Matrix-isolated Arsenic Trichloride Oxide Molecule, $OAsCl_3$: Formation and Characterization by its Infrared and Raman Spectra

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Summary Oxygen atom transfer, best effected in a noble gas matrix held at 8–30 K, leads to the formation of the hitherto unknown arsenic trichloride oxide, $OAsCl_3$; the matrix-isolated molecule has been detected by its i.r. and Raman spectra which, with the aid of polarization measurements and isotopic variations, serve to characterize its stoicheiometry, geometry, and vibrational properties.

ALTHOUGH there are conflicting reports about arsenic trifluoride oxide,[1] arsenic analogues of the familiar molecules OPX_3 (X = F, Cl, or Br) have virtually eluded characterization. In view of this and of the recently attested formation at low temperatures of arsenic pentachloride,[2] we are prompted to outline the spectroscopic evidence afforded by noble gas matrices held at 8–30 K for the formation of the discrete oxohalide molecule $OAsCl_3$.

When a gaseous mixture of arsenic(III) chloride, oxygen,

TABLE. Frequencies (in cm^{-1}) of vibrational fundamentals of matrix-isolated $OAs^{35}Cl_3$

Ar matrix		Kr matrix				
Raman (obs.)[a] ^{16}O	I.r. (obs.)[a] ^{16}O	I.r. ^{16}O		I.r. ^{18}O		
		obs.[a]	calc.[b]	obs.[a]	calc.[b]	Assignment
997·0 (0·5)	996·2 (0·2)	994·2 (0·5)	994·2	949·2 (0·2)	948·6	ν_1 (a_1)
434·3 (0·5)	435·0 (1·0)	433·5 (0·5)	433·5	433·2 (0·2)	433·1	ν_4 (e)
373·1 (0·5)	—	376·0 (0·5)	375·9	—	374·8	ν_2 (a_1)
247·1 (0·5)	248·1 (0·1)	250·0 (1·0)	250·0	239·2 (0·2)	240·2	ν_5 (e)

[a] Numbers in parentheses denote the uncertainty in measured frequencies. [b] Assuming $F_{11} = 760{\cdot}5$, $F_{22} = 241{\cdot}5$, $F_{33} = 80$, $F_{44} = 234{\cdot}0$, $F_{55} = 74{\cdot}98$, and $F_{66} = 50$ N m^{-1}; bond distances, As=O 160 and As–Cl 210 pm; ∠ Cl–As–Cl, 102°.

and argon, typically in the proportions 1 : 1 : 70, respectively, is passed at a pressure of *ca.* 1 Torr through a microwave discharge, the i.r. spectrum of the condensate formed at 8 K shows not only bands attributable to the presence of unchanged arsenic(III) chloride, but also additional features originating from a single molecule at *ca.* 996, 435, and 248 cm^{-1}. To aid the identification of the species responsible for these absorptions, we have had recourse to a second, more selective method of formation involving u.v. photolysis of matrix-isolated ozone; the oxygen atoms thus produced have been shown to undergo addition readily to a suitable molecular reagent, *e.g.* ClF,[3] HX ($X = Cl$ or Br),[4] or PCl_3,[5] also entrained within the matrix.

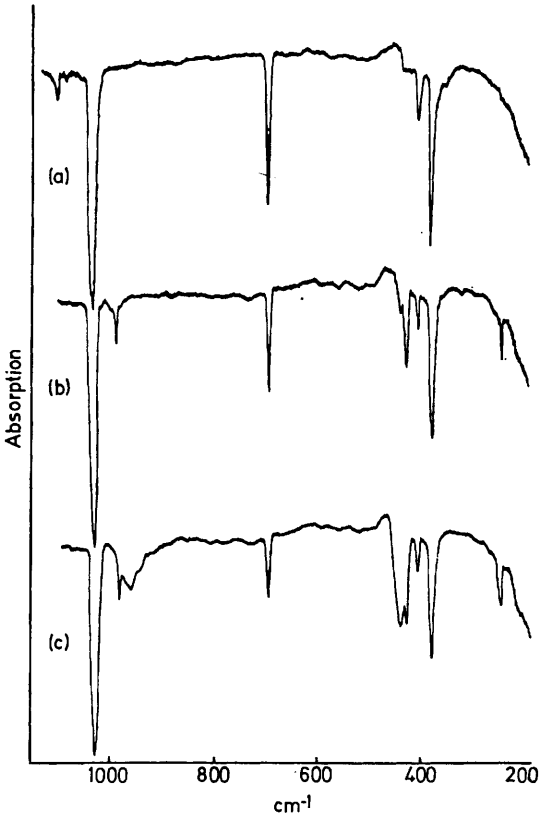

FIGURE 1. (a) I.r. spectrum of the condensate formed by isolating arsenic(III) chloride and ozone in solid argon at 8 K. (b) I.r. spectrum of the same condensate after photolysis for 30 min at 8 K using u.v. radiation with wavelengths in the range *ca.* 240–300 nm. (c) I.r. spectrum of the same condensate after photolysis for a further 30 min at 30 K.

