

Heats of Ionization of Arsenious and Arsenic Acids

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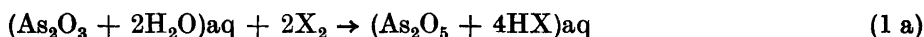
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Heats of ionization have been determined for arsenious acid (first step, $\Delta H_i = + 6.58 \pm 0.03$ kcal/mole) and arsenic acid

(first step, $\Delta H_i = -1.69 \pm 0.04$ kcal/mole
 second step, $\Delta H_i = + 0.77 \pm 0.03$ »
 third step, $\Delta H_i = + 4.35 \pm 0.05$ »)

The heat of ionization of arsenic acid has been discussed with respect to combustion calorimetry of organic chlorine and bromine compounds.

Ever since the days of Berthelot, arsenious oxide solution has been used in combustion calorimetry for organic chlorine and bromine compounds to reduce the free halogen that is formed during the combustion process (see Ref.¹, Chapters 8 and 9):



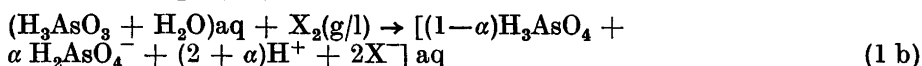
The heat effect accompanying this reaction must of course be known with sufficient accuracy — the correction applied for chlorine compounds usually amounts to *ca.* 20 cal, for bromine compounds it is approximately 80 cal (15–20 % of the chlorine content of an organic substance is converted to elemental chlorine, the corresponding figure for bromine is 90–97 %).

Bjellerup, Sunner and Wadsö² determined the heat of reaction (1 a), $\text{X}_2 = \text{Br}_2(\text{liq})$, and measurements are now in progress in this laboratory with $\text{X}_2 = \text{Cl}_2(\text{g})$ (Sunner, Thorén).

Arsenic acid has a $\text{p}K_a$ value of 2.25³ and is partly ionized in an aqueous solution. As the final solution in a combustion experiment contains varying amounts of either of the strong acids HCl or HBr the degree of ionization of the arsenic acid will differ from experiment to experiment. Thus in an ordinary combustion experiment it may well vary from *ca.* 1 to 15 %, a fact which, surprisingly enough, has never been taken into account. Arsenious acid is very weak, $\text{p}K_a = 9.23$ ³ and its dissociation can be neglected. The same is true for the second ionization of arsenic acid, $\text{p}K_a = 6.77$.³

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In order to get a better representation of the reaction taking place in the bomb solution, eqn. (1 a) should rather be written in the form



To arrive at the hypothetical reaction



it is therefore necessary to correct for the heat of ionization of arsenic acid. No reliable heat of ionization data for this acid seem to be known and it was therefore felt important to undertake a calorimetric determination. Also, in connection with calorimetric studies of ionization reactions carried out in this laboratory it was of interest to determine the enthalpy changes connected with the second and third ionization steps of arsenic acid as well as with the first step of arsenious acid. Heats of ionization of the second and third step of the latter acid cannot easily be determined calorimetrically as corresponding pK_a values are very high.⁴

EXPERIMENTAL

Materials. Arsenious oxide was of acidimetric standard grade (National Bureau of Standards, Washington, Lot No. 83b), arsenic oxide of Baker's analytical grade and sodium chloride, Merck, analytical grade. The water was glass distilled and free from carbon dioxide. In preparing the calorimetric buffer solutions, 0.050 M As_2O_3 and As_2O_5 solutions, respectively, were partly neutralized by NaOH pellets (Bohus Eka, analytical grade, 0.04 % Na_2CO_3). Solutions were prepared and handled with precautions taken to avoid uptake of carbon dioxide.

Apparatus and calorimetric procedure. The calorimetric measurements were carried out in an isothermal-jacket glass calorimeter which has been described in detail elsewhere.⁵ The heat equivalent of the calorimetric system was determined electrically by passing a known current for a given time (240 sec) through the heater. Calibrations were performed on the systems after the reaction had taken place.

The calorimeter was charged with 100 ml of the appropriate buffer solution, and the sealed glass ampoule contained about 1 mmole of dilute hydrochloric acid (1.690 mmole HCl per g of solution). The calorimeter reached thermal equilibrium 1 min after breaking the ampoule, and initial and final thermistor resistance values were evaluated graphically. Blank experiments were performed by measuring the heat of dilution of the HCl used in 0.1 M NaCl solution.

pH measurements were made on the calorimetric liquids before and after the experiments using glass electrodes (Radiometer Type 202 B IP in the acid and neutral range, and Type 200 B AH in the alkaline range) and a Radiometer pH meter 22. The pH meter was calibrated against standard buffer solutions (± 0.02 pH units).

Units of measurement. The results of the calorimetric experiments are expressed in terms of the defined calorie, equal to 4.1840 abs. joules, and refer to the isothermal process at 25°C.

RESULTS

In order to arrive at the enthalpy change accompanying the ionization reaction (the measured quantity refers to the reverse reaction!) the following corrections must be applied.

1. The heat of dilution of HCl. This quantity is obtained from the blank experiments (V, Table 1).

2. For the experiments performed in the high pH-range (I, IV) the neutralization reaction between H^+ and OH^- must be considered. The amounts neutralized were calculated from the measured pH-values and the enthalpy change was taken to be $\Delta H = -13.5$ kcal/mole.

3. In the experiments carried out on the acid side (II) part of the added H^+ ions did not react. This amount was again calculated from the pH-measurements and subtracted from the total amount of added HCl.

The experimental results are summarized in Table 1. The following symbols have been used:

$\log R_i/R_f$ is the expression proportional to the corrected temperature change;
 q_{exp} is the experimentally determined heat effect;
 q_{corr} is the heat effect referring to the reversed ionization reaction investigated: $A_{aq}^- + H_{aq}^+ \rightarrow HA_{aq}$;
 ΔH is $q_{corr}/\text{mmole HCl}(\text{corr})$ which is the negative enthalpy of ionization.

Table 1.

Calorimetric liquid	Ampoule content mmole of HCl	Final pH	$10^4 \times \log R_i/R_f$	q_{exp} cal	q_{corr} cal	mmole of HCl, corr.	ΔH kcal/mole
0.050 M As_2O_3 Initial pH = 9.15 I	0.8644	9.00	5270	6.090	5.713	0.8640	-6.61
	0.9414	8.99	5698	6.585	6.176	0.9410	-6.56
	1.0513	8.97	6344	7.331	6.874	1.0509	-6.54
	0.9613	9.00	5843	6.752	6.334	0.9609	-6.59
						Mean	-6.58 \pm 0.03
0.050 M As_2O_3 Initial pH = 4.32 II	1.0958	3.20	-1111	-1.283	-1.754	1.038	1.69
	0.9227	3.28	-949	-1.096	-1.493	0.875	1.71
	1.0507	3.22	-1074	-1.240	-1.692	0.995	1.70
	0.9502	3.26	-949	-1.096	-1.505	0.900	1.67
						Mean	1.69 \pm 0.03
0.050 M As_2O_5 Initial pH = 6.80 III	1.0475	6.67	1093	1.262	0.812	1.0475	-0.78
	1.0357	6.65	1076	1.242	0.794	1.0357	-0.77
	1.0292	6.67	1092	1.261	0.818	1.0292	-0.79
	1.0249	6.69	1040	1.201	0.760	1.0249	-0.74
						Mean	-0.77 \pm 0.03
0.050 M As_2O_5 Initial pH = 10.54 IV	0.9996	9.98	4352	5.025	4.258	0.975	-4.37
	0.9734	9.98	4231	4.885	4.129	0.948	-4.36
	0.8585	10.06	3774	4.323	3.630	0.835	-4.35
	0.8872	10.06	3834	4.427	3.722	0.863	-4.31
						Mean	-4.35 \pm 0.05
Blank experiment	0.9739		376	0.434			
0.100 M NaCl	1.0590		376	0.434			
V	0.9785		358	0.413			
	0.9621		358	0.413			

Table 2.

Reaction	pK_a	ΔG° kcal/mole	ΔH kcal/mole	ΔS e.u.
$H_3AsO_3 \rightarrow H_2AsO_3^- + H^+$	9.23	+ 12.59	+ 6.58	-20.2
$H_2AsO_4^- \rightarrow HAsO_4^{2-} + H^+$	2.25	+ 3.07	-1.69	-16.0
$HAsO_4^{2-} \rightarrow AsO_4^{3-} + H^+$	6.77	+ 9.23	+ 0.77	-28.4
$HAsO_4^{2-} \rightarrow AsO_4^{3-} + H^+$	11.53	+ 15.82	+ 4.35	-38.5
$H_3PO_4 \rightarrow H_2PO_4^- + H^+{}^a$	2.15	+ 2.93	-1.83	-16.0
$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+{}^b$	7.20	+ 9.82	+ 0.99	-29.6

^a Bates, R. G. *J. Res. Natl. Bur. Std.* **47** (1951) 127.

^b Bates, R. G. and Acree, S. F. *Ibid* **30** (1943) 127.

DISCUSSION

In Table 2 are compiled pK_a -values, free energies, enthalpies and entropies of ionization for arsenious acid, arsenic acid and, for comparison, phosphoric acid.

The pK_a -values given in Table 2 are not strictly comparable with the enthalpy data arrived at here as the latter are measured at an ionic strength of 0.1 to 0.3 (as a necessary condition of the experiments) and the dissociation constants refer to zero or very low ionic strength. However, it is judged that these inconsistencies are insignificant for the present discussion (see, e.g., Ref.⁶).

Recently, Flis, Mishchenko and Tumanova⁷ determined potentiometrically the ionization constants for arsenic acid at temperatures between 10 and 50°C and derived the corresponding heats of ionization. They obtained (25°C) + 0.6, + 2.8 and -5.4 kcal/mole for the first, second and third dissociation steps, respectively. The agreement is indeed very poor, which is not surprising as the precision of their experimental results does not seem to allow calculation of accurate heat values, especially as the heats of ionization are very temperature sensitive.

The enthalpy data given in Table 2 follow the general pattern for ionization processes for acids: strong acids have slightly negative heat of ionization values, weak acids values close to zero, and very weak acids pronounced endothermic heats of ionization. As expected, heat and entropy changes for arsenic acid are very nearly the same as for phosphoric acid.

In combustion calorimetry of organic chlorine and bromine compounds using As_2O_3 solution as reductant, the final state in the bomb will contain a mixture of arsenic acid and the corresponding halogen acid (+ unreacted As_2O_3 solution). At the concentrations formed in the process arsenic acid would be dissociated to either 10-30 % for chlorine compounds (bomb solution 10 ml) or 20-50 % for bromine compounds (bomb solution 30 ml). However, the presence of the halogen acids will decrease this dissociation to between 1 and 15 %. The degree of dissociation is thus quite low and since the heat of ionization for the first step is only -1.69 kcal/mole the correction to be made for this ionization to the combustion calculations is small. It is, however, significant. The value at present in use for the heat of reaction of arsenious

oxide solution with bromine is -28.46 ± 0.06 kcal/mole.² If this is corrected to account for the ionization a value of -28.30 ± 0.05 is obtained for the defined reaction (1 c).

In combustion calorimetry of organic chlorine and bromine compounds it is recommended that the pH of the final solution is measured and used to correct for ionization of the arsenic acid.

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