Preparation and Characterization of the First Binary Arsenic Azide Species: $As(N_3)_3$ and $[As(N_3)_4][AsF_6]$†

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Reaction of $AsCl_3$ with activated sodium azide in $CFCl_3$ gave $As(N_3)_3$ in quantitative yield. Reaction of $[AsCl_4][AsF_6]$ in liquid SO_2 led to $[As(N_3)_4][AsF_6]$. The identity of both new compounds was established by ^{14}N NMR, IR and Raman spectroscopy and in addition for $As(N_3)_3$ by microanalysis and mass spectrometry. The heat of decomposition of $[As(N_3)_4][AsF_6]$ was estimated on the basis of a Born–Haber energy cycle.

We have recently been studying the reactions of various main-group chlorine compounds with activated sodium azide.[1,2] It was possible to establish that the high reactivity of activated sodium azide is partly due to the presence of traces of hydrazinium azide, $[N_2H_5][N_3]$, and we have synthesized pure hydrazinium azide on a convenient one-pot high-yield laboratory scale.[2]

In contrast to the chemistry of halogen azides, which has been extensively explored in the last years, studies on binary Group 15 azide compounds are very limited.[1] To our knowledge the only structurally characterized molecular arsenic azide is the trifluoromethyl derivative $As(CF_3)(N_3)_2$.[3] Here we report on the reaction of $AsCl_3$ and $[AsCl_4][AsF_6]$ with activated sodium azide. Reaction of neutral $AsCl_3$ in $CFCl_3$ results in the formation of the binary arsenic triazide $As(N_3)_3$ [equation (1)]. The arsonium azide cation $[As(N_3)_4]^+$ is obtained as the salt $[As(N_3)_4][AsF_6]$ from the reaction of $[AsCl_4][AsF_6]$ with activated NaN_3 in liquid sulfur dioxide [equation (2)].

$$AsCl_3 + 3NaN_3 \xrightarrow{CFCl_3,\ 0\ ^\circ C} As(N_3)_3 + 3NaCl \qquad (1)$$

$$[AsCl_4][AsF_6] + 4NaN_3 \xrightarrow{SO_2,\ 0\ ^\circ C} [As(N_3)_4][AsF_6] + 4NaCl \qquad (2)$$

Experimental

CAUTION: $[As(N_3)_4][AsF_6]$ and $As(N_3)_3$ are explosive and can explode on contact with a metal spatula or a metal syringe; $[As(N_3)_4][AsF_6]$ immediately explodes upon exposure to an electrical discharge.

Activated sodium azide was prepared from commercially available NaN_3 (Aldrich) by treatment with hydrazinium hydroxide (Merck) as described previously.[4] Arsenic trichloride (Aldrich, 99.99%) was used without further purification. The salt $[AsCl_4][AsF_6]$ was prepared from $AsCl_3$, Cl_2 (Air Products) and AsF_5 by literature methods[5] and identified by X-ray crystallography.[6,7] All solvents were dried [$CFCl_3$ (Merck), P_4O_{10}; SO_2 (Air Products), CaH_2] and distilled prior to use. All manipulations were performed under an inert atmosphere (Ar).

Preparations.—$As(N_3)_3$. Activated sodium azide (1.05 g, 16.15 mmol) was suspended in $CFCl_3$ (10 cm^3) and treated with $AsCl_3$ (0.50 g, 2.76 mmol) at 0 °C and the slurry stirred for 12 h. The solution was allowed to warm to 15 °C. Filtration through a fine glass frit afforded a colourless solution. This was allowed to warm to room temperature with the $CFCl_3$ being evaporated off under a stream of argon to leave a light yellowish liquid, $As(N_3)_3$ (0.51 g, 92%) (Found: N, 61.4; Calc. 62.7%). Electron-impact (EI) mass spectrum (70 eV, 25 °C): $m/z = 201$ (M^+). ^{14}N NMR (28.9 MHz, $CDCl_3$, relative to $MeNO_2$, 22 °C): δ −318.0 (1, $\Delta\nu$ 150, N_a), −165.2 (1, $\Delta\nu$ 30, N_c), and −131.1 (1, $\Delta\nu$ 15 Hz, N_b) IR (KBr, cm^{-1}): 2082vs [$\nu_{asym}(N_3)$], 1238s [$\nu_{sym}(N_3)$], 561m [$\gamma(N_3)$] and 441m [ν(As–N)].