We find that ozone isolated in an argon or krypton matrix undergoes photolysis in the presence of arsenic(III) chloride (O_3 : $AsCl_3$: noble gas, 1 : 1 : 1000–2000) when the matrix is exposed to u.v. irradiation at *ca.* 250 nm. The i.r. spectrum of the matrix witnesses the appearance and growth with photolysis of the absorptions at *ca.* 996, 435, and 248 cm^{-1} with the simultaneous decrease in intensity of the absorptions due to the $AsCl_3$ and O_3 molecules (see Figure 1); under optimum conditions using a krypton matrix it was possible to discern an additional weak feature at *ca.* 375 cm^{-1} which was otherwise obscured by the intense absorption near 390 cm^{-1} due to $\nu_3(e)$ of $AsCl_3$.[6] The reaction can also be induced by laser irradiation at 514·5 nm, and the Raman spectrum of an argon matrix reveals the development of four new lines virtually coincident in frequency with the new i.r. absorptions. The Raman features at 996 and 373 cm^{-1} were found to be polarized, those at 435 and 248 cm^{-1} depolarized.

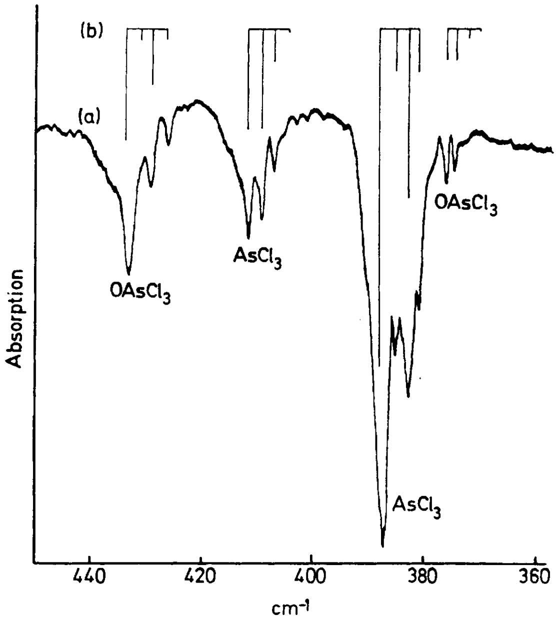

FIGURE 2. (a) Frequency range 360–450 cm^{-1} in the i.r. spectrum of a krypton matrix containing arsenic(III) chloride and ozone after photolysis for 30 min. (b) Calculated spectrum for the As–Cl stretching fundamentals of the molecules $AsCl_3$ and $OAsCl_3$.

The circumstances of the experiments are consonant with the number, frequencies, intensities, and polarization characteristics of the vibrational features in pointing to the formation of the new molecule $OAsCl_3$ presumably possessing C_{3v} symmetry, and for which the vibrational fundamentals $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_4(e)$, and $\nu_5(e)$ have thus been defined. Confirmation of the molecular identity is provided by (i) the significant decrease in frequency of two of the bands (see Table) when ^{18}O-enriched ozone (90 atom%) is used in place of the isotopically natural reagent, and (ii) the $^{35}Cl/^{37}Cl$ isotopic patterns exhibited under optimum conditions by the i.r. absorptions due to the As–Cl symmetric and antisymmetric stretching fundamentals, $\nu_2(a_1)$ and $\nu_4(e)$ respectively, of the isotopically natural product (see Figure 2).[7]

Normal co-ordinate analysis employing a simple potential function with zero off-diagonal force constant values accommodates all the observed frequencies within ± 1 cm^{-1} and suggests that $\nu_3(a_1)$ and $\nu_6(e)$ of $OAsCl_3$ may be sufficiently close to $\nu_4(e)$ of $AsCl_3$ to escape detection so long as unchanged $AsCl_3$ persists in the matrix. With an As=O stretching force constant of 760·5 N m^{-1} (*cf.* 1007 N m^{-1} for the P=O bond in $OPCl_3$ and 760·4 N m^{-1} for the V=O bond in $OVCl_3$[8]) and a principal As–Cl stretching constant of *ca.* 238 N m^{-1} (*cf.* 231 N m^{-1} in $AsCl_3$[6]), the $OAsCl_3$ molecule gives no hint of intrinsic instability; as with perbromates,[9] it is possible that the failure so far to isolate a simple molecular species of this kind is as much a kinetic as a thermodynamic problem. Whereas ozone reacts with arsenic(III) chloride at ambient temperatures to give white, highly moisture-sensitive solids with compositions ranging from AsO_4Cl to AsO_2Cl_2, attempts to preserve unco-ordinated arsenic trichloride oxide under normal conditions have so far met with failure.

Preliminary i.r. measurements encourage us to believe that the photolysis of noble gas matrices incorporating ozone in the presence of the appropriate trihalide MX_3 (M = P, As, Sb, or Bi; X = halogen) offers considerable scope for the synthesis and characterization of other discrete molecules of the type OMX_3 hitherto unfamiliar; now convincingly identified in this way, for example, is the previously vexed molecule $OAsF_3$.[1]

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