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Adducts of Arsenic Trihalides with Heterocyclic Amines: Synthesis, Characterization, and Thermochemistry

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The adducts $AsX_3 \cdot nL$ [X = Cl, Br, or I; n = 1, 1.5, or 2; L = pyridine (py), β-picoline (β-mpy), or γ-picoline (γ-mpy)] were prepared and characterized by melting points, elemental analysis, thermogravimetric analysis, and infrared spectroscopy. From the enthalpies of dissolution of the adducts in ethanol or 10% aqueous diethanolamine, arsenic trihalides, and ligands at 298.15 K, the standard enthalpies ($\Delta_r H^\ominus$) for the reactions $AsX_3(s,l) + nL(l) = AsX_3 \cdot nL(s)$ were determined, giving the following values ($\Delta_r H^\ominus$/kJ mol^{-1}): $AsCl_3 \cdot py$ = −110.1 ± 0.4; $AsCl_3 \cdot \beta$-mpy = −120.6 ± 0.7; $AsCl_3 \cdot \gamma$-mpy = −120.2 ± 0.9; $2AsBr_3 \cdot 3py$ = −91.1 ± 0.6; $AsBr_3 \cdot 3\beta$-mpy = −216.6 ± 1.1; $AsBr_3 \cdot 2\gamma$-mpy = −144.6 ± 0.6; $AsI_3 \cdot 2py$ = −107.0 ± 0.5; $AsI_3 \cdot \beta$-mpy = −60.0 ± 0.9; and $AsI_3 \cdot \gamma$-mpy = −72.6 ± 1.5. From $\Delta_r H^\ominus$, the enthalpies of formation of arsenic trihalides and the enthalpies of formation of ligands, the enthalpies of formation of adducts were calculated. The standard enthalpies of reaction for $AsCl_3(g) + nL(g) = AsX_3 \cdot nL(s)$ ($\Delta_M H^\ominus$) and for $AsX_3 \cdot nL(s) = AsX_3(s,l) + nL(g)$ ($\Delta_D H^\ominus$) were calculated and the standard enthalpies of arsenic–nitrogen bonds were estimated.

Introduction

The acceptor properties of arsenic trihalides are well established in the literature (*1–6*) and the synthesis of numerous adducts have been reported, many of them in the early part of this century (*1–3*, *7–10*). However, there is a lack of thermochemical data for these compounds. No information about the enthalpy of the arsenic–donor atom bond is available. Pyridine and substituted pyridines have been used as ligands and several adducts of the salts of transition elements have been studied (*11–13*). Adducts of arsenic trihalides and pyridine were synthesized for the first time in 1926 by Dafert and Melinski (*2*). In the following years, several authors (*7–10*) prepared and characterized these adducts by means of melting points and elemental analysis. The interaction of arsenic trihalides and α-picoline in several solvents has also been studied (*14–16*).

The adducts of arsenic trihalides are generally unstable to atmospheric moisture and decompose in the sequence $AsCl_3 > AsBr_3 \gg AsI_3$. In this paper we report the synthesis, characterization, and thermochemical study of adducts of arsenic trihalides with pyridine, β-picoline, and γ-picoline with the purpose of obtaining the enthalpies involved in the formation of the adducts.

Experimental Section

***Chemicals*.** Arsenic trichloride (Carlo Erba) was purified by distillation in vacuo through an efficient column. Arsenic tribromide was prepared from arsenic trioxide (Carlo Erba), sulfur (Baspol Produtos Quimicos Ltda), and bromine (Baker), according to the method described by Oddo and Giachery (*17*). The product was purified by distillation in vacuo through an efficient column. Arsenic triiodide was prepared from arsenic trioxide (Carlo Erba), hydrochloric acid (Merck), and potassium (Carlo Erba) according to the method described by Bailar (*18*). The product was purified by recrystallization from carbon disulfide. Pyridine (Reagen), β-picoline (Baker), and γ-picoline (Baker) were dried and purified by distillation through an efficient column and stored over 4 Å molecular sieves. Ethanol, carbon disulfide, petroleum ether, and chloroform were dried via methods outlined in the literature and stored over 4 Å molecular sieves. Diethanolamine (Merck) was used as obtained without further purification. Due to the moisture sensitivity and toxic nature of the compounds involved, all the preparations and manipulations were carried out in polyethylene glovebags under a dry nitrogen atmosphere.

