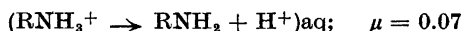


## Heats of Ionization of Some Alkylammonium and Hydroxy Alkylammonium Compounds

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Aqueous heats of dissociation,  $\Delta H_i$ , for a number of aliphatic ammonium compounds have been determined calorimetrically at 25°C.



Amine	$\Delta H_i$ , kJ/mole
$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$	$57.76 \pm 0.03$
$(\text{CH}_3)_2\text{CHNH}_2$	$58.24 \pm 0.07$
$\text{CH}_3(\text{CH}_2)_3\text{NH}_2$	$58.51 \pm 0.03$
$(\text{CH}_3)_3\text{CNH}_2$	$60.16 \pm 0.08$
$\text{HOCH}_2(\text{CH}_2)_2\text{CNH}_2$	$54.10 \pm 0.03$
$(\text{HOCH}_2)_2\text{CH}_2\text{CNH}_2$	$49.91 \pm 0.03$
$(\text{HOCH}_2)_3\text{CNH}_2$	$47.48 \pm 0.03$
$\text{HOCH}_2\text{CH}_2\text{NH}_2$	$50.50 \pm 0.04$
$\text{HOCH}_2(\text{CH}_2)_2\text{NH}_2$	$53.13 \pm 0.04$

Comparisons are made with literature data.  $\Delta H$  and  $\Delta S$  values for the dissociation reactions are discussed.

The present study is part of a program aiming at the determination of thermodynamic data for simple organic compounds in aqueous solution. Here, results are reported from a calorimetric investigation on the protonation of some aliphatic amines: simple alkyl amines and some of their hydroxy derivatives. Heats of dissociation of the ammonium compounds have been calculated from the calorimetric results.

### EXPERIMENTAL

*Materials.* All compounds used in the calorimetric experiments were of commercial origin. The alkyl amines,  $\text{PrNH}_2$ ,  $\text{BuNH}_2$ ,  $t\text{-BuNH}_2$  (Fluka; *purissimum*), and  $i\text{-PrNH}_2$  (Eastman), were purified by fractional distillation at atmospheric pressure through a 20-plate column until their purities as judged by gas chromatography and titration with standard hydrochloric acid were 99.9 % or better.

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Ethanol amine (Eastman) and propanol amine (Fluka, *purissimum*) were fractionated at 12 mm Hg. Titration gave the equivalent weights 61.17 (calc. 61.08) and 75.12 (calc. 75.11), respectively.

2-Amino-2-methyl-propanol-1 (Fluka, *purissimum*) was purified by fractional freezing out twice, at 27.9°C and 27.4°C, respectively. Titration with hydrochloric acid gave the equivalent weight 88.77 (calc. 89.14).

2-Amino-2-methyl-1,3-propanediol (Fluka, *purum*) was purified by recrystallization twice from a methanol-ether (1:3) mixture. The measured equivalent weight was 104.52 (calc. 105.14).

2-Amino-2-hydroxymethyl-1,3-propanediol ("Tris" or "THAM") was a standard sample for the "THAM-test reaction" prepared according to the procedure in Ref. 1.

Constant boiling hydrochloric acid was prepared<sup>2</sup> from analytical grade concentrated acid. Titration with standard sodium hydroxide solution showed the concentration to be  $20.26 \pm 0.01$  % by weight.

*Calorimetric apparatus.* The calorimetric experiments were carried out in isothermal jacket calorimeters with 100 ml reaction vessels made from thinwalled glass. Measurements on *i*-PrNH<sub>2</sub> and *t*-BuNH<sub>2</sub> were made with the calorimeter described in Refs. 3, 4. For the other compounds, an LKB Precision Reaction Calorimeter 8700 was used. (This latter calorimeter was based on the design in Ref. 3.)

*Calibration experiments.* In the experiments where the "prototype" calorimeter<sup>4</sup> was used, electrical calibrations were performed on the system before the reaction had taken place. Both for the reaction and the calibration experiments the final temperature was 25.00°C and calculated enthalpy values will thus refer to this temperature.

With the LKB Calorimeter reaction experiments were performed symmetrically around 25.00°C. Electrical calibrations were made, over the same temperature range, both before and after the reaction had taken place. Mean calibration values were used and derived  $\Delta H$  values will thus refer to 25.00°C.

*Calorimetric calculations.* For the reaction experiments the reaction period was about 1 min and corrected resistance values were computed by extrapolating the fore and after linear parts of the calorimetric curve to the time corresponding to 63 % of the heat evolution (Dickinson's extrapolation method). For the electrical calibrations extrapolations were taken to the time corresponding to 50 % heat evolution.