$[As(N_3)_4][AsF_6]$. In a two-bulb vessel a solution of $[AsCl_4][AsF_6]$ (1.12 g, 2.75 mmol) in SO_2 (15 cm^3) was poured onto activated sodium azide (1.50 g, 23.07 mmol) at −40 °C. The reaction mixture was allowed to warm to 0 °C and stirred at this temperature for 4 h. The resulting colourless supernatant over a white precipitate (unreacted NaN_3, NaCl) was filtered through a fine glass frit and the SO_2 was pumped off leaving a white (**highly explosive**) solid (0.90 g, 76%). ^{14}N NMR (28.9 MHz, $CDCl_3$, relative to $MeNO_2$, 22 °C): δ −279.8 (1 $\Delta\nu$ 375, N_a), −162.1 (1, $\Delta\nu$ 125, N_c) and −135.4 (1, $\Delta\nu$ 30 Hz, N_b) Raman ($\lambda = 647.09$ nm, 25 °C, 10 mW, SO_2 solution): 2127 [1, $\nu_{asym}(N_3)$], 1638 (1), 1338 [2, $\nu_3(SO_2)$], 1242 [1, $\nu_{sym}(N_3)$), 1155 [10, $\nu_1(SO_2)$], 672 [2, $\nu_1(AsF_6)$], 519 [3, $\nu_2(SO_2)$], 482 (1), 426 [4, ν(As–N)] and 357 (1). IR (KBr, cm^{-1}): 2125s [$\nu_{asym}(N_3)$], 1240m [$\nu_{sym}(N_3)$], 699vs [$\nu_3(AsF_6)$] and 395vs [$\nu_4(AsF_6$].

Results

The two new binary arsenic–nitrogen species $As(N_3)_3$ and $[As(N_3)_4]^+$ were prepared according to equations (1) and (2) and identified unequivocally on the basis of their vibrational and ^{14}N NMR spectra. The azide part of the IR and Raman spectra was assigned by comparing the observed frequencies with those obtained for ClN_3 and BrN_3 (Table 1).[1,8] For both covalently bound azide species three well resolved resonances have been found in their ^{14}N NMR spectra and assignment of the individual resonances to N_a, N_b and N_c was made on the basis of the arguments given in early work by Witanowski[9] and a report on ^{14}N data of covalent azides given by us[10] (Fig. 1). Presumably as a result of the large quadrupole moment of ^{14}N spin–spin splitting which has been estimated to be less than 30 Hz was not observed (*cf.* linewidths given in the Experimental section).[11]

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† *Non-SI units employed:* kcal = 4.184 J, Å = 10^{-10} m, eV ≈ 1.60×10^{-19} J.

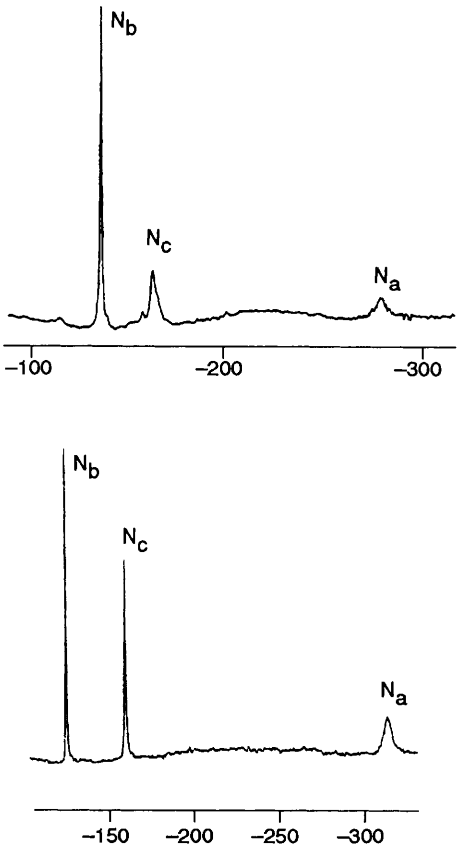
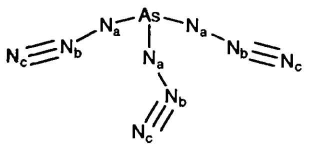
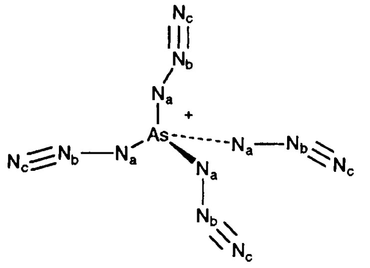


