation and solvation of the ions formed. In other solvents heat of solution of fluorosulphuric

1. R. C. Paul, R. Kaushal and S. S. Pahl, *J. Ind. Chem. Soc.*, 1965, 42, 485.
2. R. C. Paul, R. Kaushal and S. S. Pahl, (communicated).
3. R. C. Paul, R. Kaushal and S. S. Pahl, (communicated).
4. R. C. Paul, R. Kaushal and S. S. Pahl, (communicated).

Fluorosulphuric acid is known to be the strongest acid in various solvents. In nitromethane dissolution of fluorosulphuric acid is accompanied by the evolution of 21.26—29.77 Kcal/mole as compared to 16.32—40.31 Kcal/mole (Table II) in the case of antimony(V) chloride in the same solvent, the concentration ranges studied in the two being almost the same. Apparently antimony(V) chloride seems to be stronger than fluorosulphuric acid in its reaction with nitromethane which occurs in an entirely different way and involves formation of a dative bond ($O \rightarrow Sb$) between the solvent and the solute apart from the ionisation of the complex to give off a hydrogen ion and its subsequent solvation.

TABLE II

Heat of solution of various protonic and Lewis acids in nitromethane (25 ml.) at varying concentrations at 26.9°.

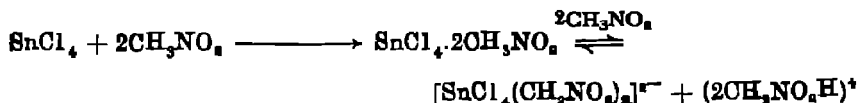
Acid	Wt. of acid (g. moles $\times 10^3$)	Heat of solution ($-\Delta H$ Kcal/mole)
HSO_3F	0.442	29.77
	0.646	27.45
	0.708	27.21
	1.29	23.02
	2.05	21.26
H_2SO_4	0.496	11.12
	0.616	6.11
	0.698	6.00
	1.286	4.33
	1.939	2.13
$SbCl_3$	0.172	40.31
	0.333	36.55
	0.596	24.71
	0.663	20.55
	0.685	16.32
$SnCl_4$	0.197	27.99
	0.323	19.85
	0.353	16.56
	0.411	11.30
	0.628	10.55
$AsCl_3$	0.848	8.59
	4.151	1.14
	4.618	0.82
	5.276	0.79
	8.350	0.78

It is of interest to compare the heat of solution of antimony(V) chloride in different solvents. A perusal of Table III suggests that the heat evolved in all the cases is nearly the same at lower concentrations of the solution. Small differences may be due to increase or decrease in the basic character of the solvent and the subsequent ionisation of the solvate and solvation of ions formed, but the overall reaction of the formation of a dative bond ($O-Sb$) is the same in all the cases.

TABLE III

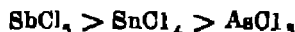
Solvent	Heat of solution of SbCl_5 ($-\Delta H$ Kcal/mole)	Ref.
Nitromethane	20.55—40.9	
Dimethyl formamide	43.40—44.24	11
Ethyl acetate	37.10—38.40	12
Acetic acid	20.54—37.70	13
Acetyl chloride	35.10—44.9	14

Thermochemical studies have shown that heat of solution of tin (IV) chloride in nitromethane varies from 8.59 to 28.00 Kcal/mole in the concentration range studied (Table II). These values are also low as compared to the values obtained in other solvents. The heat effect may be attributed to the following reaction as has already been proposed on the basis of the conductance of the solutions:



Heat of solution of the same Lewis acid in acetic acid where a similar bond is formed varies between 19.55—42.73 Kcal/mole.¹³

Comparatively much less heat is evolved on the dissolution of arsenic(III) chloride in nitromethane indicating that it is an extremely weak Lewis acid. The enthalpy value has been found to be 0.78—1.14 Kcal/mole (Table II). The heat of solution of these Lewis acids in nitromethane thus suggests the following order of the strength of these acids:



This is in agreement with the results of similar studies in other solvents reported in literature^{11,12,15,16} and also agrees with conductance work carried out by Paul and coworkers¹ in these laboratories.

