# The Electron Spin Resonance of the Anion Radicals Formed on Metal Oxides*

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The formation of cationic species adsorbed on surfaces has been established by studies[1-3] of the adsorption of hydrocarbons on silica-alumina catalysts. It is also probable that an anionic species will be formed on an adsorbent of an electron donor if a strong electron acceptor is used as the adsorbate.[4]

The present authors will here report on the formation of such anionic species in the cases of tetracyanoethylene and benzophenone adsorbed on zinc oxide or alumina.

Tetracyanoethylene[5] and benzophenone, which are known to be strong electron acceptors and which can easily form stable anion radicals,[6,7] were adsorbed on zinc oxide or alumina in vacuo.

All the samples gave ESR signals which were stable for a week or more. The signals quickly dissappeared, however, upon the introduction of air.

A fairly well-resolved hyperfine structure of the ESR spectrum of tetracyanoethylene was observed when tetracyanoethylene was adsorbed on alumina from a benzene solution with a $10^{-1}$ mol. concentration and evacuated under a high vacuum (Fig. 1.)

The spectrum is the same as that for the anion of a solid state, and shows the characteristic feature of a nine-line hyperfine structrue for the solution of the anion.[4]

In the case of benzophenone, the hyperfine structure was not resolved so well and so was not

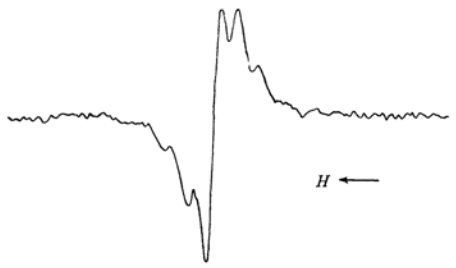


Fig. 1. ESR spectrum of tetracyanoethylene adsorbed on alumina.

confirmative evidence for the formation of aion radicals; however, the most probable paramagnetic species formed from benzophenone is its anion radical.

In an attempt to accelerate the electron transfer from donor to acceptor, the samples were exposed for several tens of minutes to a strong illumination of ultraviolet light from a high pressure mercury lamp. An increase in the signal intensity was observed in both cases upon irradiation.

A transfer of the trapped electrons from oxides to adsorbates will decrease the paramagnetic centers in the oxides; experimental evidence of this was, however, obtained only in the case of zinc oxide by the decrease of the signal at $g=1.96$.

It is interesting to observe the anion radical of tetracyanoethylene on alumina in contrast to the fact that aromatic hydrocarbons are easily oxidized into cation radicals on silica-alumina.[1-3] The milder treatment of the alumina samples in this experiment (evacuation for 3 hr. at 350°C) may be a reason for its poor oxidative tendency.

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