Table I. Melting Points and Yields of the Adducts[a]

adducts	mp[b]	appearance[c]	% yield
$AsCl_3 \cdot py$	114–115	wh cr	65
$AsCl_3 \cdot \beta$-mpy	90–91	wh cr	53
$AsCl_3 \cdot \gamma$-mpy	131–132	wh cr	66
$2AsBr_3 \cdot 3py$	144–145	pa ye cr	70
$AsBr_3 \cdot 3\beta$-mpy	91–92	pa ye cr	78
$AsBr_3 \cdot 2\gamma$-mpy	104–105	pa ye cr	66
$AsI_3 \cdot 2py$	162	br pw	88
$AsI_3 \cdot \beta$-mpy	90–91	br pw	60
$AsI_3 \cdot \gamma$-mpy	110–111	br pw	72

[a] Elemental analysis (C, H, N, As, halogens) in agreement with theoretical values were obtained and submitted for review. [b] °C, uncorrected. [c] Key: wh, white; pa, pale, ye, yellow; br, brown; cr, crystals; pw, powder.

***Adducts Synthesis*.** Adducts were prepared by combining solutions of the donor and the acceptor in 1:1 molar ratios, using petroleum ether as a solvent for the adducts of arsenic trichloride; 1:2 molar ratios in petroleum ether for adducts of arsenic tribromide (a molar relation 1:1 yielded compounds of indefinite stoichiometry) and 1:1 molar ratios in carbon disulfide for adducts of arsenic triiodide. In the case of the adduct of pyridine, a molar ratio of 1:2 was used, because the 1:1 molar ratio led to a product of indefinite stoichiometry. A typical procedure is given below.

***Arsenic Trichloride–Pyridine*.** To a solution of 6.48 mL of $AsCl_3$ (77.3 mmol) in 50 mL of petroleum ether, 6.11 g (77.3 mmol) of pyridine was added slowly and dropwise with stirring. The stirring was maintained for at least 3 h. After removal of the solvent, the white crystals formed were washed with three portions of 20 mL of petroleum ether, and dried for several hours in vacuo. The compound obtained was stored in a desiccator over calcium chloride.

***Analytical Section*.** Carbon, hydrogen, and nitrogen were determined by microanalytical procedures. Halogen analysis was obtained by potentiometric titration with standard N/10 $AgNO_3$ solution (*19*), after the adducts were dissolved in water. Arsenic content was determined by redox titration of the aqueous solution of the adduct samples, with standard 0.05 N iodine solution, to the appearance of the blue color of starch used as an indicator (*20*).

***Spectra*.** Infrared spectra were obtained with sample mulls in Nujol sandwiched between NaCl plates for the adducts, and by using a liquid cell with NaCl windows for the ligands, on a Perkin-Elmer 180 spectrophotometer.

***Thermogravimetric Studies*.** These were made in a nitrogen atmosphere in a Perkin-Elmer TGS-1 system using samples

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Table II. Main Infrared Absorption Bands (cm^{-1}) of Adducts and Ligands[a]

