

Interactions of Aromatic Hydrocarbons with Heavy-metal Halides in the Solid State Studied by Electron Spin Resonance

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Summary Very stable e.s.r. signals have been observed in solid aromatic hydrocarbon-heavy metal halide mixtures and their origin is discussed.

AROMATIC hydrocarbons have previously been shown to give radical cations on oxide and related surfaces,¹ with group VIII metal chlorides,^{2,3} and other Lewis-acid catalysts including CdCl₂,⁴ in solid mixtures, some examples of which required heating to give the e.s.r. signal.

While studying the photo- and thermo-chemical behaviour of naphthalene, anthracene, phenanthrene, tetracene, thianthrene, acridine, and anthraquinone with, or in the presence of, heavy-metal halides, MX₂ (where M = Cd, Hg, or Pb and X = Cl, Br, or I) we have found very stable e.s.r. signals in solid mixtures of organic and inorganic components. Such mixtures when heated (with or without prior evacuation of the samples) below the melting point of the hydrocarbon, ground by hand, or compressed become paramagnetic. The observed e.s.r. signal intensity is found to depend more on the treatment of the sample than its composition. No detectable paramagnetic species is

generated in identically treated pure hydrocarbon or metal halide.

In general the observed spin concentration (estimated to be $\leq 6\%$ of the hydrocarbon molecules present in mixtures with composition ranges 100:1—1:5 hydrocarbon:halide) increases with temperature and duration of heating, or with duration of grinding. The signal intensity of the compressed samples increases with pressure applied (so far ≤ 10 kbar) and also incrementally by successive compression to a given pressure.

Samples treated as described have retained their paramagnetism for at least six months even if left open to the atmosphere. Soxhlet extraction of the paramagnetic mixtures (CH₂Cl₂, 48 h) gives a quantitative recovery of the organic component and leaves the residual inorganic halide with an e.s.r. signal of somewhat reduced intensity. In suitable cases the inorganic halide has been similarly extracted with water to leave the hydrocarbon weakly paramagnetic. A CH₂Cl₂ solution of this residue also gives an e.s.r. signal but unless the solution is kept sealed under vacuum it decays slowly. Similarly mixed and treated

samples have also had the hydrocarbon present sublimed out to leave the metal halide paramagnetic.

In almost all instances the e.s.r. signal is a symmetric isotropic relatively narrow single line with a g -factor very close to the spin-only value. A few examples of low spin-concentration cases do give a line which is marginally asymmetric but none show any hyperfine structure. The e.s.r. line-shapes formed are of mixed type, *i.e.* Gaussian in the wings of the line changing to Lorentzian as the line centre is approached. As expected⁴ for those samples with higher spin-concentrations the line is progressively more Lorentzian in character as exchange narrowing increases.

Some representative g -values and peak-to-peak line-widths are given below for ground and compressed anthracene:halide samples; heated aliquots of the same mixtures give very similar e.s.r. data.

TABLE. E.s.r. resonances in anthracene:MX₂ mixtures

1:5 mixture	g -value (± 0.001)	line-width ^a /mT
Anthracene: CdCl ₂	2.001	0.32
Anthracene: CdI ₂	2.001	0.37
Anthracene: PbI ₂	2.001	0.35
Anthracene: HgBr ₂	2.002	0.38
Anthracene: HgI ₂	2.001	0.34

^a These are virtually insensitive to temperature over the range 77—490 K as is the line intensity.

The heterogeneous nature of the systems suggests that the observed behaviour of the mixtures involves interaction of the hydrocarbon with inorganic halide at contiguous microcrystalline surfaces during grinding, compression, or

heating. Such an interaction, presumably of charge-transfer Lewis acid–Lewis base type (*e.g.* the pale yellow anthracene:PbI₂ mixture turns orange when treated as indicated) could give a chemisorbed hydrocarbon radical cation more than usually stabilised by its surface environment.

The inorganic halides used have crystal structures which suggest that unless radical cation formation occurs only at exposed metal ions or other active sites chemisorption will occur on a two-dimensional array of halogen atoms. The transferred electron may in turn be trapped in the inorganic lattice with a spin-only g -value. Hence a superposition of radical cation and trapped electron resonances may be present, each to be affected to a greater or lesser extent by the extraction sequence or sublimation described.

In the present work preliminary analyses of anthracene or naphthalene: CdI₂ or PbI₂ mixtures have failed to show any iodination. In contrast, chlorination³ of naphthalene by PtCl₄ has been reported. It would seem also that the process producing the e.s.r. signals in the hydrocarbon: MX₂ mixtures is confined to the solid since cyclohexane solutions of anthracene in contact with CdI₂ or PbI₂ have been found to be spin free, as are solutions of HgCl₂, HgBr₂, and HgI₂ in methylbenzenes which do show⁵ u.v. charge-transfer bands. The observed behaviour is perhaps more akin to that in the solid charge-transfer complexes:—tetracene:I₂⁶ or perylene and pyrene:I₂ complexes⁷ in which marked pressure effects have been observed.⁸

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