

## An ESR Investigation of Nitrobenzene Adsorbed on Zinc Oxide

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An ESR study of the interaction of nitrobenzene with nonstoichiometric ZnO surfaces was made. A 3-line spectrum with  $g$  values 1.9840, 2.0055 and 2.0225 was observed and was identified as due to nitrobenzene anion radicals strongly held to the surface. An unidentified signal at  $g = 2.0050$  was left behind after heating the sample at 300°-500° in a vacuum.

Of the many aromatic radicals which can be formed on surfaces by electron transfer processes, the formation of nitro radicals has received particular attention. A relatively simple analysis of the spectra is possible on the basis of an interaction of the unpaired spin of the electron with the nucleus (or nuclei) of nitrogen. The adsorption of mono- and polynitrobenzenes from solution in benzene, cumene, or CCl<sub>4</sub> on catalytic aluminas (1) and from the vapor-phase on surfaces of MgO (2) have been shown to yield anion radicals at the surface. In the present work, the adsorption of nitrobenzene from the vapor state on a typical  $n$ -type oxide semiconductor, nonstoichiometric ZnO, has been studied. An analysis of the ESR spectra obtained has been made to identify the radical formed and to understand the mechanism of the adsorption process.

High-purity zinc oxide (New Jersey Zinc Co., Palmerton, Pennsylvania; surface area 3 m<sup>2</sup>/g) was outgassed for 2 hr at 500° and 10<sup>-6</sup> torr before treatment with nitrobenzene in a conventional adsorption apparatus. The nitrobenzene (Baker Analyzed Reagent Grade) was purified from dissolved gases by repeated freezing and thawing *in vacuo*. Since the vapor pressure of nitrobenzene is low (<1 mm at 25°) sufficient excess of the vapors were transferred onto the sample by briefly cooling the sample vessel in liquid nitrogen. The ESR spectra were recorded with

an X-band Varian spectrometer (V-4502) fitted with a TE<sub>104</sub> mode dual cavity and DPPH (1,1-diphenylpicrylhydrazyl) was used in the reference cavity as a standard for  $g$  measurements. The spectra were recorded both at room temperature and at -195°.

The ESR spectrum of vacuum-outgassed ZnO (500°, 2 hr) in Fig. 1A shows a principal signal at  $g \sim 1.96$  which has been attributed

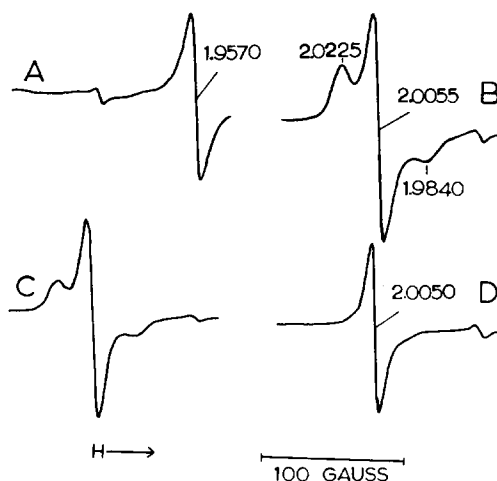


FIG. 1. ESR (X-band) spectra of nitrobenzene adsorbed on ZnO. A, sample outgassed at 500° for 2 hr at 10<sup>-6</sup> torr (SL 100, -195°); B, exposed to excess nitrobenzene vapors and reoutgassed for 15 hr at 25° (SL 50; 25°); sample further outgassed C, for 1 hr at 200° (SL 50, 25°); and D, for 1 hr at 300° (SL 50, 25°). (All spectra were recorded at approximately 22 mW.)

to  $Zn^{2+}$  ions (3, 4), or oxygen ion vacancies with trapped electrons (5), or to both (6). The adsorption of excess nitrobenzene vapors markedly reduced the intensity of the  $g \sim 1.96$  signal and simultaneously produced a 3- $g$  value signal corresponding to  $g = 1.9840, 2.0055,$  and  $2.0225$  in which the satellites were somewhat asymmetrically located with respect to the central signal. Removal of excess nitrobenzene by outgassing at  $25^\circ$  for 15 hr increased the intensity of the spectrum by about 50% (Fig. 1B). Power variation studies indicated that the entire spectrum changed uniformly in intensity, suggesting that the spectrum is due to a single species. The intensity of the spectrum at  $-195^\circ$  was about 40% higher than that at  $25^\circ$ . No increase in the separation of outer peaks occurred on cooling the sample to  $-195^\circ$ . Outgassing at temperatures up to  $200^\circ$  reduced the intensity of the triplet without any change in the  $g$  values (Fig. 1C). However, following treatment at higher temperatures ( $300\text{--}500^\circ$ ) only a singlet corresponding to a  $g$  value of 2.0050 could be observed in the spectrum (Fig. 1D). That the singlet was a new signal and did not result simply by a broadening of the satellites at  $g = 1.9840$  and  $2.0225$  of the triplet was shown from a study of the variation in intensity of the spectra with temperature, in the range  $-195^\circ$  to  $25^\circ$ .

The three-line spectrum produced by the ZnO-nitrobenzene system in the present study suggests an anisotropic interaction of the unpaired electron with the  $^{14}N$  nucleus of nitrobenzene. In fact, the shape of the triplet and the asymmetry of the satellites with

respect to the central signal are very similar to those reported for adsorbed nitro radicals on either high-area alumina (1) or MgO (2). Therefore, our results show that the adsorption of nitrobenzene on the low-area ZnO apparently also leads to the formation of nitrobenzene anions on the surface.