Heat of neutralisation: It is well known that almost constant values of the heat of neutralisation of various strong acids against strong bases in water is due to the fact that the heat effect is largely due to the combination of H^+ and OH^- ions, resulting in the formation of feebly ionised water molecules.

In order to study the nature of the reactions and to understand the influence of the solvent on the course of the reaction, heats of neutralisation of fluorosulphuric, sulphuric and formic acids with the organic bases piperidine, α -picoline, and dimethylaniline have been determined and the results are given in Table IV.

Fluorosulphuric acid has been reported to be the strongest acid. Its reaction with piperidine, α -picoline and dimethylaniline (taking both the components in nitromethane)

11. R. C. Paul, S. C. Ahluwalia and S. S. Pahil, *Indian J. Chem.*, 1965, 3, 300.

12. R. C. Paul, S. C. Ahluwalia and S. S. Pahil, (private communication).

13. R. C. Paul, S. C. Ahluwalia, S. K. Rehani and S. S. Pahil, *Indian J. Chem.* 1965, 3, 207.

14. R. C. Paul, P. S. Gill and J. Singh, *Indian J. Chem.*, 1964, 2, 219.

results in the evolution of 40.97—42.30; 33.12—34.89 and 29.06—30.414 Kcal/mole respectively. The enthalpy change may be due to the following reaction:

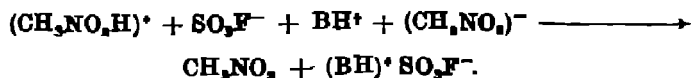
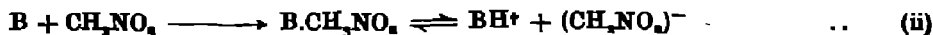
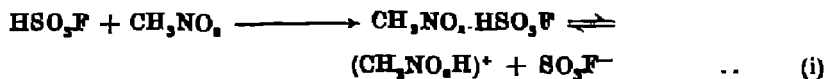


TABLE IV

Heat of neutralisation of various bases with protonic and Lewis acids in nitromethane (25 ml.) at 26.9°

Acid	Base	Heat of reaction (-ΔH Kcal/mole)
HSO ₃ F	Piperidine	41.54
	α-picoline	34.36
	D. M. A.	29.59
H ₂ SO ₄	Piperidine	48.32
	α-picoline	26.78
	D. M. A.	26.30
HCOOH	Piperidine	21.29
	α-picoline	10.18
	D. M. A.	2.71
SbCl ₅	Piperidine	36.39
	α-picoline	33.65
	D. M. A.	20.95
SnCl ₄	Piperidine	39.34
	α-picoline	30.61
	D.M.A.	26.95
AsCl ₃	Piperidine	22.38
	α-picoline	20.53
	D.M.A.	17.52

(D.M. A. is dimethyl aniline)

where B is a base (piperidine, α-picoline or dimethylaniline). This reaction is more highly exothermic as compared to similar reactions in the other solvents. This may be due to the fact that combination of (CH₃NO₂)⁻ and (CH₃NO₂H)⁺ may be more exothermic. The product of neutralisation i.e. BH⁺(SO₃F)⁻ may be much less soluble, thus the heat of precipitation also may be involved. In a few cases the neutralisation product separates out as a solid and thus involves the heat of precipitation. Heat evolved at higher concentrations of the base has been found to be slightly lower than that at lower concentrations. As the heat of solution of the acid shows a marked concentration effect, it is possible that at higher concentrations of the acid some heat is absorbed as the acid ionises as a result of the consumption of the ionised part of the acid due to neutralisation. Basicity of α-picoline is enhanced due to the inductive effect of methyl group in the α-position whereas

in dimethylaniline, steric hindrance may weaken its basic character. Thus enthalpy values for the neutralisation reaction with the same acid in nitromethane are higher for α -picoline than for dimethylaniline. Heat of neutralisation of sulphuric acid and formic acid in nitromethane with piperidine, α -picoline and dimethylaniline are lower as compared to those with fluorosulphuric acid as is evident from the Table V.

