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The Nature of the Blue Species Formed by the Interaction of 1,1-Diphenylethylene with Silica-Alumina

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The surface complexes formed by the interaction of 1,1-diphenylethylene and tetraphenylethylene, respectively, with activated silica-alumina have been investigated using spectrophotometric and ESR techniques. Differences in behavior of these olefins support the conclusion that the blue complex obtained from 1,1-diphenylethylene is not a cation-radical but is a stable carbonium ion formed by hydride ion removal from a dimeric product.

Further support for this conclusion was obtained from infrared absorption spectra of products, desorbed by acetone or ammonia, and also from the adsorption characteristics of these products on fresh catalyst or on anhydrous magnesium perchlorate.

The interaction of 1,1-diphenylethylene (DPE) with silica-alumina has aroused considerable interest in the field of adsorption of hydrocarbons on acidic solids. When DPE is added to dry silica-alumina the yellow carbonium ion $\phi_2C^+ CH_3$, absorbing at 423 mμ is first obtained, followed by formation of a blue species with an absorption band at 605 mμ. The presence of both species imparts a green color to the catalyst.

Leftin and Hobson (*1*) have recently reviewed the application of spectrophotometry to this and related problems. While they summarize several observations in support of the conclusion that the blue species is a cation-radical formed by electron transfer from DPE to Lewis acid or oxidizing centers in the surface of silica-alumina, not all the known facts are in agreement with this view. There is evidence that the carbonium ion is involved in the formation of the blue species in acidic solvents (*1*). While the green DPE–catalyst system contains a low concentration of cation-radicals (*2*) sufficient water may be added to eliminate both the carbonium ions and cation-radicals but still leave the catalyst bright blue. Further addition of water causes complete bleaching, but on pumping the system at room temperature the blue species is quickly restored. The carbonium ion and paramagnetic species are regained simultaneously by further evacuation for a few minutes at 100°C. Hirschler (*3*) has also noted that the blue species can be desorbed as a colorless compound in acetone and when this compound is added back to fresh catalyst the blue complex is formed immediately. These observations cannot be explained by the assumption that only electron transfer is required to form the blue species from DPE.

Experiments and Results

In view of the uncertainty about the identity of the blue species the DPE–catalyst system was again carefully investigated and the results compared with those obtained from corresponding experiments using tetraphenylethylene (TPE).

Controlled amounts of DPE were added to dry oxidized silica-alumina in dry car-

bon tetrachloride and electronic spectra recorded, using a reflectance technique, while the catalyst remained immersed in the solvent in an optical quartz cell. Only the 423 mμ band was obtained on addition of a minute quantity of DPE. Addition of DPE was continued until the 605 mμ band had clearly developed and the variation of both bands over a period of 25 min recorded. On addition of a minute quantity of water the 423 mμ band decreased with a simultaneous increase in the 605 mμ band (Fig. 1). In another experiment sufficient DPE was added to give a high surface concentration of adsorbed species with the 605 mμ band very strongly developed. Addition of a trace of water decreased the 423 mμ band considerably but the 605 mμ band was not altered. These experiments were repeated and the effects of adding water confirmed, i.e., at low surface concentrations the carbonium ions are eliminated, and the olefins obtained readsorbed at different sites with an increase in the concentration of the blue species. At high surface concentrations removal of the yellow species does not affect the blue species as the sites required to readsorb the desorbed olefins are already fully occupied.

Adsorption of TPE resulted in the immediate appearance of strong absorption bands at 360 and 490 mμ with a weaker band at approximately 600 mμ. The adsorbed species were very sensitive to the presence of water, all the bands decreasing at approximately equal rates. The dry TPE–catalyst system also showed a strong unresolved ESR signal and addition of a trace amount of water was sufficient to cause complete removal of the paramagnetic species. The 360 mμ band may be assigned to the carbonium ion, ϕ_2C^+–$CH\phi_2$, and the remaining absorption bands to the cation-radical of TPE.

A series of experiments was carried out in which 20 g quantities of activated catalyst were saturated with DPE in dry carbon tetrachloride and the surface species then desorbed by addition of dry acetone, or by bubbling ammonia through the catalyst–solvent system. The solutions of desorbed material were freed from catalyst, the solvents removed by vacuum distillation at room temperature, and the residues taken up in 1-ml portions of dry carbon tetrachloride, giving yellow-colored solutions. The infrared absorption spectra of these solutions revealed that in all cases polymers had been formed. The presence of an alcohol was also detected, but only in those solutions where acetone had been used as the desorbing agent.

