J. Chem. Eng. Data **1994,** *39,* 667−669

Thermochemistry of Benzenamine Adducts of Arsenic Trihalides

P. Oliver Dunstan

Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, CEP 13081-970,
Campinas, São Paulo, Brazil

The adducts $AsX_3{\cdot}3L$ [where L = benzenamine (An), 2-nitrobenzenamine (*o*-NO_2An), 3-nitrobenzenamine (*m*-NO_2An), or 4-nitrobenzenamine (*p*-NO_2An) and X = Cl, Br, or I] were synthesized and characterized by melting points, elemental analysis, thermal studies, and infrared spectroscopy. From calorimetric studies in solution, the mean standard enthalpies of the arsenic−nitrogen bond were determined.

Introduction

Benzenamine is known to form a coordination compound with arsenous chloride, and its preparation and characterization have been reported (*1*, *2*).

It is expected that substituted benzenamines will also form coordination compounds with arsenic trihalides. The substitution of one hydrogen atom in the phenyl group by the electronic withdrawing nitro group will cause the decrease of the electronic density in the aromatic ring. Consequently by an inductive effect, the electronic density on the nitrogen atom will also be decreased. This paper describes the interaction of arsenic trihalides with benzenamine and 2-, 3-, and 4-nitrobenzenamine to form adducts in which the nitrogen atom is the coordinating atom of the ligands. Calorimetric measurements were made to determine the mean strength of As−N bonds. The effect of introducing a nitro group into the phenyl group on the energy of the As−N bond is also studied.

Experimental Section

Chemicals. Arsenic trihalides were prepared as described in a previous paper (*3*), benzenamine (Química Fina Ltd., 99.5%), 2-nitrobenzenamine (Carlo Erba, 98.5%), 3-nitrobenzenamine (Fluka, 98%), and 4-nitrobenzenamine (Aldrich, 99%) were used as obtained without further purification. Solvents used in the synthesis of the adducts were purified by distillation and stored over Linde 4-Å molecular sieves. Ethanolamine (Nuclear, 98.0−100%) was used as obtained without further purification. Due to the moisture sensitivity and toxic nature of the compounds involved, all the preparation and manipulations were carried out in polyethylene glovebags under a dry nitrogen atmosphere.

Adduct Synthesis. The adducts were prepared by the reaction of arsenic trihalides and ligands in solutions. A typical procedure is given below.

Arsenic Bromide−Benzenamine. To a solution of 1.09 g of $AsBr_3$ (3.5 mmol) in 10 cm^3 of chloroform was added 0.3 cm^3 of benzenamine (3.5 mmol) in 3 cm^3 of chloroform slowly and dropwise with stirring. The stirring was maintained for at least 3 h. After filtration, the white solid formed was washed with one portion of 20 cm^3 of chloroform and two portions of 20 cm^3 of petroleum ether, and dried for several hours in vacuo. The compound obtained was stored in a desiccator over calcium chloride. All adducts were prepared with a molar ratio of donor to acceptor of 1:1. The purity of the adducts was 99.5−100% as their chemical analysis showed.

Analytical Section. The carbon, hydrogen, and nitrogen contents were determined by microanalytical procedures. Halogen analysis was made by gravimetry using standard N/10 $AgNO_3$ solution, after the adducts were dissolved in water (*4*).

Spectra. Infrared spectra were obtained using samples of the adducts in a KBr matrix in the region 4000−400 cm^{-1} using a Perkin-Elmer 1600 Series FTIR spectrophotometer.

Thermal Studies. These were made under an argon atmosphere using a Du Pont 951 TG analyzer, with samples varing in mass from 3.08 to 4.85 mg and a heating rate of 10 $K{\cdot}min^{-1}$.

Calorimetric Measurements. All the solution calorimetric determinations were made in an LKB 8700−1 precision calorimeter as described previously (*3*). The accuracy of the calorimeter was carried out by determining the heat of dissolution of tris[(hydroxymethyl)amino]methane in 0.1 $mol{\cdot}dm^{-3}$ hydrochloric acid. The result (−29.78 ± 0.03 $kJ{\cdot}mol^{-1}$) is in agreement with the value recomended by IUPAC (*5*) (−29.763 ± 0.003 $kJ{\cdot}mol^{-1}$). The