Fig. 1 The ^{14}N NMR spectra of $[As(N_3)_4]^+$ (top) and $As(N_3)_3$ (bottom) (chemical shifts δ in ppm relative to $MeNO_2$)





Tetraazidoarsonium hexafluoroarsenate, $[As(N_3)_4][AsF_6]$, which can be handled safely in SO_2 solutions, is very sensitive in the solid state and detonates upon exposure to mechanical stress or a high-frequency discharge. Using a Born–Haber cycle (Scheme 1), the reaction enthalpy for its decomposition was estimated to be −406 kcal mol^{-1}.

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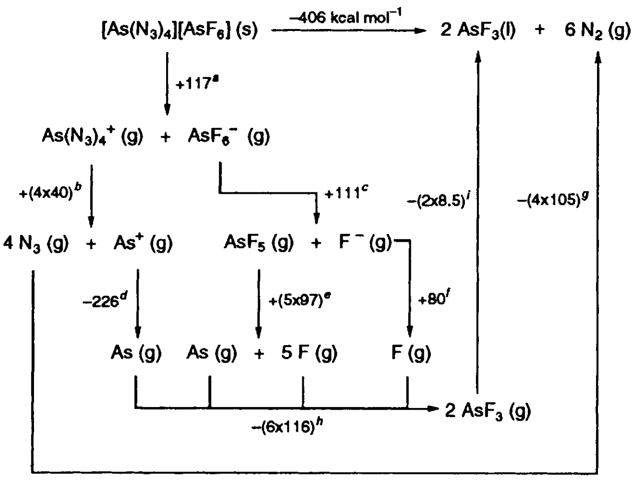
Table 1 Frequencies of $As(N_3)_3$ and $[As(N_3)_4]^+$ in comparison with ClN_3 and BrN_3

$As(N_3)_3$*	$[As(N_3)_4]^{+a}$	ClN_3[1,8]	BrN_3[1,8]	Assignment
2082	2126	2075	2058	$\nu_{asym}(N_3)$
1238	1241	1145	1150	$\nu_{sym}(N_3)$
561	n.o.	522	n.o.	$\gamma(N_3)$
n.o.	n.o.	719	682	$\delta(N_3)$
n.o.	n.o.	223	n.o.	$\delta(N_3)$
441	426	545	452	$\nu(X-N_3)$

n.o. = Not observed. * This work.



Scheme 1 Energy cycle for the decomposition of $[As(N_3)_4][AsF_6]$. [a] Crystal lattice energy (U_L/kcal mol^{-1}), calculated from the molecular volume ($V_M/Å^3$) using the linear relationship for $[A]^+[B]^-$ salts:[12,13] $U_L = 556.3 \sqrt[3]{V_M} + 26.3$; $V_M\{[As(N_3)_4][AsF_6]\}$ was assumed to be equal to $V_M\{[AsCl_4][AsF_6]\} = 231$ $Å^3$ [6,7] [*cf.* $U_L(KCl) \approx U_L(KN_3)$; $U_L(KCl) = 168$ kcal mol^{-1},[14] $U_L(KN_3) = 164$ kcal mol^{-1} [14]] which gives $U_L([AsCl_4][AsF_6]) = U_L\{[As(N_3)_4][AsF_6]\} = 117$ kcal mol^{-1}. [b] The bond dissociation energy D(As–N) was estimated from 0.5 [D(As–As) + D(N–N)] = 0.5 (42.6 + 37.8) kcal mol^{-1},[14] *i.e.* 40 kcal mol^{-1}. [c] Fluoride-ion affinity of AsF_5.[15] [d] Ionization energy of As.[15] [e] $D(As^V-F) = 97$ kcal mol^{-1}.[15] [f] Electron affinity of fluorine.[15] [g] $\Delta H^\circ_f(N_3, g) = +105$ kcal mol^{-1}.[16] [h] $D(As^{III}-F) = 116$ kcal mol^{-1}.[15] [i] Heat of vaporization, $\Delta H_{vap}(AsF_3) = 8.5$ kcal mol^{-1} [17]

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