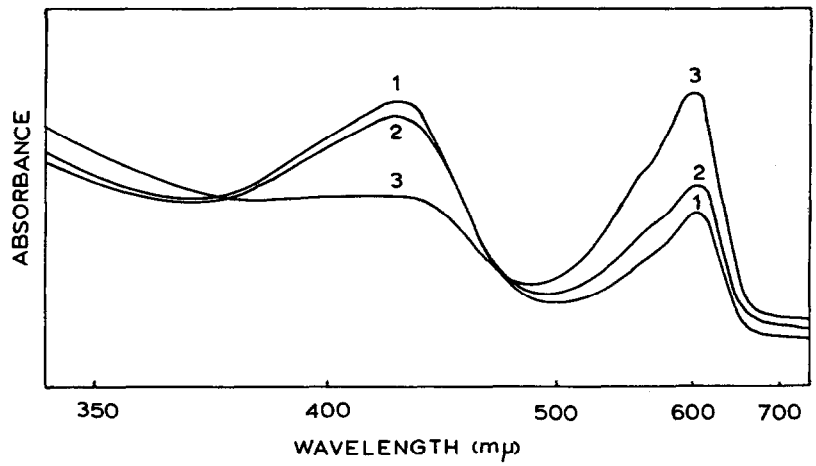


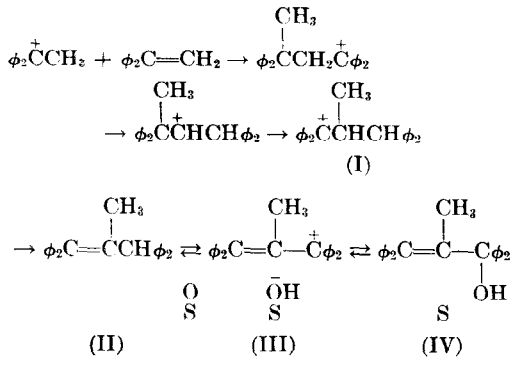
FIG. 1. Electronic spectra of 1,1-diphenylethylene adsorbed on silica-alumina; (1), initial spectrum; (2), change in (1) after period of 25 min; (3), immediate effect of added water on (2).

When the acetone-desorbed material was added to fresh catalyst immediate intense formation of the blue species was noted, in agreement with Hirschler's observations (*3*). On the other hand the ammonia-desorbed material behaved in a manner similar to that of DPE with much slower development of the blue complex on fresh catalyst.

A more striking demonstration of these color tests was obtained when the solutions of desorbed material were added to anhydrous magnesium perchlorate. The acetone-desorbed material gave rapid development of a bright blue color on the solid particles of the salt, but only a faint blue coloration was observed using the ammonia-desorbed material. The effects of magnesium perchlorate on a variety of compounds in dry carbon tetrachloride were then examined. Triphenylmethanol was readily converted to the corresponding carbonium ion, the particles of the solid assuming an intense yellow color, but only a faint coloration was obtained from triphenylmethane over a period of 24 hr. There was no visible interaction with 1,1-diphenylmethanol, diphenylmethanol, TPE, DPE, or anthracene within a period of 12 hr.

Discussion

These results are more compatible with the identification of the blue species as a stable carbonium ion, which may be formed according to the following sequence of reactions.



(I)

(II) (III) (IV)

The formation of the carbonium ion (I) takes place at the strongly acidic Bronsted sites, with excess DPE facilitating the displacement of (I) as the olefin (II). Small amounts of water are also very effective in aiding this desorption. The desorbed olefin (II) is readsorbed at the oxidizing centers where it is converted in part to cation-radicals and mainly to the carbonium ion (III) by hydride ion abstraction. The carbonium ion (III) is the blue species, and it is desorbed from the surface at least to some extent as the alcohol (IV) by acetone, and as the olefin (II) by ammonia. Hirschler (*4*) also claims that triphenylmethanol can be obtained by reaction of triphenylmethane with chemisorbed oxygen in the surface of silica-alumina. On the other hand Leftin and Hall (*5*) found that desorbing the triphenylmethyl cation using ammonia only gave back the original triphenylmethane.

The absence of visible interaction of the hydrocarbons with magnesium perchlorate shows that this solid is not active in forming cation-radicals and thus the blue species is not a cation-radical. The inert behavior of 1,1-diphenylethanol and diphenylmethanol in contrast with triphenylmethanol reveals that only particularly labile molecules react with magnesium perchlorate. The postulated olefin (II) and alcohol (IV), would be expected to fulfill this condition and to react similarly to triphenylmethane and triphenylmethanol, respectively. The formation of the carbonium ion (III) by hydride ion abstraction from the olefin (II) also explains why traces of oxidizing agents accelerate the formation of the blue species from DPE in weak acids (*1*). Cookson, Rosenbaum, and Symons (*6*) have also shown that a blue carbonium ion, very similar in structure to (III), is obtained from the reaction product of 1,1-di(*p*-methoxyphenyl)ethylene and formic acid. A carbonium ion of this type would be expected to absorb at a longer wavelength than less conjugated ions.

The exact identification of the cation-radicals in the green DPE–catalyst system is still a problem. Leftin and co-workers (*1*) found that exposing the system to

water vapor results in a pronounced enhancement of the ESR signal. Since the present results indicate that the initial effect of water, at low concentrations of DPE on dry catalyst, is to displace olefins from the highly acidic Bronsted sites to the oxidizing centers, it is probable that the increase in cation-radical concentration, noted by Leftin and his associates, is also due to the same transfer process. Because the formation of cation-radicals requires strongly electron-accepting centers of fairly high acid strength, further addition of water eliminates these species, but still leaves a detectable concentration of the blue carbonium ion on the surface. The experiments with magnesium perchlorate suggest that the latter ion can be obtained from (II) or (IV) at sites of lower acid strengths and should therefore be less subject to the addition of water. The behavior of TPE on silica-alumina confirms this view since the cation radicals, formed directly on the surface, are about as sensitive to water as the carbonium ion on the Bronsted site. Interpretation in this case is not complicated by polymerization.

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