The spectrum observed shows no hyperfine splitting due to protons such as reported (2) for nitrobenzene on MgO at  $293^\circ K$ . Also, once formed, the spectrum of the nitrobenzene anion is quite stable and is unaffected by subsequent contact with oxygen. An analysis of the spectrum following Fox, Gross, and Symons (7) supports the suggested views on the origin of the spectrum. It appears that the satellites of the triplet at  $g$  values 2.0225 and 1.9840 are the outer hyperfine features of the component parallel to the field. The middle hyperfine line for the parallel component expected at  $g = 2.0033$  along with the three perpendicular features are apparently contained within the broad central signal at  $g = 2.0055$  ( $\Delta H = 12$  gauss). Using the known solution value for  $g_{av}$  (7) and the value of  $g_{\parallel}$  obtained from an analysis of the position of the satellites of the signal, it is possible to calculate  $g_{\perp}$ . The value thus calculated and other spectral parameters for nitrobenzene adsorbed on ZnO are given in Table 1. Also, included for comparison are the corresponding values obtained for nitrobenzene anions in the solid state and for the species adsorbed on catalytic aluminas and MgO. The similarity in values of the various parameters confirms the formation of nitrobenzene anions on ZnO. Further, the observation that there is

TABLE I  
ANISOTROPIC PARAMETERS FOR NITROBENZENE RADICAL ANION

| Adsorbent                      | $A_{\parallel}^N$<br>(gauss) | $A_{\perp}^N$<br>(gauss) | $g_{\parallel}$    | $g_{\perp}$        | $g_{av}$            | References   |
|--------------------------------|------------------------------|--------------------------|--------------------|--------------------|---------------------|--------------|
| ZnO                            | 30                           | 5.9 <sup>a</sup>         | 2.0033             | 2.005 <sup>c</sup> | 2.0044 <sup>c</sup> | Present work |
| MgO                            | 28                           | $\sim 3$                 | 2.003 <sup>b</sup> | 2.006              | 2.005 <sup>b</sup>  | 2            |
| Al <sub>2</sub> O <sub>3</sub> | 33.0                         | $\leq 10.6$              | 2.0023             | 2.006              | 2.0048              | 1            |
| Radicals in<br>solid state     | 27.4                         | 6.9                      | 2.0018             | 2.0055             | 2.0044              | 7            |

<sup>a</sup> Value calculated using  $A_{iso}^N = 13.9$  [see ref. (9)]. An approximately similar value for  $A_{\perp}^N$  is also obtained as an upper limit on using the width of the central signal ( $\Delta H \sim 12$  gauss).

<sup>b</sup> Values calculated from data given in the paper.

<sup>c</sup> Value for  $g_{av}$  assumed (equal to solution value) to calculate  $g_{\perp}$ .

no increase in the separation of the outer peaks in the spectrum on cooling the sample from 25° to -195° indicates that the nitrobenzene anion lies flat on the surface, a conclusion also reached by Tench and Nelson in their investigations on MgO.

ESR studies were also made on nitrobenzene adsorbed on oxygen-treated samples of zinc oxide. In these experiments ZnO was pretreated in vacuum ( $10^{-6}$  torr) at 500° for 2 hr and then heated in oxygen ( $\sim 1$  atm) for 8 hr at 500°. The sample was subsequently cooled in oxygen to 25° and outgassed for 10 min to remove excess oxygen. Subsequent adsorption of nitrobenzene under otherwise identical conditions gave no signals in the ESR spectrum. Therefore, the nonstoichiometry in ZnO (indicated by the ESR signal at  $g \sim 1.96$ ) is necessary for the formation of nitrobenzene anions at the surface. A transfer of electrons from lattice oxide ions ( $O^{2-}$ ) at the surface has been suggested in the formation of nitrobenzene anions on MgO (8). Our experiments, however, indicate such a process is unlikely on ZnO where the  $Zn^{+}$  ions or the oxide ion vacancies (with trapped electrons) function as electron donors.

The nature and origin of the signal at  $g = 2.0050$  produced when ZnO with adsorbed nitrobenzene is heated in vacuum at 300°, is not very clear. This signal persists even after heating in vacuum at 500° for 30 min. While a possibility that the signal is related to adsorbed nitrobenzene cannot be ruled out, it seems more likely that this is not the case. It may be pointed out here that recently Ueda (8) has noticed the formation of two signals with  $g$  values of 1.96 and 2.004 when ZnO was heated with various organic compounds at 300°. While some or-

ganic compounds gave a more intense 1.96 signal, with others the 2.004 signal was of greater intensity. It was suggested that the two signals were not from two independently existing species but from species such as  $Zn_i^{+}$  and  $(ZnO)_\nu^{-(2\nu-1)}$  (where  $\nu$  is an integer), in equilibrium with each other. The signal at  $g = 2.004$  is very similar to the signal obtained in the present study at  $g = 2.0050$ , despite the small difference in the cited  $g$  values. While we do not wish to comment on the identity of the signal, it appears at the present time that it is associated with the desorption of the adsorbate anion and a consequent return of the electron to ZnO.

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