SHORT COMMUNICATIONS

Paramagnetic Chemical Species of Triphenylmethane and Diphenylamine Formed on the Surface of Several Oxides[1]

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In a previous communication[2] it was reported that some paramagnetic chemical species were formed if anthracene, naphthalene, benzene and hydroquinone were adsorbed in the presence of air on powdered vanadium pentoxide (V_2O_{5-x}). On the basis of their stabilities and for other reasons, the species were hypothesized to be mainly paramagnetic intermediates in the oxidation process of these aromatic hydrocarbons, e. g. radicals of the semiquinone type; rather than the molecule cations such as have been proposed in the research papers[3] when these hydrocarbons were adsorbed on silica-alumina, especially in the absence of air.

In order to confirm the above hypothesis, the research was extended to other adsorbents besides vanadium pentoxide, i. e., cupric oxide, cuprous oxides and alumina. Moreover, instead of aromatic hydrocarbons, triphenylmethane and diphenylamine were used as the adsorbates, because these compounds are known to give radicals by oxidation easily. The experimental procedure and the ESR apparatus used were the same as in the previous paper.

As is shown in Fig. 1, triphenylmethane, when adsorbed on V_2O_{5-x} and heated in air, gave a signal at $g=2.00$ superposed on a broad signal with incompletely resolved hfs of the vanadium ion, in a way similar to that of

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[1] Paper presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[2] K. Hirota and K. Kuwata, This Bulletin, **36**, 229 (1963).

[3] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, **70**, 70 (1961); J. K. Fogo, *J Phys. Chem.*, **65**, 1919 (1961); D. M. Brouwer, *Chem. & Ind.*, **1961**, 177; *J. Catalysis*, **1**, 372 (1962); H. P. Leftin et al., *J. Phys. Chem.*, **66**, 1214 (1962).

[4] Unpublished.

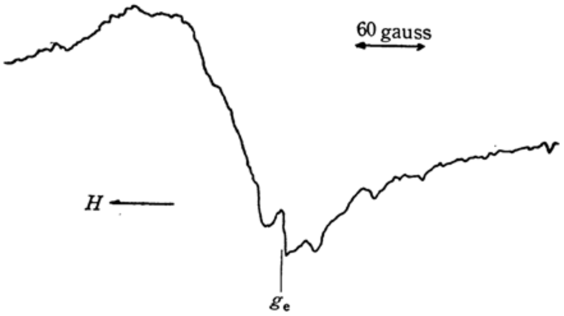

Fig. 1. ESR spectrum of triphenylmethane/V_2O_{5-x} system heated in air for 2.5 hr. at 200°C.

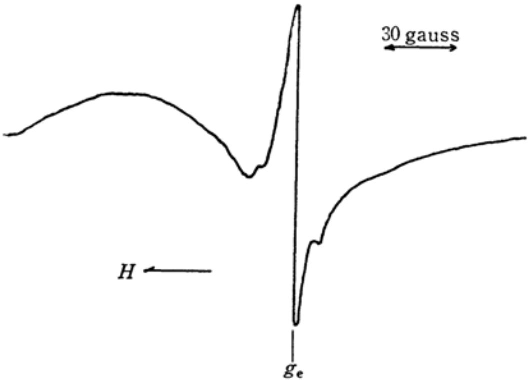

Fig. 2. ESR spectrum of diphenylamine/V_2O_{5-x} system heated in air for 1 hr. at 150°C.

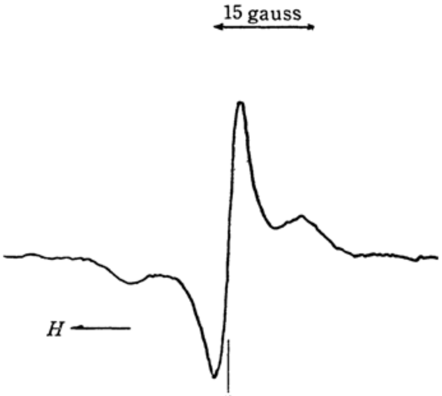

Fig. 3. ESR spectrum of diphenylamine/Cu_2O system heated in air for 15 min. at 200°C.

hydroquinone4), but it gave no signal when adsorbed on cuprous oxide, cupric oxide, or aluminum oxide. The hfs here observed may be due to the decrease in the number of paramagnetic vanadium ions in the oxide. This finding may be explained by the following process:

$$(C_6H_5)_3CH + 2(\dot{V}) + 2O_2 \rightarrow$$
$$(C_6H_5)_3CO\dot{O} + (\dot{V})OH + V^{(v)}O \qquad (1)$$

occurring in connection with the oxidation of triphenylmethane by air, where $(\dot{V})$ denotes the paramagnetic-valency state of vanadium.

Diphenylamine, however, gave signals at $g=2.00$ for all these oxides. Judging from their shape, all the paramagnetic species produced may not be the same. An interesting point is the splitting of the signal into a triplet of unequal height in the case of cuprous oxide (Fig. 3). This may be brought about by the nuclear spin of ^{14}N of the adsobed species and by the anisotropic effect5). A similar tendency was observed, though not so clearly, in the spectrum of diphenylamine adsorbed on V_2O_{5-x} (Fig. 2), while no splitting could be observed in the spectra of cupric oxide and aluminum oxide. From such a difference it may be concluded that the adsorptive power of aluminum oxide is stronger than that of cuprous oxide. The reason why hfs of the adsorbent did not appear can be explained by the constancy in quantity of $(\dot{V})$ during the oxidation, if the following mechanism be assumed in the case of diphenylamine:

$$(C_6H_5)_2NH + (\dot{V}) + O_2 \rightarrow$$
$$(C_6H_5)_2N\dot{O} + (\dot{V})OH \qquad (2)$$

After the ESR measurement had been made, the adsorbates were extracted with carbon disulfide in the cases of triphenylmethane/V_2O_{5-x} and diphenylamine/V_2O_{5-x}. Both extracted substances were found to show ESR signals at $g=2.00$, suggesting the formation of stable radicals by oxidation.

For the sake of comparison, DPPH was similarly adsorbed at room temperature on V_2O_{5-x}; it was found to give no signal. The extract also gave no signal of radicals, suggesting the perfect oxidation of DPPH. Mechanisms (1) and (2) are, therefore, plausible.

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5) A. van Roggen, L. van Roggen and W. Gordy, *Phys. Rev.*, **105**, 50 (1957).