TABLE V

Heat of neutralisation ($-\Delta H$ Kcal/mole) of bases with different protonic acids in nitromethane

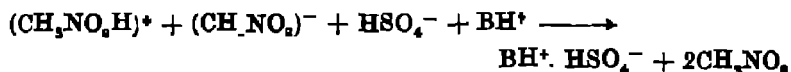
Base	HSO ₃ F	H ₂ SO ₄	HCOOH
Piperidine	40.97-42.8	47.9-48.7	20.6-22.0
α -Picoline	33.12-34.69	28.95-29.1	9.86-10.69
Dimethylaniline	29.05-30.4	26.1-26.4	2.4-2.9

Except in the case of neutralisation of piperidine with sulphuric acid, the higher heat of neutralisation may be due to some turbidity which appears in the solution on neutralisation, indicating the lower solubility of the neutralisation products, thereby introducing heat of precipitation also.

Lower heats of neutralisation in the case of formic acid are due to its being a very weak acid and absorbs large amount of heat for its own ionisation as the neutralisation proceeds to completion. The general order of basic strength as observed in the neutralisation enthalpies with protonic acids is as:

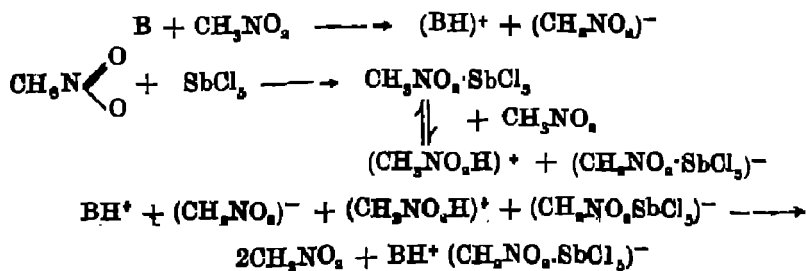


The reactions with sulphuric acid are similar to those of fluorosulphuric acid and since sulphuric acid was taken in excess only one of the protons may take part in neutralisation.



Neutralisation of Lewis acids like antimony(V) chloride, tin(IV) chloride and arsenic (III) chloride with bases like piperidine, α -picoline and dimethylaniline has been carried out in nitromethane and the results are given in Table IV.

Antimony (V) chloride which is the strongest acid among the Lewis acids used, reacts with piperidine, α -picoline and dimethylaniline with an evolution of 35.87-37.23; 32.97-34.00 and 19.97-20.83 Kcal/mole respectively. The heat effect may be attributed to the following reactions:

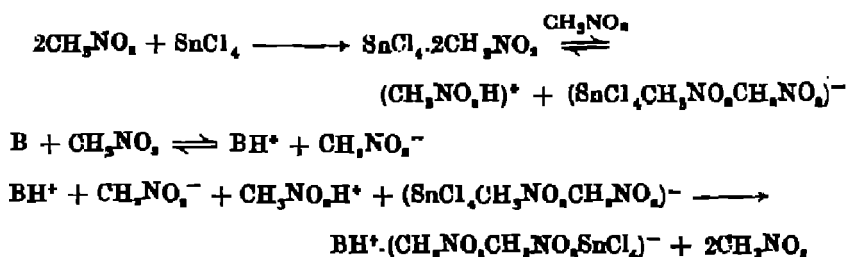


The heat evolved is higher in nitromethane as compared to that obtained in other solvents for the same acid-base pair. This may partially be due to high heat of combination of H^+ and $(CH_3NO_2)^-$ ions and the heat of formation of the insoluble neutralisation product. The order of the strength of bases is as:



Dimethylaniline is a weaker base as compared to the other two bases which is most probably due to steric hindrance as has already been stated.

Tin(IV) chloride reacts with the organic bases, piperidine, α -picoline and dimethylaniline in nitromethane with the evolution of 39.10—40.10; 30.40—30.7'; 26.06—27.27 Kcal/mole respectively. The reactions may be represented as:

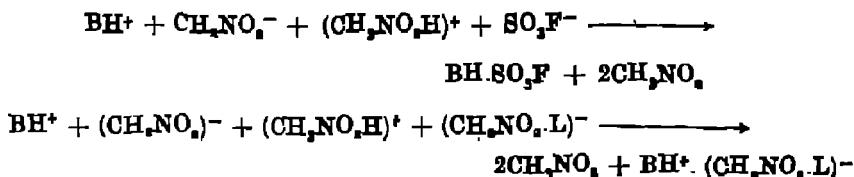


The order of basic strength remains the same as obtained with other acids i.e.,



Neutralisation enthalpies in the case of arsenic(III) chloride (a weak Lewis acid) with usual bases mentioned earlier have been found to vary between 17.26-22.83 Kcal/mole. The order of the strength of bases is the same as in other cases. Since it has been presumed that differences in the heat of neutralisation of different acids are due to the energy needed to ionise more of the acid, and in this case, the acid is less ionised even at low concentration this factor affects the enthalpy causing much less variations in the results.

Since the heat of neutralisation of the solutions of Lewis and protonic acids with organic bases in nitromethane is of the same order, it may be assumed that the behaviour of the solutions of Lewis acids is similar to that of the solution of protonic acids and the course of neutralisation reaction is therefore similar.



In both the cases the major part of heat of reaction may be due to the combination of $(CH_3NO_2H)^+$ and $(CH_3NO_2)^-$.

In cases where the neutralisation product is insoluble, heat of precipitation is also involved.

EXPERIMENTAL

Nitromethane, Lewis and protonic acids and organic tertiary bases were purified as reported earlier¹. Diphenyl ether used as the dilatometric fluid in the isothermal phase-change calorimeter, was purified by repeated crystallisation. It was finally distilled under vacuum into the calorimeter and was sealed with mercury.

Calorimeter: An isothermal phase-change calorimeter described by Dainton *et al.*¹⁷ was used. Diphenyl ether was used as the dilatometric fluid so that all determinations were conducted at its freezing point (26.9°). The calorimeter was placed in a water thermostat which was itself kept in an air thermostat. Both the water and air thermostats were maintained at 26.8°. It was thus possible to control the temperature of the water thermostat to $\pm 0.005^\circ$. The vacuum jacket of the calorimeter further reduced the temperature fluctuations. In this way, a drift rate of the mercury meniscus in the calibrated capillary was controlled within ± 0.001 cm./min. for a few hours. The calibration factor of the calorimeter defined as the amount of mercury displaced when 1 cal. of the heat is evolved or absorbed, was found to be 0.04854 g. shift in the mercury meniscus in the capillary by 1 cm. corresponded to 3.15 cal. The reaction vessel of the calorimeter was thoroughly cleaned and dried. A current of dry nitrogen was passed through it for 10-15 min. before use, to expel traces of moisture. The reaction vessel was fitted with a mercury seal stirrer.

Heats of solution: Freshly distilled solvent (25 ml.) was transferred to the reaction vessel and a known amount of the solute, taken in a fragile glass bulb, was then transferred to the reaction vessel. The thermostats were then operated for 4 hrs. during which the contents of the vessel attained the temperature of the thermostat as indicated by uniform drift rate of mercury meniscus in the calibrated capillary which was invariably zero. The dissolution of the solute was then initiated by breaking the bulb with the sharp end of the glass rod which also acted as the stirrer. The heat change could be found from the displacement of the mercury meniscus of the calibrated capillary. Various amounts of solute were tried, keeping the amount (25 ml.) of the solvent same every time.

Heat of Neutralisation: For neutralisation reactions, standard solutions of the acid and base were prepared. Acid solution (25 ml.) was transferred to the reaction vessel and a known amount of the base solution taken in a sealed fragile glass bulb, was then transferred to the reaction vessel. In some cases 25 ml. of the base solution was transferred to the reaction vessel and a known amount of the acid solution was sealed in a fragile glass bulb and transferred to the reaction vessel. The heat of neutralisation was calculated as the heat evolved on the neutralisation of one mole of the base or acid whichever was taken in the sealed bulb in the presence of an excess of the other component.

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15. R. G. Paul and J. Singh, *Indian J. Chem.*, 1964, 2, 262.
16. S. Sud., M. Sc. Thesis, Panjab University (1965).
17. F. S. Dainton, J. Diaper, K. J. Ivin and D. R. Shcared, *Trans. Faraday Soc.*, 1957, 53, 1269.