Table 1. Melting Points, Yields, Appearance, and Analytical Data of the Adducts

				% C		% H		% N		% halogen	
compound	yield/%	mp/K	appearance[a]	calcd	found	calcd	found	calcd	found	calcd	found
$AsCl_3{\cdot}3An$	20	466	wh cr	46.93	47.08	4.59	4.77	9.13	9.13	23.09	23.19
$AsBr_3.3An$	28	435	wh cr	36.40	36.41	3.56	3.72	7.07	6.99	40.36	40.45
$AsBr_3{\cdot}3o$-NO_2An	12	468	ye pw	29.66	29.51	2.49	2.62	11.53	11.28	32.88	32.66
$AsBr_3{\cdot}3m$-NO_2An	30	359	wh pw	29.66	29.78	2.49	2.60	11.53	11.41	32.88	33.03
$AsBr_3{\cdot}3p$-NO_2An	7	443	wh pw	29.66	29.06	2.49	2.51	11.53	11.38	32.88	32.69
$AsI_3{\cdot}3An$	15	394	ye pw	29.41	29.52	2.87	2.94	5.72	5.51	51.80	52.01

[a] Key: wh, white; ye, yellow; cr, crystals; pw, powder.

0021-9568/94/1739-0667$04.50/0 © 1994 American Chemical Society

Table 2. IR Spectral Data[a]

compound	N−H$_{stretching}$/cm^{-1}	N−H$_{deformation}$/cm^{-1}
$AsCl_3 \cdot 3An$	3428 m, b	1600 m
$AsBr_3 \cdot 3An$	3448 m, b	1599 m
$AsI_3 \cdot 3An$	3418 m, b	1598 m
$AsBr_3 \cdot 3$*o*-NO_2An	3447 m, b, 3344 m	1614 m
$AsBr_3 \cdot 3$*m*-NO_2An	3447 m, b	1588 m
$AsBr_3 \cdot 3$*p*-NO_2An	3416 m, b	1602 m

[a] Intensity of bands: s, strong; m, medium, b, broad.

Table 3. Thermoanalytical Data of the Compounds

compound	apparent melting point/K	weight loss/%		temperature range/K	species lost
		calcd	obsd		
$AsCl_3 \cdot 3An$	466	100	99.12	415−464	$AsCl_3 \cdot 3An$
$AsBr_3 \cdot 3An$	435	100	97.86	423−464	$AsBr_3 \cdot 3An$
$AsI_3 \cdot 3An$	468	100	97.33	394−478	$AsI_3 \cdot 3An$
$AsBr_3 \cdot 3$*o*-NO_2An	359	100	75.69	364−425	$AsBr_3 \cdot 3$*o*-NO_2An
			24.31[a]	425−1073	?
$AsBr_3 \cdot 3$*m*-NO_2An	443	100	100	436−488	$AsBr_3 \cdot 3$*m*-NO_2An
$AsBr_3 \cdot 3$*p*-NO_2An	394	100	76.80	403−468	$AsBr_3 \cdot 3$*p*-NO_2An
			23.20[a]	468−1073	?

[a] Residue.

Table 4. Enthalpies of Dissolution at 298.15 K

m/mg	*n* × 10^3/mol	Q_r/J	*m*/mg	*n* × 10^3/mol	Q_r/J
$AsCl_{3(l)}$ + 25% EA−EtOH[a]					
12.08	66.64	−22.70	50.17	276.8	−102.8
27.10	149.5	−55.67	52.39	289.0	−109.0
28.81	158.9	−57.83	61.15	337.3	−133.0
30.05	165.8	−64.30	81.71	450.7	−175.3
38.66	213.3	−83.63			
$\Delta_1H°/(kJ \cdot mol^{-1}) = -384.19 \pm 3.46$					
$3An_{(l)} + AsCl_3 - $ 25% EA−EtOH					
18.62	199.9	−0.3549	80.74	867.0	−2.626
44.06	473.1	−1.588	340.15	3652.4	−6.423
59.58	639.9	−1.700			
$\Delta_2H°/(kJ \cdot mol^{-1}) = -8.61 \pm 0.22$					
$AsCl_3 \cdot 3An_{(s)}$ + 25% EA−EtOH					
2.25	4.88	−0.9602	8.36	18.2	−3.606
4.52	9.81	−1.992	9.40	20.4	−3.971
$\Delta_3H°/(kJ \cdot mol^{-1}) = -197.05 \pm 1.67$					
$AsBr_{3(s)}$ + 25% EA−EtOH					
21.23	67.47	−19.14	46.04	146.3	−40.60
37.86	120.3	−33.94	51.08	162.3	−45.09
40.08	127.4	−35.24			
$\Delta_1H°/(kJ \cdot mol^{-1}) = -278.53 \pm 1.09$					
$3An_{(l)} + AsBr_3 - $ 25%EA−EtOH					
16.57	177.9	−0.4826	36.34	390.2	−1.024
23.88	256.4	−0.6755			
$\Delta_2H°/(kJ \cdot mol^{-1}) = -7.91 \pm 0.06$					
$AsBr_3 \cdot 3An_{(s)}$ + 25% EA−EtOH					
5.48	9.23	−0.923	7.60	12.8	−1.219
6.75	11.4	−1.071	19.13	32.20	−3.035
$\Delta_3H°/(kJ \cdot mol^{-1}) = -94.72 \pm 0.80$					
3*o*-$NO_2An_{(s)} + AsBr_3 - $ 25% EA−EtOH					
27.90	201.9	2.593	60.00	434.4	6.474
32.40	174.6	3.891	99.69	721.8	9.549
53.40	382.2	7.486	171.96	1245.0	15.62
$\Delta_2H°/(kJ \cdot mol^{-1}) = 40.11 \pm 2.35$					
$AsBr_3 \cdot 3$*o*-$NO_2An_{(s)}$ + 25% EA−EtOH					
1.82	2.50	−0.4783	6.43	8.82	−1.725
5.05	6.93	−1.299			
$\Delta_3H°/(kJ \cdot mol^{-1}) = -192.46 \pm 2.69$					
3*m*-$NO_2An_{(s)} + AsBr_3 - $ 25% EA−EtOH					
48.07	348.0	4.768	76.74	555.6	7.742
52.42	379.5	5.347	113.50	821.70	12.06
57.06	413.1	5.674			
$\Delta_3H°/(kJ \cdot mol^{-1}) = 42.78 \pm 0.62$					
$AsBr_3 \cdot 3$*m*-$NO_2An_{(s)}$ + 25% EA−EtOH					
4.75	6.52	−1.141	6.85	9.40	−1.175
5.00	6.86	−0.8784	11.30	15.50	−2.139
$\Delta_3H°/(kJ \cdot mol^{-1}) = -133.70 \pm 3.37$					
3*p*-$NO_2An_{(s)} + AsBr_3 - $ 25% EA−EtOH					
27.96	202.4	1.956	244.55	1770.5	11.00
52.82	382.4	2.761			
$\Delta_2H°/(kJ \cdot mol^{-1}) = 18.87 \pm 0.86$					
$AsBr_3 \cdot 3$*p*-$NO_2An_{(s)}$ + 25% EA−EtOH					
1.41	1.93	−0.3261	9.97	13.7	−2.339
5.41	7.42	−1.273			
$\Delta_3H°/(kJ \cdot mol^{-1}) = -171.12 \pm 0.27$					
$AsI_{3(s)}$ + 25% EA−EtOH					
6.66	14.6	−3.629	27.75	60.90	−15.16
12.92	28.36	−7.034	55.04	120.8	−29.05
13.30	29.19	−7.554	61.49	135.0	−33.00
$\Delta_1H°/(kJ \cdot mol^{-1}) = -243.83 \pm 1.58$					
$3An_{(l)} + AsI_3 - $ 25% EA−EtOH					
7.04	75.6	−0.2596	33.75	362.4	−0.7910
7.92	85.0	−0.2993	35.23	378.3	−0.8213
16.50	177.2	−0.2839			
$\Delta_2H°/(kJ \cdot mol^{-1}) = -6.52 \pm 0.48$					
$AsI_3 \cdot 3An_{(s)}$ + 25% EA−EtOH					
3.71	5.05	−0.7765	14.23	19.36	−2.724
4.80	6.53	−1.008			
$\Delta_3H°/(kJ \cdot mol^{-1}) = -154.13 \pm 0.23$					

[a] 100 mL of 25% (*v*/*v*) ethanolic ethanolamine.

uncertainty intervals are twice the standard deviations of the means of about five replicate measurements on each compound.

Results and Discussion

All the adducts were solids. The yields range from 7 to 30%. The interaction of arsenic trichloride or arsenic triiodide with NO_2An did not lead to the formation of solid compounds. The capillary melting points, yields, colors, appearance, and analytical data are summarized in Table 1.

Infrared Spectra. The infrared spectra of the adducts show dislocation of some bands and the appearance of new ones when compared with the spectra of free ligands. The pattern of the spectra of the adducts is similar to that of the free ligands. There is a shift of the N−H stretching and bending modes of the adducts to lower frequencies, indicating a weakening of this bond by coordination through the nitrogen atom (*6−14*). Table 2 presents the extracted infrared spectral data for N−H stretching and bending frequencies of the adducts.

Thermogravimetric Data. The thermogravimetry of the An adducts and $AsBr_3 \cdot 3$*m*-NO_2An shows a similar behavior. All evolve both the ligand and trihalide in a single step. The adducts $AsBr_3 \cdot 3$*o*-NO_2An and $AsBr_3 \cdot 3$*p*-NO_2An lose most of their masses in a unique step, leaving a residue that is probably carbon as the degradation product of the adducts. Table 3 presents the thermoanalytical data of the adducts.

Calorimetric Measurements. The standard enthalpies of dissolution of arsenic trihalides, ligands, and adducts ($\Delta_iH°$) were obtained as previously reported (*3*, *15*). Table 4 gives these standard thermochemical values. From $\Delta_iH°$ values the standard enthalpies of acid/base reactions ($\Delta_rH°$) were determined. Using appropriate thermochemical cycles and applying Hess's law, the standard enthalpies of formation ($\Delta_fH°$), the standard enthalpies of decomposition ($\Delta_DH°$), the standard lattice enthalpies ($\Delta_MH°$), and the standard enthalpies of acid/base reactions in the gaseous phase ($\Delta_rH°(g)$) were calculated. The $\Delta_rH°(g)$ values can be used to calculate the standard enthalpy of the arsenic—nitrogen bond ($\bar{D}(As-N) = \Delta_rH°(g)/n$) if the values

Table 5. Summary of the Thermochemical Results

compound	$\Delta_r H°$/ (kJ·mol^{-1})	$\Delta_f H°$/ (kJ·mol^{-1})	$\Delta_{s,1}^{g} H°$/ (kJ·mol^{-1})	$\Delta_M H°$/ (kJ·mol^{-1})	$\Delta_D H°$/ (kJ·mol^{-1})	$\Delta_r H°$(g)/ (kJ·mol^{-1})	$\bar{D}$(As—N)/ (kJ·mol^{-1})
$AsCl_{3(l)}$		-305.0^a	43.5^a				
$AsBr_{3(s)}$		-197.5^a	67.5^a				
$AsI_{3(s)}$		-58.2^a	95.0^a				
$An_{(l)}$		31.3 ± 0.7^b	55.8 ± 1.1^b				
o-$NO_2An_{(s)}$		-26.2 ± 0.4^b	90.0 ± 4.2^b				
m-$NO_2An_{(s)}$		-38.2 ± 0.4^b	96.7 ± 1.4^b				
p-$NO_2An_{(s)}$		-42.0 ± 0.6^b	101.5 ± 2.5^b				
$AsCl_3 \cdot 3An_{(s)}$	-195.75 ± 3.85	-407.7 ± 4.5		-406.7 ± 5.1	363.2 ± 5.0	-350.9 ± 5.2	117.0 ± 1.7
$AsBr_3 \cdot 3An_{(s)}$	-191.72 ± 1.35	-295.3 ± 2.7		-426.6 ± 3.6	359.1 ± 3.5	-370.8 ± 3.8	123.6 ± 1.3
$AsBr_3 \cdot 3o$-$NO_2An_{(s)}$	-45.96 ± 3.73	-322.1 ± 4.0		-383.5 ± 13.2	224.0 ± 13.1	-293.5 ± 13.8	97.8 ± 4.6
$AsBr_3 \cdot 3m$-$NO_2An_{(s)}$	-102.05 ± 3.60	-414.2 ± 3.9		-459.2 ± 4.5	392.2 ± 5.5	-363.0 ± 5.8	121.0 ± 1.9
$AsBr_3 \cdot 3p$-$NO_2An_{(s)}$	-88.54 ± 1.41	-412.0 ± 2.5		-460.5 ± 7.7	393.0 ± 7.6	-359.0 ± 8.1	119.7 ± 2.7
$AsI_3 \cdot 3An_{(s)}$	-96.22 ± 1.67	-61.3 ± 2.9		-358.6 ± 3.7	263.6 ± 3.6	-302.8 ± 3.9	100.9 ± 1.3

[a] Reference 16. [b] Reference 17.

of the standard enthalpy of sublimation of each adduct are known (*3*). The values of these parameters are listed in Table 5.

The melting points and the thermogravimetric studies of the adducts showed that they are unstable in the liquid phase and decompose on heating. For the determination of $\Delta_r H°$(g), it was assumed that the molar standard enthalpy of sublimation of each adduct ($\Delta_s^g H°$) was equal to the enthalpy of vaporization or sublimation of 1 mol of ligand. Measurements on some adducts that sublime and correlation between $\Delta_s^g H°$ (adduct) calculated in several forms and $\bar{D}$(As—donator atom) confirm this assumption (*7, 15, 18–22*). From the $\Delta_r H°$ and $\bar{D}$(As—N) values for a series of adducts with the same stoichiometry and the same trihalide, the basicity order An > m-NO_2An > p-NO_2An > o-NO_2An can be obtained. The expected order would be An > o-NO_2An ≈ m-NO_2An > p-NO_2An due to a major inductive effect of para substitution in the phenyl group. A steric hindrance would be in action, decreasing the basicity of o-NO_2An.

