The Stabilisation of Radicals by Magnesium Chloride

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Summary Magnesium chloride forms complexes containing a substantial concentration of very stable free radicals when vigorously milled with an aromatic or polymeric material such as naphthalene, durene, or polyethylene, some of which are highly coloured and they are all typified by intense e.s.r. spectra; a few other metal halides, notably manganese(II) chloride and magnesium bromide, behave similarly to magnesium chloride in this respect although the spin density of their complexes is much inferior to those of the latter prepared under equivalent conditions.

We have noticed that suitable milling of anhydrous magnesium chloride with naphthalene causes a progressive change in the colour of the mixture from white to purple followed by the formation of free radicals; we report here our observations on the change.

Our experiments were originally carried out using a McCrone micronising mill with agate or carborundum grinding elements. Similar results were obtained using a larger 'Megapact' stainless steel vibration ball mill.[1] In each case the mill was loaded under an inert atmosphere with a 1:1 mixture by weight of anhydrous magnesium chloride and naphthalene using a total of 1 g of mixture in the McCrone or 30 g in the Megapact mill. The milling chambers were then sealed and agitated for 30 min—17 h, while the purple colouration of the reactants developed.

It is well known that polycyclic aromatic species (*e.g.* naphthalene and anthracene) can react with the Lewis acid sites of various supports (*e.g.* silica–alumina,[2,3] boron phosphate,[4] and mordenite[5]) to form highly coloured cation radicals. The e.s.r. spectrum of our $MgCl_2$–naphthalene complex from the Megapact mill strongly resembled that of the silica–alumina–naphthalene complex[6] with $g = 2\cdot0027$. However, in the former case, the e.s.r. signal was so intense that most of the resolution was lost and the spectrum frequently appeared as a singlet with width equal to 20 G. The width of the singlet was extremely variable and depended on the milling conditions and radical density produced. Values of 10—20 G were typical for $MgCl_2$–naphthalene complexes. The unusually high concentration of radical species capable of being supported on magnesium chloride by this novel milling technique, compared with the usual method of depositing the aromatic species on to the support from solution,[2–4] was further investigated.

The e.s.r. spectra indicated that there were *ca.* 10^{17}—10^{19} spins per g of $MgCl_2$–naphthalene complex. In order to determine this figure more precisely, a known weight of the complex was titrated against a standard solution of diphenylpicrylhydrazyl (dpph) in chloroform. However, it proved to be difficult to determine the end point of this titration. Thus, the method of Weil and Anderson[7] was adopted. This involves adding excess of dpph to the complex and back titrating with a standard solution of thiosalicylic acid in chloroform. The results indicated a spin density of *ca.* $7\cdot5 \times 10^{18}$ spins per g of $MgCl_2$. Since the surface area of anhydrous magnesium chloride milled under similar conditions was found, by nitrogen adsorption, to be *ca.* 14 $m^2 g^{-1}$, there are *ca.* 5×10^{13} spins cm^{-2} of support. These spin density figures can be compared with estimates of 10^{10}—2×10^{12} spins cm^{-2} for typical silica–alumina–anthracene systems.[2]

The most striking feature of these complexes, apart from their high spin density, is their stability. The radicals were not affected by oxygen, carbon dioxide, hydrogen, or chlorine. Most dry solvents had no effect or simply dissolved away the excess of naphthalene while leaving the radicals stabilised on the support. The excess of naphthalene could even be sublimed off without diminishing the purple colour of the complex. Only water and the lower alcohols succeeded in dissolving away the support and destroying the complex.

We have also found that a whole new range of stabilised cation radical–support complexes may be prepared using the milling technique. It is well known that comminution of polymers, for example, gives rise to free radical formation[8] and we have found that these radicals may be stabilised on the surface of anhydrous magnesium chloride. Thus, when polypropylene, polythene, polysiloxanes, polyester, *etc.* are milled with $MgCl_2$ as above, then the resulting powder possesses a high concentration of radicals as determined by e.s.r. spectroscopy. Materials found to form a strong radical with $MgCl_2$ on milling were: durene, sulphur, tetrasulphur tetraimide $S_4N_4H_4$, phosphonitrilic chloride, thiazyl chloride, cyanuric chloride, benzoyl peroxide, phosphorus pentasulphide, trichloroborazole, phenoxathiin, red phosphorus, boron nitride (graphitic form), *N*-ethylphenothiazine, *p*-diaminobenzene, phosphorus sequisulphide (P_4S_3), and naphthalene. Materials which formed a weaker radical were: hydroxylamine hydrochloride and nitric oxide, which gave a weak signal at 25 °C which became very intense at −20 °C. Materials which did not form detectable radicals were: graphite, heptasulphur monoimide, triphenylphosphine, melamine, phospham $[P_3N_3(NH)_3]$, $P_3N_3(NH_3)_6$, diaminophosphonitrilic chloride, diphenyl sulphone, sulphamide and tri(*p*-bromo)-phenylamine. It is interesting to note that several amino compounds, such as melamine, diaminophosphonitrilic chloride, and tris-*p*-bromophenylamide do not give stabilised radicals with $MgCl_2$ despite the propensity of aromatic amines to radical formation with silica–alumina.[9]

Having found that a wide variety of organic and inorganic compounds give cation radicals when milled with $MgCl_2$, we investigated the possibility of using other materials as supports for these radical species. It became clear that only a limited number of materials were capable of stabilising these radical complexes and that $MgCl_2$ was by far the most efficient support in terms of the number of stabilised radicals per unit of surface area. Only $MnCl_2$, $MgBr_2$, and MgI_2 functioned as supports. Compounds such as $CoCl_2$ and $FeCl_2$ showed no activity despite having the same crystal structure as $MgCl_2$ and $MnCl_2$.[10]

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