Perylene Cation-radicals on the Surface of Catalytic Aluminas

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Summary E.s.r. evidence is presented that it is the cation radical, not the anion radical, of perylene that is generated on the surface of catalytic aluminas.

ION-RADICAL formation at the alumina surface was first reported[1] in 1964. The e.s.r. spectra, obtained when polycyclic aromatic hydrocarbons such as perylene were adsorbed on a suitably prepared alumina surface, were attributed to the cation-radical of the parent molecule.[1,2] It was later demonstrated that suitably activated alumina also possesses electron-donor properties; thus, tetracyanoethylene and 1,3,5-trinitrobenzene (TNB) were reduced to the corresponding anion-radical at the catalyst surface.[3,4] Evidence was subsequently presented to show that the sites responsible for oxidation and for reduction were to some degree mutually dependent.[5] Most of the information at present available on the radical-forming characteristics of alumina has been discussed on the basis of these ideas.

In a recent paper,[6] however, Muha has challenged the entire basis of this work and has argued extensively that the radical formed from perylene, on the activated alumina surface, is not the cation but the corresponding anion-radical. We have submitted for publication elsewhere[7] a letter rebutting some of these arguments, but we have now obtained additional experimental evidence which suggests strongly that the original interpretation based on the cation radical is correct.

We have found that the electron-transfer sites responsible for radical formation on alumina can readily be blocked by either Lewis acids or Lewis bases, and that the results of this blocking can be shown by e.s.r. spectroscopy to be dependent upon the organic adsorbate. When alumina activated in air at 700 °C is blocked by the adsorption of sulphur dioxide (or hydrogen chloride gas), the surface will no longer convert TNB into the corresponding ion-radical, but will still convert perylene to a radical form; when a benzene solution containing both perylene and TNB is added to the alumina + sulphur dioxide system, only the perylene spectrum is seen [Figure (a), (b), and (c)]. Conversely, if the surface is blocked by ammonia (or n-butylamine or pyridine), TNB is converted into the ion-radical but there is no reaction with perylene; with the mixed solution of perylene and TNB, only the TNB-ion spectrum is seen [Figure (d), (e), and (f)]. On an alumina surface treated in turn with both sulphur dioxide and ammonia no radicals are observed [Figure (g)], whereas on the untreated surface the usual spectrum containing signals of both radicals is obtained [Figure (h)].

These blocking experiments demonstrate, beyond reasonable doubt, the existence of two different electron-transfer sites on the activated alumina surface: an electron-donor site that can reduce TNB, and is poisoned by Lewis acids but not by Lewis bases; and a site that can generate a free-radical form of perylene, and is poisoned by Lewis bases but not by Lewis acids. Since there is no doubt that the radical formed from TNB is the anion, the simplest interpretation of these findings is that perylene molecules adsorbed on an alumina surface are held at electron-deficient sites as cation radicals.

In our earlier experiments we reported a twofold enhancement of the TNB anion-radical signal when perylene was added to an alumina + TNB system and a 70% enhancement of the perylene ion-radical concentration in the presence of adsorbed TNB.[5] This assessment of the separate radical concentrations involved the measurement of peak amplitudes and integrated intensities. Muha[6] confirmed the enhancement effect, but claimed that the magnitude of the effect was much less (*ca.* 10%). In the experiments now reported, using integrated intensities only (the method employed by Muha) we have found an enhancement factor of 1.7 ± 0.3 when the concentrations of perylene and TNB in the supernatant solution lay in the ranges 10^{-4}—10^{-2} M and 10^{-3}—10^{-1} M, respectively. A factor of this magnitude is not easy to account for if both TNB and perylene are converted into the anion radical. On the other hand, if it is the cation radical of perylene that is formed on the surface, the explanation could be simple.[5]

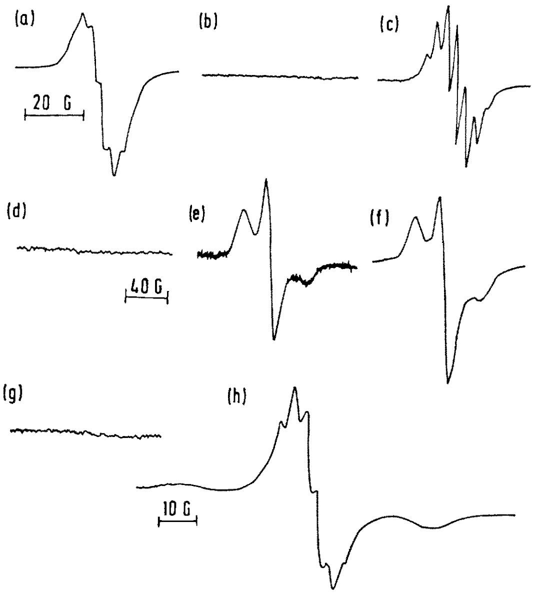

FIGURE. E.s.r. spectra (first derivative) of organic reagents adsorbed from benzene at 20 °C on alumina activated at 700 °C. Catalyst exposed to sulphur dioxide at 20 °C: (a) perylene, (b) TNB, (c) perylene + TNB. Catalyst exposed to ammonia at 20 °C: (d) perylene, (e) TNB, (f) perylene + TNB. (g) Catalyst exposed in turn to ammonia and sulphur dioxide at 20 °C: perylene + TNB. (h) Catalyst was not exposed to inorganic adsorbates: perylene + TNB.

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