Considering adducts with the same stoichiometry and the same ligand, from $\bar{D}$(As—N) values, the acidity order $AsBr_3$ > $AsCl_3$ > AsI_3 is obtained. The order expected from the electronegativity values of halogen atoms would be $AsCl_3$ > $AsBr_3$ > AsI_3. The $\bar{D}$(As—N) values show that $AsBr_3$ is the best acid for An, as the stronger bond is formed with the stronger acid. The inversion in the expected order would be due to the nature of the bond formed between the donor and acceptor atoms (*3, 7, 23, 24*). It was also observed that nitroanilines only form adducts with arsenic tribromide, neither with arsenic trichloride nor with arsenic triiodide.

Benzenamine is a weak Lewis base. Substitution of one hydrogen atom in the phenyl group by a nitro group leads to the decrease of the electronic density on the nitrogen atom of benzenamine, by an inductive effect. It is then expected that nitroanilines would be weaker bases than aniline. This is confirmed by the thermochemical results.

Literature Cited

(1) Montignie, E. *Bull. Soc. Chim. Fr.* **1935**, *5* (2), 1365.
(2) Okuda, T.; Gima, S.; Ishihara, H.; Negita, H. *J. Mol. Struct.* **1982**, *81*, 261.
(3) Dunstan, P. O.; Airoldi, C. *J. Chem. Eng. Data* **1988**, *33*, 93.
(4) Vogel, A. I. *A Text book of Quantitative Inorganic Analysis*; Pergamon: Oxford, U. K., 1973; p 322.
(5) Henrigton, E. F. G. *Pure Appl. Chem.* **1974**, *40*, 391.
(6) Ahuja, I. S.; Rastogi, P. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2665.
(7) Srivastava, P. C.; Ansari, B. J., Banerjee, B. K. *Indian J. Pure Appl. Phys.* **1976**, *14* (15), 384.
(8) Ripan, R.; Várhelyi, Cs.; Szotyori, L. Z. *Anorg. Allg. Chem.* **1968**, *357* (3), 149.
(9) Delgado, S.; Moran, M.; Fernandez, V. *J. Coord. Chem.* **1982**, *12*, 105.
(10) Sellman, D.; Müller, J. *J. Organomet. Chem.* **1984**, *277*, 379.
(11) Okeya, S.; Yoshimatsu, H.; Hakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 483.
(12) Mathis, R.; Pellizzari, A. M.; Bouisson T., Revel, M. *Spectrochim. Acta, Part A* **1981**, *37A* (8), 677.
(13) Laurence, C.; Wojtkowiak, B. *Bull. Soc. Chim. Fr.* **1971**, *9*, 3124.
(14) Ahuja, I. S. *Indian J. Chem.* **1969**, *7*, 509.
(15) Dunstan, P. O.; Dos Santos, L. C. R. *Thermochim. Acta* **1989**, *156*, 163.
(16) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttail, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, 2–77.
(17) Pedley, J. B.; Rylance, J. *Sussex-N-P.L. Computer Analysed Thermochemical Data Organic and Organo-Metallic Compounds*; Sussex University: Brighton, England, 1970.
(18) Simoni, J. A.; Airoldi, C.; Chagas, A. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1102.
(19) Airoldi, C.; Chagas, A. P.; Assunção, F. P. *J. Chem. Soc., Dalton Trans.* **1980**, 1823.
(20) Burkinshaw, P. M.; Mortimer, C. T. *Coord. Chem. Rev.* **1983**, *48*, 101.
(21) Burkinshaw, P. M.; Mortimer, C. T. *J. Chem. Soc., Dalton Trans.* **1984**, *75*.
(22) Ashcroft, S. J. *J. Chem. Soc. A* **1970**, 1020.
(23) Ochiani, E. *J. Org. Chem.* **1953**, *18*, 534.
(24) Feely, W. E.; Evanega, G.; Beavers, E. M. *Org. Synth. Collect.* **1973**, *5*, 1286.

Received for review August 30, 1993. Revised January 21, 1994. Accepted June 27, 1994.® The author thanks Conselho Nacional de Desenvolvimento Científico e Tecnolōgico (CNPq) for financial support.

® Abstract published in *Advance ACS Abstracts*, September 1, 1994.