Spectrum attributed to the AsCN Free Radical

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A NEW absorption spectrum attributed to the AsCN free radical has been observed in the flash photolysis of mixtures of cyanogen with arsine or arsenic trichloride and nitrogen as inert gas.

Cyanogen was prepared by reacting potassium cyanide with copper sulphate[1] and arsine was prepared according to Gunn *et al.*[2] $AsCl_3$(B & A) was purified by distillation *in vacuo*. A mixture of AsH_3 (or $AsCl_3$),C_2N_2, and N_2 (0·2 : 40 : 210 mm. Hg pressure) was flash photolysed at an energy of ~1000 J. The electronic absorption spectrum was recorded on Ilford HP3 plate using a Hilger quartz spectograph, model E742, with an absorption path of 50 cm. The AsCN band rises to maximum intensity at ~3 μsec. and lasts for ~150 μsec.

The spectrum (Table) is attributed to the three sub-bands of the 000–000 band of a $^3\Pi(a)$–$^3\Sigma^-$ transition of the linear AsCN by analogy with NCN

TABLE

Wavelengths of AsCN [$^3\Pi(a)$–$^3\Sigma^-$]

Sub-band	λ_{air}(Å)	ν_{vac}(cm.$^{-1}$)
	2916·6	34277
	2914·2	34305
$^3\Pi_2$–$^3\Sigma^-$	2913·4	34314
	2910·1	34353
	2869·0	34845
	2868·1	34856
$^3\Pi_1$–$^3\Sigma^-$	2863·4	34913
	2862·6	34923
	2861·4	34938
	2824·5	35394
	2823·4	35408
$^3\Pi_0$–$^3\Sigma^-$	2830·9	35439
	2817·5	35482

($A^3\Pi_u \leftarrow X^3\Sigma_g^-$).[3] The larger triplet splitting for AsCN (~550 cm.$^{-1}$), as compared with the triplet splitting of ~40 cm.$^{-1}$ for NCN and ~104 cm.$^{-1}$ for PCN[4] is expected for the heavier molecule because of increased spin–orbit interaction. In the absence of a complete spectroscopic analysis, however, the assignment of the spectrum to AsCN must be considered as tentative.

The formation of AsCN can be explained by a mechanism, similar to that proposed for NCN[5] and PCN,[4] involving the reactions

$$CN(X^2\Sigma) + AsH(X\,^3\Sigma) \rightarrow H(^2S) + AsCN(\tilde{X}\,^3\Sigma)$$

$$CN(X^2\Sigma) + AsCl \rightarrow Cl(^2P) + AsCN(\tilde{X}\,^3\Sigma)$$

From its mode of formation and the analogous reaction of CN with NH,[5] the structure of AsCN is preferred to that of CNAs. The spectrum of the HAsCN free radical which like HNCN and HPCN might also be expected to result from the combination of the radicals was not observed.

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