Heat evolved in an experiment,  $Q$ , was calculated from the expression  $Q = \Delta R \cdot \epsilon / R_m$  where  $\Delta R$  is the corrected thermistor resistance change and  $R_m$  is the mean resistance value in the reaction experiment. The value for the calibration constant,  $\epsilon$ , was calculated from the expression  $\epsilon = Q_c \cdot R_{mc} / \Delta R_c$  where  $Q_c$  is the electrical energy introduced in the calibration experiment,  $\Delta R_c$  is the change in thermistor resistance and  $R_{mc}$  the mean resistance.

In the main experiments aqueous solutions of the amines were protonated by hydrochloric acid. The calorimetric liquids consisted of amine buffers which were prepared from 0.05 M hydrochloric acid by addition of amine until the pH value was nearly equal to the  $pK_a$  value of the ammonium compound formed. Care was taken to avoid carbon dioxide uptake by the buffer solution. The calorimeter vessel was charged with 100 ml of buffer solution and the sealed glass ampoule contained about 2.5 mmole of constant boiling hydrochloric acid. The amine was in excess and small amounts of impurities should therefore not interfere with the measurements.

For most of the compounds investigated, the pH of the calorimetric liquid was rather high and a significant amount of hydroxyl ions was also reacted. This quantity was calculated from pH values measured before and after the reaction had taken place. pH-Measurements were made with a Radiometer pH meter, Type PHM 22 p, and the equipment was standardized with NBS standard samples of potassium biphthalate and potassium hydrogen tartrate.

Heat of dilution of constant boiling hydrochloric acid was determined in several series of experiments where the ionic strength of the calorimetric liquid was the same as in the protonation experiments. Dilutions were performed in 0.05 M solutions of BuNH<sub>2</sub>Cl, HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>Cl, (HOCH<sub>2</sub>)<sub>2</sub>CNH<sub>2</sub>Cl and, as a comparison, NaCl. In the experiments with the ammonium compounds the calorimetric liquids were prepared by neutralization of amine solution. A slight excess of acid was added to make the pH about 3.

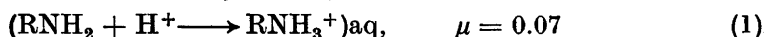
*Units of measurements.* Results of the calorimetric experiments are expressed in terms of absolute joules and refer to isothermal processes at 25.00°C.

## RESULTS

To arrive at enthalpy changes for the dissociation of the ammonium compounds in dilute aqueous solution,  $\Delta H_i$ , corrections must be applied to account for heat evolution caused by hydroxyl ion neutralization and for the heat of dilution of the ampoule content. In the main experiments pH values were rather high and in most cases a significant amount of hydroxyl ions,  $m_{\text{OH}^-}$ , was also neutralized. This quantity was calculated from the volume of the calorimetric liquid and the pH values measured. The difference between the amount of acid contained in the ampoule,  $m$ , and  $m_{\text{OH}^-}$  gives the amount of acid which will protonate the amine,  $m_{\text{corr}}$ . Heat of neutralization of hydroxyl ions at the final ionic strength of the experiments,  $\Delta H_n$ , was taken to be  $-56.4$  kJ/mole.<sup>5</sup>

Results from measurements of heat of dilution of constant boiling hydrochloric acid,  $\Delta H_{\text{dil}}$ , are summarized in Fig. 1. It is seen that, in the range investigated, linear relationships are obtained. For solutions of  $\text{BuNH}_3\text{Cl}$  and  $\text{HOCH}_2\text{CH}_2\text{NH}_3\text{Cl}$  the results are identical whereas a slightly lower value was obtained for the  $(\text{HOCH}_2)_3\text{CNH}_3\text{Cl}$  solution. For the dilution corrections (eqn. 2) the line for the  $(\text{HOCH}_2)_3\text{CNH}_3\text{Cl}$  solution was used for  $\text{HOCH}_2(\text{CH}_3)_2\text{CNH}_2$ ,  $(\text{HOCH}_2)_2\text{CH}_3\text{CNH}_2$ , and  $(\text{HOCH}_2)_3\text{CNH}_2$  whereas the other line was used for all the other compounds.

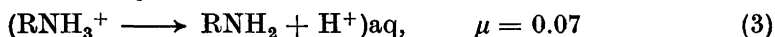
Heat evolved in the idealized process ( $Q_{\text{corr}}$ ):



was calculated from the expression

$$Q_{\text{corr}} = Q_{\text{exp}} + (m - m_{\text{corr}})\Delta H_n + m\Delta H_{\text{dil}} \quad (2)$$

The enthalpy change,  $\Delta H_i$ , at the idealized dissociation reaction:



is equal to  $Q_{\text{corr}}/m_{\text{corr}}$ .

Results of the main calorimetric experiments and the calculations are summarized in Table 1. Uncertainties given are the standard deviation of the mean.

*Comparison with previous measurements.* In Table 2 a comparison is made between the present  $\Delta H_i$  values and literature data. The present calorimetric

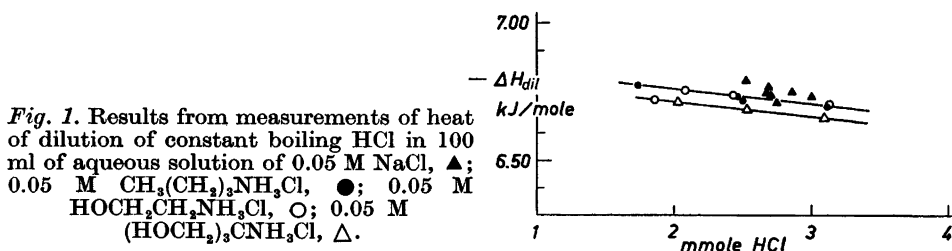


Table 1. Results of calorimetric measurements of the heat of ionization,  $\Delta H_i$ , for some ammonium compounds.

Calorimetric liquid	HCl mmole		$Q_{\text{expt}}$ joule	$Q_{\text{corr}}$ joule	$\Delta H_i$ kJ/mole
	$m$	$m_{\text{corr}}$			
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =10.91	1.8822	1.8455	121.39	106.60	57.76
	1.7099	1.6743	110.27	96.71	57.76
	1.6900	1.6544	109.00	95.49	57.72
	1.9241	1.8855	124.08	108.91	57.76
	1.9080	1.8684	123.16	108.00	57.80
					57.76 ± 0.01
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =10.71	2.6307	2.5956	171.67	152.00	58.56
	2.4228	2.3893	158.00	139.80	58.51
	2.2898	2.2567	149.40	132.11	58.54
	2.4924	2.4570	162.43	143.71	58.49
	2.1907	2.1580	142.77	126.09	58.43
					58.51 ± 0.02
(CH <sub>3</sub> ) <sub>2</sub> CHNH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =10.78	2.9629	2.9168	192.83	170.31	58.39
	2.4925	2.4574	161.43	142.70	58.07
	2.8057	2.7586	181.70	160.19	58.07
	3.0881	3.0420	200.62	177.29	58.28
	2.6420	2.6017	171.94	151.89	58.38
	3.2721	3.2218	212.29	187.61	58.23
					58.24 ± 0.06
(CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =10.74	3.0014	2.9585	199.72	177.21	59.90
	2.8628	2.8220	191.47	170.00	60.24
	3.0115	2.9680	201.49	178.91	60.28
	2.9985	2.9550	200.03	177.51	60.07
	2.9644	2.9215	198.51	176.20	60.31
					60.16 ± 0.08
HOCH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CNH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =9.70	2.2654	2.2622	137.75	122.41	54.11
	1.9442	1.9412	118.30	105.10	54.14
	1.9549	1.9519	118.88	105.60	54.10
	2.0503	2.0472	124.65	110.69	54.07
	2.5199	2.5163	153.09	136.11	54.09
					54.10 ± 0.01
(HOCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> CNH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =9.04	1.6170	1.6165	91.57	80.60	49.86
	2.0167	2.0161	114.19	100.60	49.90
	2.0354	2.0349	115.26	101.60	49.93
	2.2975	2.2969	130.12	114.71	49.94
					49.91 ± 0.02
(HOCH <sub>2</sub> ) <sub>3</sub> CNH <sub>2</sub> buffer, $\mu=0.05$ pH <sub>start</sub> =8.19	2.3444	2.3443	127.09	111.40	47.52
	2.4265	2.4264	131.44	115.21	47.48
	2.3824	2.3823	129.09	113.11	47.48
	2.5012	2.5011	135.47	118.70	47.46
	2.4411	2.4410	132.24	115.90	47.48
					47.48 ± 0.01

Table 1. Continued.

HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	2.1221	2.1197	121.36	106.90	50.43
buffer, $\mu=0.05$	2.0525	2.0501	117.45	103.41	50.44
pH <sub>start</sub> =9.60	2.4349	2.4323	139.42	122.90	50.53
	2.1218	2.1194	121.53	107.09	50.53
	2.0583	2.0560	118.01	104.00	50.58
					50.50 ± 0.03
HOCH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	1.7524	1.7449	105.00	92.71	53.12
buffer, $\mu=0.05$	1.7839	1.7763	106.74	94.20	53.03
pH <sub>start</sub> =10.24	1.8252	1.8168	109.38	96.60	53.17
	2.2432	2.2326	134.21	118.51	53.08
	2.5896	2.5780	155.28	137.20	53.22
					53.13 ± 0.03

results refer to an ionic strength of about 0.07 and a total buffer concentration of 0.1 mole/l. Most of the literature values are obtained from equilibrium measurements and refer to infinite dilution. However, as the idealized process ( $\text{RNH}_3^+ \rightarrow \text{RNH}_2 + \text{H}^+$ )<sub>aq</sub> is an isoelectric reaction, only a minor influence from the ionic strength on the  $\Delta H_i$  values is to be expected.

Inspection of Table 2 shows a good agreement between the present calorimetric values and those derived from equilibrium measurements. The present  $\Delta H_i$  value for  $\text{BuNH}_3^+$  is in excellent agreement with the calorimetric value ( $\mu=0.2$ ) reported earlier.<sup>4</sup> However, the recent calorimetric  $\Delta H_i$  values<sup>23</sup> for  $\text{EtNH}_3^+$  and, in particular,  $\text{HO}(\text{CH}_2)_2\text{NH}_3^+$  are considered to be seriously in error. (These values will be still lower if due consideration is taken to the dilution of 1 M HCl and to neutralization of hydroxyl ions presumably present.)

## DISCUSSION

It is generally recognized that thermodynamic data for an aqueous ionization must be interpreted in terms of changes in solute-solvent interactions as well as in parameters characteristic for the acid-base system under investigation. It is frequently noted that it is easier to correlate  $\Delta G_i$  values with changes in structural parameters than to make corresponding correlations with  $\Delta H_i$  or  $\Delta S_i$ . This is explained by the fact that  $\Delta H_i$  and  $T\Delta S_i$  terms tend to compensate each other to a large extent; the "compensation law".<sup>13</sup> Splitting up  $\Delta G_i$  into an enthalpy and an entropy term will often make the energetics look more complex but will at the same time bring about a more realistic picture of the studied process.

For the purpose of discussion some thermodynamic quantities for the investigated compounds have been summarized in Table 2. As a comparison data are also given for  $\text{MeNH}_3^+$  and  $\text{EtNH}_3^+$ . Where available, the calorimetrically determined  $\Delta H_i$  values have been used to calculate the entropy data.

*Entropy changes.* The pattern observed for the alkyl ammonium compounds is similar to what has been noted for other ionization processes. For an acid ionization process involving carboxylic acids (see, e.g., Ref. 10) or thiols<sup>11</sup>



Table 2. Thermodynamic data for the ionization process  $(\text{RNH}_3^+ \rightarrow \text{RNH}_2 + \text{H}^+)_{\text{aq}}$ . Data refer to 25°C except for EtNH<sub>3</sub><sup>+</sup>. Uncertainties for the present  $\Delta H_1^\circ$  values include estimates of systematic errors.

Amine	$\Delta G_1^\circ$ kJ/mole	$\Delta H_1^\circ$ kJ/mole		$\Delta S_1^\circ$ J/mole, °C
		Lit. data	This work	
CH <sub>3</sub> NH <sub>2</sub>	60.72 <sup>a</sup>	55.00 <sup>a</sup>		-19.2 <sup>a</sup>
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	60.65 <sup>b</sup>	56.82 <sup>b</sup> 47.57 <sup>c</sup>		-13.0 <sup>b</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	60.29 <sup>d</sup>	57.18 <sup>d</sup>	57.76 ± 0.03	-10.5 <sup>d</sup> -8.5
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	60.70 <sup>d</sup>	58.09 <sup>d</sup> 58.45 ± 0.12 <sup>e</sup>	58.51 ± 0.03	-8.9 <sup>d</sup> -7.3
(CH <sub>3</sub> ) <sub>4</sub> CHNH <sub>2</sub>	60.47 <sup>f</sup> 60.64 <sup>g</sup>		58.24 ± 0.07	-7.8 <sup>h</sup>
(CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub>	60.98 <sup>i</sup>	60.07 <sup>i</sup>	60.16 ± 0.08	-3.1 <sup>i</sup> -2.8
HOCH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CNH <sub>2</sub>	55.32 <sup>i</sup>	53.93 <sup>i</sup>	54.10 ± 0.03	-4.6 <sup>i</sup> -4.1
(HOCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> CNH <sub>2</sub>	50.24 <sup>j</sup>	49.86 <sup>j</sup>	49.91 ± 0.03	-1.3 <sup>j</sup> -1.1
(HOCH <sub>2</sub> ) <sub>3</sub> CNH <sub>2</sub>	46.07 <sup>d</sup> 46.06 <sup>p</sup>	47.60 <sup>d</sup> 47.40 <sup>p</sup>	47.48 ± 0.03	5.1 <sup>d</sup> 4.7
HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	54.21 <sup>k</sup> 53.90 <sup>l</sup>	50.54 <sup>k</sup> 50.50 <sup>l</sup> 34.31 <sup>m</sup>	50.50 ± 0.04	-12.3 <sup>k</sup> -11.3 <sup>l</sup> -11.9 <sup>n</sup>
HOCH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	56.82 <sup>o</sup>		53.13 ± 0.04	-12.3

<sup>a</sup> Ref. 18; <sup>b</sup> Ref. 19, 30°C; <sup>c</sup> Ref. 23. Calorimetric determination,  $\mu=0.03$ ; <sup>d</sup> Ref. 6; <sup>e</sup> Ref. 4. Calorimetric determination,  $\mu=0.2$ ; <sup>f</sup> Ref. 20; <sup>g</sup> Ref. 24; <sup>h</sup>  $\Delta S^\circ$  value derived using the mean of the  $\Delta G^\circ$  values <sup>20,24</sup>; <sup>i</sup> Ref. 7; <sup>j</sup> Ref. 8; <sup>k</sup> Ref. 21; <sup>l</sup> Ref. 9; <sup>m</sup> Ref. 23. Calorimetric determination,  $\mu=0.015$ ; <sup>n</sup>  $\Delta S^\circ$  value derived by use of the mean  $\Delta G^\circ$  values;<sup>9,21</sup> <sup>o</sup> Ref. 22. <sup>p</sup> Ref. 25.

alkyl substitution is known to make the  $\Delta S_1$  value more negative, *i.e.* the soluted acid anion will lose entropy relative to that of the neutral molecule.

For a dissociation process involving, *e.g.*, ammonium or thiazolium acids<sup>12</sup>



increased alkyl substitution will make the  $\Delta S_i$  value less negative, *i.e.* the ionic form of the compound will also in this case lose entropy relative to that of the neutral molecule. For the straight chain alkyl ammonium compounds the increase in  $\Delta S_i$  with increasing chain length will rapidly level off and it might be expected that  $\Delta S_i$  will be constant after  $C_4$ , as is the case for carboxylic acids.  $t\text{-BuNH}_3^+$  has a slightly less negative  $\Delta S_i$  value than  $\text{BuNH}_3^+$  which is in line with observations made for carboxylic acids.<sup>10</sup>

Current molecular interpretations of these effects include the hypothesis by King and King<sup>10</sup> suggesting a solvent exclusion effect together with structure promotion in the disordered region outside the primary hydration shell of the ion. Another interpretation is offered by Ives and Marsden<sup>13</sup> who suggest that alkyl groups will promote hydration on the "watery" side of the ionic charge by field perturbation due to the exclusion of water and thereby change of dielectric constant.

For carboxylic acids and thiols,<sup>11</sup> a hydroxyl group close to the acid group will increase the  $\Delta S_i$  value, *i.e.* oppose the effect exerted by alkyl groups. This has been explained on the basis of a preferred orientation of water molecules already existing before the ionization and thus a reduction in the gross orientation effect accompanying the charge generation.<sup>10</sup>

Substitution of a  $\beta$  hydrogen in  $\text{EtNH}_3^+$  and a  $\gamma$  hydrogen in  $\text{PrNH}_3^+$  with a hydroxyl group, has a small effect on the  $\Delta S_i$  values. Comparison between  $\Delta S_i$  values for  $t\text{-BuNH}_3^+$  and its hydroxy derivatives shows a small negative increment for the first hydroxyl group followed by slightly larger positive increments for the second and third groups.

For the present hydroxy ammonium compounds the picture is thus rather mixed and one might assume the existence of opposing effects which nearly balance each other.

*Enthalpy changes.* The alkyl ammonium compounds have all very similar  $\Delta G_i$  values and the difference in the  $T\Delta S_i$  terms are thus largely compensated by corresponding differences in the enthalpy values.

Substitution in the  $\beta$ -position by a hydroxyl group causes a decrease in  $\Delta H_i$  of about 6 kJ/mole both for the ethyl and the *t*-butyl compounds. A saturation effect is noted for additional substitution in the *t*-butyl group. A slight falling off effect (factor=1.3) is found when hydroxy substitutions in the  $\beta$  and  $\gamma$  positions are compared.

For carboxylic acids and thiols the effect of hydroxy substitution is near zero ( $\text{HOCH}_2\text{COOH}$ ,  $\text{CH}_3\text{COOH}$ ,<sup>14</sup>  $\text{HOC}_2\text{H}_4\text{SH}$ ,  $\text{C}_2\text{H}_5\text{SH}$ <sup>11</sup>) or will slightly increase the  $\Delta H_i$  value (several pairs of amino acids,<sup>14</sup>  $\Delta\Delta H \approx 2.5$  kJ/mole). As for the  $\Delta S_i$  values it thus appears that, with regard to the effect of OH-substitution, several factors are at work and will contribute differently for the different types of acids considered here.

The difference between the enthalpy values for the hydroxy substituted compounds and the alkyl compounds is demonstrated by Fig. 2, where  $\Delta H_i$  values are plotted *versus*  $\Delta S_i$  values. It is seen that an "isokinetic" line<sup>15</sup> with a  $\beta$  close to 298°C is found for the alkyl ammonium compounds whereas the hydroxy compounds fall below the line and do not show any linear relationship.

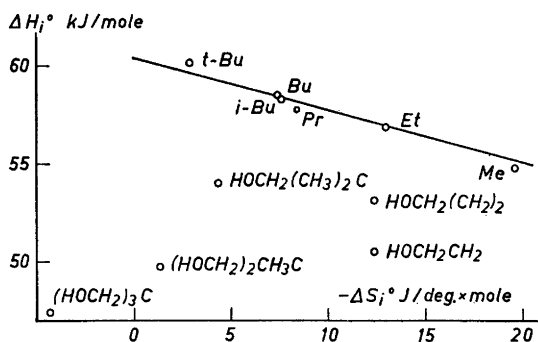


Fig. 2.  $\Delta H_i^\circ$  versus  $\Delta S_i^\circ$  for some ammonium compounds,  $\text{RNH}_3^+$ .

The polar nature of the influence exerted by the hydroxyl groups is, for the present reactions, demonstrated by the linear relationship obtained when  $\Delta G_i^\circ$  is plotted versus Taft's  $\sigma^*$  constants,<sup>16</sup> Fig. 3.

We may in this connection note that  $\Delta G$  for a symmetrical proton transfer reaction like



can be equated with Hepler's "internal enthalpy change",  $\Delta H_{\text{int.}}$ <sup>17</sup> ( $\Delta H_{\text{ext.}} = \beta \Delta S_{\text{ext.}}$ ;  $\beta = T$ <sup>13</sup>). If  $\Delta G$  for eqn. 6 is plotted versus  $\sigma^*$ , a line parallel to that in Fig. 3 is obtained and the polar effect of the hydroxyl groups may be identified with an "internal" enthalpy effect.

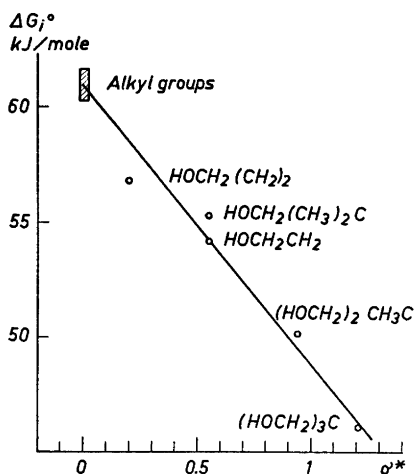


Fig. 3.  $\Delta G_i^\circ$  versus  $\sigma^*$  for some ammonium compounds,  $\text{RNH}_3^+$ .  $\sigma^*$  for R=alkyl groups taken as zero.<sup>16</sup> Saturation effect for the hydroxymethyl groups according to Taft as quoted in Ref. 16:

$$\sigma^*(\text{CH}_2\text{OH})_3: \sigma^*(\text{CH}_2\text{OH})_2: \sigma^*(\text{CH}_2\text{OH}) = 2.2:1.7:1.$$



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