J. Am. Chem. Soc. **1980**, *102*, 7511–7513

Spin Trapping of Molecules Adsorbed on Zinc Oxide

Tokuo Matsuzaki, Taizo Uda, Akio Kazusaka, George W. Keulks, and Russell F. Howe[*]

Laboratory for Surface Studies and Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201. *Received April 10, 1980*

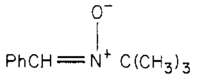
Abstract: The reactions of the spin trap PBN with hydrogen and propylene adsorbed on ZnO are reported. For hydrogen, evidence is presented that the species trapped are H atoms adsorbed on Zn sites. For propylene, the allyl anion adsorbed on Zn sites reacts with PBN, but the resulting hydroxylamine must be oxidized before a nitroxide radical can be observed. Less than 1% of the adsorbed species are detected by the spin trapping technique.

The spin trapping technique has been widely used to identify radicals formed in homogeneous systems.[1,2] The method involves reaction of a short-lived radical with a spin trap to produce a stable radical which may be identified from its EPR spectrum:

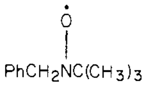
$$\mathrm{R\cdot + T \rightarrow RT\cdot} \qquad (1)$$

A number of radicals formed photochemically at the solid–solution interface have been detected by means of spin trapping. For example, $\mathrm{CH_3\cdot}$ has been trapped during photodecarboxylation of acetates over platinized $\mathrm{TiO_2}$.[3] The $\mathrm{O_2^-}$ radical anion has been detected during photolysis of various pigment suspensions.[4,5] The $\mathrm{HO\cdot}$ radical has been trapped during photosynthesis of $\mathrm{H_2O_2}$ in aqueous ZnO dispersions,[6] and both $\mathrm{HO\cdot}$ and $\mathrm{HO_2\cdot}$ have been detected during photodecomposition of $\mathrm{H_2O}$ at $\mathrm{TiO_2}$ surfaces.[7]

We recently reported the first application of the spin trapping technique to the solid–gas interface.[8] Adsorption of $\mathrm{H_2}$ on a ZnO surface, followed by reaction with the spin trap *N-tert*-butyl-α-phenylnitrone (PBN, I), produced the stable radical II on the surface, which could be extracted into solution.


I

$\mathrm{PhCH{=}\overset{O^-}{\overset{|}{N^+}}C(CH_3)_3}$


II

$\mathrm{PhCH_2\overset{\dot{O}}{\overset{|}{N}}C(CH_3)_3}$

The adsorption of $\mathrm{H_2}$ on ZnO has been extensively studied.[9–17] Two stages of adsorption occur at room temperature, an initial rapid and reversible process giving rise to infrared bands characteristic of ZnH and OH,[10,11] and a subsequent slow and irreversible process which apparently involves infrared inactive species. Kesavulu et al.[12,13] have suggested from conductivity measurements that the irreversibly adsorbed $\mathrm{H_2}$ is protonic, a conclusion which does not appear to have unanimous support.[16] Our preliminary spin trapping experiments suggested that part of the adsorbed $\mathrm{H_2}$ may have radical character, although free hydrogen atoms are not formed during $\mathrm{H_2}$ adsorption on ZnO. In this paper we present the results of further spin trapping experiments aimed at establishing which form of adsorbed $\mathrm{H_2}$ is trapped by PBN.

As part of an extension of the technique to systems of catalytic interest, we also report here the reaction of PBN with species formed during adsorption of propylene on ZnO. The elegant isotopic and infrared studies of Dent and Kokes[18] showed that propylene adsorption on ZnO involves loss of a hydrogen to form ZnOH and a symmetric π-allyl species. More recently, Nguyen and Sheppard presented spectroscopic evidence for the anionic nature of the allyl species on ZnO.[19]

Experimental Section

Two different experimental procedures were used to trap adsorbed species with PBN. Method A used the reaction vessel shown in Figure 1a. About 5 mL of a 0.01 M solution of PBN (Aldrich Chemical Company) in $\mathrm{CCl_4}$ (spectroscopic grade) was placed in the side arm and degassed by evacuation at −78 °C. The Teflon stopcock was then closed, and 2.0 g of Kadox-25 ZnO (5 $\mathrm{M^2\,g^{-1}}$) placed in the reactor and degassed in vacuo at 500 °C for several hours. Following adsorption of the molecule of interest at room temperature, the Teflon stopcock was opened and the PBN solution transferred onto the ZnO. The reactor was then opened to the air, the ZnO–$\mathrm{CCl_4}$ slurry filtered, and the filtrate transferred to an EPR tube following evaporation of 75% of the solvent.

Method B avoided contact of the sample with air during the filtration step, employing the reaction vessel shown in Figure 1b. A procedure similar to that given above was followed, except that filtration was carried out through a plug of glass wool, allowing direct transfer of the filtrate into an EPR tube without exposure to air.

Spectra were recorded at 9.5 GHZ on a Varian E115 spectrometer. The *g* values were obtained by comparison with a DPPH standard, and spin concentrations estimated (with an uncertainty of ±30%) by numerical double integration of signals and comparison with the standard, using a double cavity. Spectra were simulated with the program SIM 14.[20]

Results

As previously reported,[8] addition of a solution of PBN to ZnO which had been exposed to 100 torr of $\mathrm{H_2}$ at room temperature and briefly evacuated produced the H atom adduct of PBN (II). The EPR signal of II was not obtained in blank experiments with ZnO alone. Figure 2a shows the spectrum of the H atom adduct obtained by method B. This is identical with the spectrum obtained by method A.[8] The spin concentrations of II obtained by both methods were about 10^{16} spins per g of ZnO. A similar spin concentration was obtained in an experiment in which the reactor was completely shielded from daylight with aluminum foil, ruling out any photochemical reaction between PBN and adsorbed hydrogen. The EPR signal was not observed if the ZnO was evacuated for 1 h following $\mathrm{H_2}$ adsorption before admitting PBN.

Figure 2b shows the spectrum obtained by adding PBN to ZnO containing adsorbed HD (using method A). This consists of two overlapping signals, the 7-line signal of the H atom adduct, and

---

[*] Address correspondence to this author at the Department of Chemistry.

(1) E. G. Janzen in "Free Radicals in Biology", Vol. 4, W. A. Pryor, Ed., Academic Press, New York, 1979.

(2) E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971).

(3) B. Kraeutler, C. D. Jaeger, and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 4903 (1978).

(4) J. R. Harbour and M. L. Hair, *J. Phys. Chem.*, **82**, 1397 (1978).

(5) J. R. Harbour and M. L. Hair, *J. Phys. Chem.*, **81**, 1791 (1977).

(6) J. R. Harbour and M. L. Hair, *J. Phys. Chem.*, **83**, 652 (1979).

(7) C. D. Jaeger and A. J. Bard, *J. Phys. Chem.*, **83**, 3146 (1979).

(8) T. