AsF_5 Radical Anion Intermediate in the Charge-transfer Interaction with Donors

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Summary Arsenic pentafluoride interacts at low temperature with either butadiyne or nitric oxide to form the arsenic radical anion ($\cdot AsF_5^-$); this radical anion generation and subsequent annihilation at higher temperatures governs the 'overall' half-reaction: $3AsF_5 + 2e^- \rightarrow 2AsF_6^- + {:}AsF_3$.

We report the first evidence that the acceptor AsF_5 undergoes a one-electron transfer process when combined *in vacuo* at 77 K with either of the donors C_4H_2 or NO. The progress of this solid state reaction was monitored by e.s.r. spectroscopy. In the case of C_4H_2, an intense e.s.r. absorption line recorded at a magnetic field strength of *ca.* 3250 G proved the existence of the hydrocarbon radical cation ($C_4H_2{\cdot}^+$)[1] and numerous signals recorded above 5000 G demonstrated the existence of the pentafluoroarsenic radical anion ($\cdot AsF_5^-$)[2] immediately upon insertion of this solid-state mixture into the preconditioned cavity (103 K). No e.s.r. signals from other As transitions were recorded below 5000 G, a finding which supports a ^{75}As hyperfine interaction well in excess of 1700 G as inferred from the work of Colussi *et al.*[3] Although the 103 K spectrum (Figure) was complicated by numerous multiplets,[4-6] especially by the strong n.m.r. transition which is coincidentally superimposed on the high-field As transition, *all* high-field signals were observed to disappear and reappear completely at 20 and 55 K, respectively. The importance of this e.s.r. temperature dependence is to provide the first experimental evidence in support of the original proposal of Singer and Lewis that the *initial* step in the reaction occurring in solution between an aromatic hydrocarbon and $SbCl_5$ was a 'reversible one-electron transfer': $ArH + SbCl_5 \rightarrow ArH{\cdot}^+ + SbCl_5{\cdot}^-$[7a] and applies to the mechanism of aromatic hydrocarbon oxidations by SbF_5.[7b] *All* high-field absorptions were also

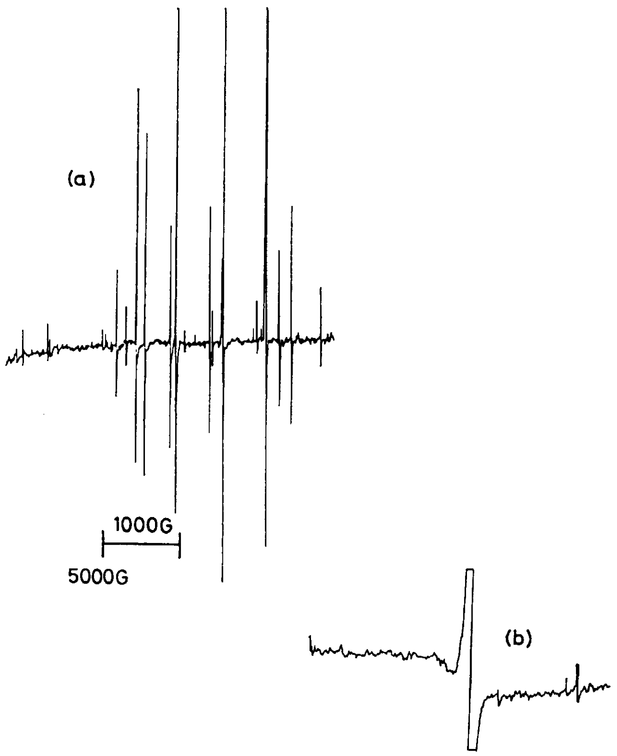

Figure. E.s.r. spectra recorded concurrently at 103 K resulting from the solid-state interaction between C_4H_2 and AsF_5 with (b) the radical cation spectrum of $C_4H_2{\cdot}^+$, centred at 3250 G (g = 2·0028; line width *ca.* 20 G); the portion of the $\cdot AsF_5^-$ spectrum centred at 6429 G (g *ca.* 2·0000) was analysed ($F = 2$) and resulted in the following value for the hyperfine constants: $a(I_{As})$ = 1889·2 G also $a(I_F)$ = 63·9 G(n.m.r.); 162·8 G(e.p.r.).

observed to disappear at *ca.* 120 K, complementing the earlier e.s.r. findings of Singer and Lewis.[7a]

Identification of AsF_3 as one of the end-products[8] of the solid-state charge-transfer interaction was based on the more accurate method of mass spectroscopic analysis.