	assignment										
compound	$\nu_{(CC)}$	$\nu_{(CC)}$	$\nu_{(CC,CN)}$	$\nu_{antisym}(CH_3)$	$\nu_{(CC,CN)}$	$\nu_{(CC,CN)}$	$\nu_{sym}(CH_3)$		ring	$\beta_{(CH)}$	$\nu_{(CC,CN)}$
pyridine	1573 sh	1561 s	1463 s		1418 s	1355 m				1193 s	1123 s
$AsCl_3$·py	1586 s	1513	1468 s		1393 w	no		1223 w		1178 s	1150 m
$2AsBr_3$·3py	1585 s	1513 s	1467 s		no	no		1225 w		1176 w	1141 w
AsI_3·2py	1580 s	1505 s	no		no	no		1226 w		1165 w	1113 w
β-picoline	1572 sh	1558 s	1456 s	1433 s	1393 s	1315 w	1363 s		1206 m	1170 s	
$AsCl_3$·β-mpy	1593 m	1532 s	no	no	no	1327 w	no		1241 m	1163 w	
$AsBr_3$·3β-mpy	1595 s	1537 s	no	1430 m	no	1333 m	no		1248 m	1151 w	
AsI_3·β-mpy	1591 m	1533 s	no	no	no	no	no		1236 m	1161 w	
γ-picoline	1585 s	1545 s	1466 s	1426 s	1393 s	1341 sh	1361 s		no	no	
$AsCl_3$·γ-mpy	1593 m	1575 m	1487 s	no	no		no		1232 w 1211 w	1180 m	
$AsBr_3$·2γ-mpy	1617 s	1595 m	1483 m 1463 w	no	no	1344 w	no		1238 w 1223 w	1180 m	
AsI_3·γ-mpy	1615 m	1572 m	1478 m	no	no	1341 sh	no		1238 w 1213 w	no	

[a] Intensity of bands: vs, very strong; s, strong;, m, medium; w, weak; sh, shoulder. Key: ν, stretching; β, bending in plane; γ, bending out of plane; α, ring deformation in plane; ϕ, ring deformation out plane; ring, ring breathing; R, rocking; sym, symmetric; antisym, antisymmetric; no, not observed.

varying in weight from 0.770 to 1.000 mg and a heating rate of 10 °C min^{-1}.

Calorimetric Measurements. All the solution calorimetric determinations were carried out in a LKB 8700-1 precision calorimeter. Each measurement was performed at 298.15 ± 0.02 K with a thin-walled ampule containing reactant being broken in a 100-mL glass reaction vessel containing 90.0 mL of calorimetric solvent. Details of the measurement procedure, the apparatus, and data processing have already been described (*21*). Uncertainty intervals associated with the variation of the enthalpy data are quoted as twice the standard deviation of the mean.

Results and Discussion

All the adducts of arsenic trichloride were prepared by using a molar ratio 1:1 between $AsCl_3$ and ligand. Relations of 1:2 or 1:3 yielded products of indefinite stoichiometry and after recrystallization led to the 1:1 adduct. For arsenic tribromide a molar ratio of 1:1 led to an indefinite product. For the adduct AsI_3·2py, a molar ratio of 1:1 also gave a product of indefinite stoichiometry.

The adducts of arsenic triiodide were obtained as orange powders, which in a few days turned brown without modifying their composition. All adducts are hydroscopic in the sequence $AsCl_3 > AsBr_3 \gg AsI_3$. The melting points, colors, yields, and analytical data are summarized in Table I.

Infrared Data. The infrared spectra of pyridine adducts show dislocation and splitting of several bands when compared with the spectrum of free pyridine although the pattern of the spectra of the adducts is similar to that of the free ligand. Qualitatively the coordinated pyridine is distinguished from free pyridine by the presence of a weak band at 1230 cm^{-1} and by dislocation of bands at 1573, 584, and 400 cm^{-1} to higher frequencies (*22*). The similarity of the spectra shows that the electronic density is the same in the aromatic ring since significant changes in the electronic density would produce large changes in the infrared spectra (*23*, *24*).

The infrared spectra of β-picoline and γ-picoline adducts are similar to those of the free ligands except for dislocations and splitting of several bands. Appreciable dislocations toward higher frequencies are observed after coordination for the absorptions at 1585, 1545, and 1206 cm^{-1}. The infrared data can be interpreted in terms of a coordination of ligands to the arsenic trihalides (*25*, *26*). The main infrared bands of the ligands and the adducts are presented in Table II.

Thermogravimetric Data. The thermogravimetry of the adducts of arsenic trichlorides shows a similar behavior. All of them evolve ligand and arsenic trichloride together in a single step. For the adduct of arsenic tribromide with pyridine, an elimination of ligand and arsenic tribromide in a single step was also observed. For the adduct with γ-picoline, the curve obtained showed the loss of mass in two steps: the first with elimination of 1 mol of ligand and the second with elimination of 1 mol of ligand and 1 mol of arsenic tribromide. The adduct of β-picoline showed two steps in the thermal decomposition: the first with elimination of 1 mol of ligand and the second with elimination of 2 mol of ligand and 1 mol of arsenic tribromide. The adducts of arsenic triiodide presented similar thermal curves, with elimination of ligand and arsenic triiodide in a single step. With the exception of AsI_3·β-mpy and AsI_3·γ-mpy, the thermoanalytical data of all the adducts of arsenic trihalides showed an instability of the adducts in the liquid phase. Table III presents the thermoanalytical data of the adducts.

Table III. Thermoanalytical Data of the Compounds of Formula $AsX_3 \bullet nL$

compound	weight loss, % calcd	weight loss, % obsd	temp range, K	mp, K
$AsCl_3$·py	100.0	96.65	311–448	387–388
$AsCl_3$·β-mpy	100.0	96.53	298–481	363–364
$AsCl_3$·γ-mpy	100.0	99.74	409–442	404–405
$2AsBr_3$·3py	100.0	95.16	419–450	417–418
$AsBr_3$·3β-mpy	15.68	19.09	298–407	364–365
	84.32	80.66	407–478	
$AsBr_3$·2γ-mpy	18.59	14.26	298–334	377–378
	81.41	84.22	334–483	
AsI_3·2py	100.0	99.28	439–471	435
AsI_3·β-mpy	100.0	95.91	429–501	363–364
AsI_3·γ-mpy	100.0	98.85	448–481	383–384

Calorimetric Measurements. The standard enthalpies of reaction ($\Delta_r H^\ominus$) can be determined for reactions 1

$$AsX_3(s,l) + nL(l) = AsX_3{\cdot}nL(s); \quad \Delta_r H^\ominus \qquad (1)$$

These standard enthalpy changes were obtained through the standard enthalpy of reactions 2–5 in solution. The application

$$AsX_3(s,l) + \text{calorimetric solvent} = \text{solution A}; \quad \Delta_1 H^\ominus \qquad (2)$$

$$nL(l) + \text{solution A} = \text{solution B}; \quad \Delta_2 H^\ominus \qquad (3)$$

$$AsX_3{\cdot}nL(s) + \text{calorimetric solvent} = \text{solution C} \quad \Delta_3 H^\ominus \qquad (4)$$

$$\text{solution B} = \text{solution C}; \quad \Delta_4 H^\ominus \qquad (5)$$

of Hess' law to the series of reactions 2–5 gives $\Delta_r H^\ominus$. Thus, $\Delta_r H^\ominus = \Delta_1 H^\ominus + \Delta_2 H^\ominus - \Delta_3 H^\ominus$ since the final B and C solutions are equivalent and $\Delta_4 H^\ominus = 0$. The enthalpies of dissolution of arsenic trihalides, ligands, and adducts are listed in

assignment										
$\beta_{(CH)}$	$\beta_{(CH)}$	$R_{(CH_3)}$	ring	ring	$\gamma_{(CH)}$	$\phi_{(CC)}$	$\phi_{(CC)}$	$\alpha_{(CCC)}$	$\alpha_{(CCC)}$	$\phi_{(CC)}$
1045 s			1011 s	973 s	923 s	729 s	685 s	657 sh	584 s	no
1063 m			1033 m	971 m	890 m	727 s	705 s	655 s	592 m	434 w
1039 sh										
no			1033 m	no	no	726 s	no	no	589 m	432 w
no			1031 m	980 w	no	725 s	717 sh	652 sh	587 w	no
1103 s	1085 s	1020 sh	1011 s		769 s	690 s		610 s	no	no
1096 m	1087 w	1026 w	1015 w		767 s	662 s		612 w	522 m	444 w
1101 s	1080 w	1023 s	1008 s		786 m	662 vs		609 m	514 w	440 m
1095 m	no	1025 w	1000 w		757 s	654 s		no	no	439 w
						647 sh				
	1048 m	1021 s		978 s	no	707 m		617 w	no	no
	1078 w	1041 w		990 w	no	730 s		no	522 w	462 sh
	1086 w	1048 w		986 w	no	725 w		654 w	552 m	454 m
	1071 w	1048 w		990 w	750 m	717 m		no	557 m	447 m

Table IV. Enthalpies of Dissolution at 298.15 K

substance	calorim solvent	no. of expts	$\Delta H^\ominus$, kJ mol^{-1}
$AsCl_3$ (l)	EtOH[a]	5	−131.89 ± 0.31
$AsBr_3$ (s)	EtOH[a]	5	−85.07 ± 0.36
AsI_3(s)	EtOH[a]	5	−49.98 ± 0.34
AsI_3(s)	DEA[b]–water	5	−135.5 ± 0.57
pyridine(l)	1:1 $AsCl_3$–EtOH[a]	5	−10.64 ± 0.09
pyridine(l)	3:2 $AsBr_3$–EtOH[a]	5	−15.65 ± 0.31
pyridine(l)	2:1 AsI_3–EtOH[a]	5	−16.93 ± 0.39
β-picoline(l)	1:1 $AsCl_3$–EtOH[a]	5	−16.49 ± 0.09
β-picoline(l)	3:1 $AsBr_3$–EtOH[a]	5	−66.52 ± 0.88
β-picoline(l)	1:1 AsI_3–DEA[b]–water	5	−9.08 ± 0.30
γ-picoline(l)	1:1 $AsCl_3$–EtOH	5	−20.55 ± 0.44
γ-picoline(l)	2:1 $AsBr_3$–EtOH	5	−31.32 ± 0.20
γ-picoline(l)	1:1 AsI_3–DEA[b]–water	5	−10.35 ± 0.12
$AsCl_3$·py(s)	EtOH[a]	5	−32.40 ± 0.21
$AsCl_3$·β-mpy(s)	EtOH[a]	5	−27.80 ± 0.67
$AsCl_3$·γ-mpy(s)	EtOH[a]	5	−32.21 ± 0.72
$2AsBr_3$·3py(s)	EtOH[a]	5	−9.61 ± 0.27
$AsBr_3$·3β-mpy(s)	EtOH[a]	5	65.02 ± 0.41
$AsBr_3$·2γ-mpy(s)	EtOH[a]	5	28.19 ± 0.42
AsI_3·2py(s)	EtOH[a]	5	40.11 ± 0.08
AsI_3·β-mpy(s)	DEA[b]–water	5	−84.58 ± 0.66
AsI_3·γ-mpy(s)	DEA[b]–water	5	−73.32 ± 0.97

[a] Ethanol. [b] Diethanolamine.

Table IV. The standard enthalpy of formation ($\Delta_f H^\ominus$) of the adducts can be determined from the standard enthalpy of formation ($\Delta_f H^\ominus$) of the arsenic trihalides and of the ligands and the $\Delta_R H^\ominus$ values obtained for reaction 1: $\Delta_f H^\ominus$(adduct) = $\Delta_r H^\ominus + \Delta_f H^\ominus(AsX_3) + n\Delta_f H^\ominus$(ligand). The standard enthalpies of reactions 6 and 7, $\Delta_D H^\ominus$ and $\Delta_M H^\ominus$, respectively, were also determined. From these

$$AsX_3\cdot nL(s) = AsX_3(l,s) + nL(g); \quad \Delta_D H^\ominus \tag{6}$$

$$AsX_3(g) + nL(g) = AsX_3\cdot nL(s); \quad \Delta_M H^\ominus \tag{7}$$

equations one derives $\Delta_D H^\ominus = -\Delta_r H^\ominus + \Delta_l^g H^\ominus$ (ligand) and $\Delta_M H^\ominus = \Delta_D H^\ominus + \Delta_s^g H^\ominus (AsX_3)$, where $\Delta_l^g H^\ominus$ is the standard enthalpy of vaporization and $\Delta_s^g H^\ominus$ is the standard enthalpy of sublimation. Table V gives these standard thermochemical values for arsenic trihalides, ligands, and adducts.

For a series of adducts with the same stoichiometry, $\Delta S^\ominus$ values can be considered constant and a direct correlation between $\Delta G^\ominus$ and $\Delta H^\ominus$ values can be obtained. Considering $\Delta_r H^\ominus$, $\Delta_f H^\ominus$, $\Delta_M H^\ominus$, $\Delta_D H^\ominus$, the sequence of stability of the adducts is γ-mpy > β-mpy > py. The values of standard enthalpy of formation of adducts in the condensed phase ($\Delta_r H^\ominus$) can be used to relate the donor strength of the ligand (*30*, *32*). For adducts of the same stoichiometry with a fixed acceptor the energy involved can be considered constant and the observed values $\Delta_r H^\ominus$ reflect the basicity order γ-mpy > β-mpy > py.

The standard enthalpy of interaction of arsenic trihalides with ligands in the gas phase ($\Delta_r H^\ominus$(g))

$$AsX_3\cdot nL(g) = AsX_3(g) + nL(g); \quad \Delta_r H^\ominus(g) \tag{8}$$

can be used to calculate the standard enthalpy of the arsenic–nitrogen bond ($\bar{D}$(As–N) = $\Delta_r H^\ominus(g)/n$) if the values of the standard enthalpy of sublimation of each adduct is known (*30*, *33–35*). The melting point and the thermogravimetry studies

Table V. Summary of the Thermochemical Results (kJ mol^{-1})

compound	$\Delta_r H^\ominus$	$\Delta_f H^\ominus$	$\Delta_s^g H^\ominus$ or $\Delta_l^g H^\ominus$	$\Delta_M H^\ominus$	$\Delta_D H^\ominus$	$\Delta_r H^\ominus$(g)	$\bar{D}$(As–N)
$AsCl_3$(l)		−305.0[a]	43.5[a]				
$AsBr_3$(s)		−197.5[a]	67.5[a]				
AsI_3(s)		−58.2[a]	95.0[b]				
pyridine(l)		101.2 ± 0.7[c]	40.2[c]				
β-picoline(l)		61.9 ± 0.5[c]	44.4 ± 0.0[c]				
γ-picoline(l)		58.5 ± 1.1[c]	45.3 ± 0.4[c]				
$AsCl_3$·py(s)	−110.1 ± 0.4	−313.9		−193.8	150.03 ± 0.6	153.7	153.7
$AsCl_3$·β-mpy(s)	−120.1 ± 0.7	−363.7		−208.5	165.0 ± 1.1	164.1	164.1
$AsCl_3$·γ-mpy(s)	−120.2 ± 0.9	−366.7		−209.0	165.5 ± 1.5	163.7	163.7
$2AsBr_3$·3py(s)	−91.1 ± 0.6	−136.8		−218.9	151.4 ± 0.9	178.7	119.1
$AsBr_3$·3β-mpy	−216.6 ± 1.1	−228.4		−417.3	349.8 ± 1.1	372.9	124.3
$AsBr_3$·2γ-mpy	−144.6 ± 0.6	−255.1		−302.7	235.2 ± 1.1	257.4	128.7
AsI_3·2py	−107.0 ± 0.5	37.2		−282.4	187.4 ± 0.8	242.2	121.1
AsI_3·β-mpy	−60.0 ± 0.9	−56.3		−199.4	104.4 ± 1.5	155.0	155.0
AsI_3·γ-mpy	−72.5 ± 1.5	−72.2		−211.8	117.8 ± 1.7	167.6	167.6

[a] Reference *27*. [b] Reference *28*. [c] Reference *29*.

of the adducts showed that most of them decompose on heating. To evaluate the relative strengths of arsenic–nitrogen bonds, it was necessary to assume that the molar enthalpy of sublimation of each adduct was equal to the enthalpy of vaporization of 1 mol of ligand (*34*, *35*). Standard enthalpies of sublimation of several adducts (that could be measured) and its respective ligands, confirmed our assumption (*36–38*). For adducts of the same stoichiometry, $\bar{D}$(As–N) values also follow the sequence py < β-mpy < γ-mpy. $\Delta_r H^{\ominus}$(g) and $\bar{D}$(As–N) values are listed in Table V.

Comparison of the same base with different acids gives the acidity order $AsCl_3 > AsI_3$ as is expected from the electronegativity values of chloride and iodine atoms.

In synthesis, the $\Delta_r H^{\ominus}$ and other parameters data indicate that the As–N bond is stronger as we go in the sequence py < β-mpy < γ-mpy. The substitution of one hydrogen in the pyridine ring by the electronic donator methyl group causes the increase of the electronic density in the aromatic ring and consequently the electronic density on the nitrogen atom. It is then expected that the electronic density available for bonding is higher in β-mpy and γ-mpy than in py. The order observed between β-mpy and γ-mpy is due to the stronger inductive effect of the *p*-methyl than the *m*-methyl group.

On the other hand, for a given ligand, the stronger bond is formed with the stronger acid as is also shown by the data on the $\Delta_r H^{\ominus}$ and other parameters.

Registry No. Py, 110-86-1; β-mpy, 108-99-6; γ-mpy, 108-89-4; $AsCl_3$·py, 112070-05-0; $AsCl_3$·β-mpy, 112087-35-1; $AsCl_3$·γ-mpy, 112070-10-7; $2AsBr_3$·3py, 112070-08-3; $AsBr_3$·3β-mpy, 112070-07-2; $AsBr_3$·2γ-mpy, 112070-06-1; AsI_3·2py, 94503-44-3; AsI_3·β-mpy, 112070-09-4; AsI_3·γ-mpy, 112070-11-8; $AsCl_3$, 7784-34-1; $AsBr_3$, 7784-33-0; AsI_3, 7784-45-4.

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Solid–Liquid Equilibria in the Reciprocal Ternary System K,Li/S,CO_3

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The solid–liquid equilibria in the molten salt system K,Li/S,CO_3 were studied as a function of composition and temperature. The lowest freezing–melting mixture of the reciprocal ternary system lies within the region bordered by the following selected four points: $X_{K_2S} = 0.20$, $X_{K_2CO_3} = 0.40$, $X_{Li_2CO_3} = 0.40$; $X_{K_2S} = 0.20$, $X_{K_2CO_3} = 0.32$, $X_{Li_2CO_3} = 0.48$; $X_{K_2S} = 0.12$, $X_{K_2CO_3} = 0.45$, $X_{Li_2CO_3} = 0.43$; and $X_{K_2S} = 0.09$, $X_{K_2CO_3} = 0.32$, $X_{Li_2CO_3} = 0.59$ at 485 °C. The precision of the liquidus temperatures is ±10 °C.

Introduction

Data concerning phase diagrams of reciprocal ternary systems, mixtures containing two cations and two anions, have received attention in recent years. Among the different measurements, those on solid–liquid equilibria are particularly important for use in fuel cells. Solid–liquid (SL) equilibria are reported, relative to the reciprocal ternary system K,Li/S,CO_3. To our knowledge, no data for this system have been previously reported, except liquidus data concerning the binary system (K,Li/CO_3), which have been measured by Janz and Lorenz (*1*).

Experimental Section

Commercially available samples of K_2S, Li_2S, K_2CO_3, and Li_2CO_3 (Alfa) were used for preparation of the binary and ternary mixtures. Particular care was devoted to the purification and drying of the salt components. The K_2S was of 44% nominal purity, the principal impurities being polysulfides as well as hydrates of the polysulfides. The method of purification

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