SHORT COMMUNICATIONS

Formation of Paramagnetic Chemical Species of Aromatic Hydrocarbons on Vanadium Pentoxide

By Kozo Hirota and Keiji Kuwata

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Recently, formation of radical or radical ion has been demonstrated repeatedly[1,3] by ESR measurement in the chemisorption of anthracene, perylene, 1, 1-diphenylethylene[4], and *p*-phenylenediamine[5] on silica-alumina catalysts in relation to the mechanism of the acid-site of catalysts. It is interesting to find among these researches some contradicted results on the effect of oxygen; i. e., the intensity of the spectrum became larger by the presence of oxygen according to Fogo[3], while the effect is reversed according to Brouwer[2] and Leftin[4]. Such a discrepancy seems not to be explained by the difference of adsorbates, since the results of Brouwer and Fogo are obtained by the same adsorbates, perylene and anthracene.

In order to investigate such an oxygen effect, we measured the ESR spectrum of benzene, naphthalene and anthracene on vanadium pentoxide which would supply oxygen chemically to the adsorbate. These aromatic hydrocarbons were brought about to the oxide surface as a vapor state and/or a *n*-heptane solution*. ESR measurements were carried out using an X-band apparatus as already reported[6], operating with 455 kc. field modulation.

A slightly asymmetric broad line could be observed always in the spectrum of vanadium pentoxide, degassed (less than 10^{-3} mmHg) at 350°C for one hour. According to the data hitherto published[7], this spectrum could be ascribed to V^{4+} or VO_2^{2+} ion, because it is characterized by a *g*-factor of 1.97, its shape and its half-width of 185 gauss. Now, if anthracene and naphthalene were brought into contact with the oxide treated at 350°C, a small but narrow signal appeared at the shoulder of the broad line, especially markedly in the case of anthracene (cf. Fig. 1). By an introduction of air the signals increased their intensity and the corresponding one appeared even in the case of benzene. It is noteworthy that the radicals produced are so stable as can be kept under the atmosphere for a long time. Their half-width and *g*-factor are as follows:

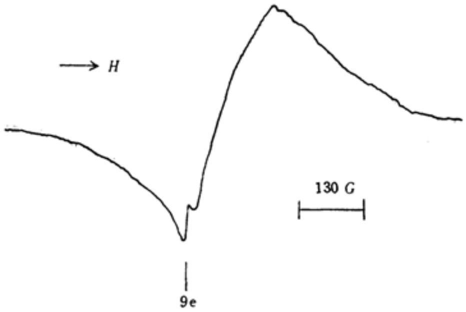

Fig. 1. ESR spectrum of anthracene on vanadium pentoxide.

Anthracene	$g=2.0025\pm0.0008$	$H_{\mathrm{msl}}=19\pm2$
Naphthalene	2.01 ± 0.005	$18._5\pm3$
Benzene	2.00 ± 0.005	$18._5\pm3$

In every case no hyperfine structure of the narrower signal could be observed as well as the color change of the adsorbate. These results are not coincident with the systems of anthracene and perylene on silica-alumina[2,4] and on aluminum chloride[8]. However, the effect of oxygen seems to coincide with Fogo's result[3]. Allotting the role of an electron-acceptor to oxygen atom, Fogo ascribed his signal to a hydrocarbon cation-radical formed on Lewis acid site, similarly as Leftin et al.[4] assumed in the chemisorption of 1, 1-diphenylethylene.

It is possible, however, that the same

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[1] J. J. Rooney and E. C. Pink, *Proc. Chem. Soc.*, **1961**, 70.

[2] D. M. Brouwer, *Chem. & Ind.*, **1961**, 77.

[3] J. K. Fogo, *J. Phys. Chem.*, **65**, 1919 (1961).

[4] H. F. Leftin, ibid., **66**, 1214 (1961).

[5] M. Okuda, *J. Chem. Soc. Japan, Pure Chem Sec.* (*Nippon Kagaku Zasshi*), **82**, 1290 (1961); M. Okuda and T. Tachibana, This Bulletin, **33**, 863 (1960).

* Spectroscopic grade of *n*-heptane free from aromatics was used.

[6] K. Kuwata and K. Hirota, ibid., **34**, 458 (1961).

[7] K. Tarama and S. Teranishi et al., ibid., **34**, 1195 (1961); R. Faber and M. Roggrs, *J. Am. Chem. Soc.*, **81**, 1849 (1959).

[8] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, **1961**, 142.

conclusion cannot be applied to the present research, because the paramagnetic species here observed may have a possibility to include some other intermediate species, e. g. semiquinone, formed as the result of oxidation of these aromatic hydrocarbons besides the cation-radical. Such a presumption is in harmony with the oxidative property of the vanadium pentoxide degassed at high temperature. In connection to the above consideration, sample-tube containing anthracene adsorbed on the oxide was heated up to 200°C in the atmosphere, in order to investigate the stability of the radical. Then the shoulder signal disappeared at all; i. e., the radical on the oxide was completely oxidized at higher temperatures.

Added in Proof. In order to investigate the nature of this signal in detail, hydroquinone which is one of the oxidation products of benzene was used as the adsorbate. A signal (g-factor$=2.002 \pm 0.001$) appeared also at once, and became very strong at 200°C. The color of the sample became dark-purple, suggesting that quinhydrone is formed, i. e, equimolar complex of quinone and hydroquinone. The signal had no hfs and was narrow as compared to that observed in the case of aromatic hydrocarbons, but it may be allowed to consider that it is due to semiquinone. A similar experiment was carried out, making p-phenylenediamine as the adsorbate, and a signal with no hfs could be obtained as reported by Okuda5) on silica-alumina. This will be another finding to support our viewpoint.

Such being the matter, it will be reasonable to propose that if anthracene, naphthalene or benzene is adsorbed, corresponding semiquinone radical is formed on the degassed vanadium radical.

Details of the study will be published elsewhere.

Science Faculty
Osaka University
Nakanoshima
Osaka