Although $\cdot AsF_5^-$ has been postulated as a radical product in the 77 K radiolysis of a solid solution of AsF_5–SF_6 (e.s.r. cavity temp. 120 K[2b]) or the room temperature γ-irradiation of either $KAsF_6$ (e.s.r. cavity temp. 293 K[2a]) or KPF_6 impurity-doped with $KAsF_6$ (e.s.r. cavity temp. not specified[2c]), we consider that both the generation technique and the e.s.r. cavity temperature[7a] as well as our e.s.r. evidence of the 'low'-temperature reversibility are of crucial importance in assigning the e.s.r. spectrum presented in the Figure (a) to $\cdot AsF_5^-$. The reported spectrum[3] of other arsenic radical species, although detected at 103 K but generated under entirely different experimental conditions (*i.e.* radiolysis), supports our argument. Recent discussions about the behaviour of donors with AsF_5 have claimed that $\cdot AsF_5^-$ is *not* a likely species in the charge-transfer interaction.[9,10] Such statements are incompatible with our e.s.r. spectral detection of the simultaneous generation of arsenic radical anions ($\cdot AsF_5^-$) and hydrocarbon cations ($C_4H_2{\cdot}^+$).

Two consecutive one-electron transfer processes govern the 'overall' half-reaction $3AsF_5 + 2e^- \rightarrow 2AsF_6^- + {:}AsF_3$,[11] and occur in the following manner: the primary low-temperature interaction generates the radical anion [*e.g.*, equation (1)], whose lifetime is remarkably long and which

$$As^{V}F_5 + e^- \overset{50\ K}{\rightleftharpoons} \cdot As^{IV}F_5^-\ \text{(red.)} \qquad (1)$$

is therefore a relatively stable radical intermediate at temperatures below 123 K. Equation (1) is analogous to the gas-phase negative-ion reactivity, 'resonance (thermal) electron capture' ($AsF_5 + e^- \rightleftharpoons \cdot AsF_5^-$), which occurs at near-zero electron energy (*ca.* 0 eV).[12a] Around 120 K, a second charge transfer process occurs which annihilates the radical anion [equation (2)], and most likely explains the formation of AsF_3. Equation (2) is comparable to gas-phase negative ion-reactivity, 'dissociative electron capture' ($AB + e^- \rightarrow A + B^-$), which occurs at higher electron energy (*ca.* 0·2 eV).[12b] Equation (3), the resultant of the low-temperature [equation (1)] and the higher temperature [equation (2)] solid-state interactions, only partially describes the 'overall' half-reaction.

$$\cdot AsF_5^- + e^- \rightarrow {:}AsF_3{\cdot}2F^- \qquad (2)$$

$$AsF_5 + 2e^- \rightarrow {:}AsF_3{\cdot}2F^- \qquad (3)$$

Concurrent with the second one-electron transfer, an additional chemical process (4) occurs that involves the fluoride affinity of AsF_5 and solely accounts for the formation of AsF_6^-,[13] the other stable end-product, where

$$2AsF_5 + {:}AsF_3{\cdot}2F^- \rightarrow 2AsF_6^- + {:}AsF_3 \qquad (4)$$

identification of AsF_6^- (and AsF_3) in the solid state has been supported by spectroscopic evidence[14] and recent micro-analytical determinations.[15]

We conclude that the *dual* electron–fluoride acceptor properties of AsF_5 (rather than the convenient, but less definitive oxidant–dopant label) account for the 'overall' half-reaction [equations (3) + (4) = equation (5)], which

$$3AsF_5 + 2e^- \rightarrow 2AsF_6^- + {:}AsF_3 \qquad (5)$$

is applicable to the 'general' donor (D)–AsF_5 charge transfer interaction (6).[9,10,16]

$$2D + 3AsF_5 \rightarrow 2D{\cdot}^+,\ 2AsF_6^- + AsF_3 \qquad (6)$$

It is recognized that certain aromatic hydrocarbons (anthracene, perylene, *etc.*, and most likely graphite) are easily oxidized not only to the monoradical cation but also to the dication;[7a,17] presumably equation (6) also accounts for this case *via* one-electron transfer: $2D{\cdot}^+ + AsF_5 \rightarrow 2D^{2+}$, $AsF_3{\cdot}2F^-$.

Low-temperature e.s.r. studies of the $:\dot{N}O$–XF_5 (X = P, As, Sb) and other solid state donor–AsF_5 charge transfer interactions are continuing.

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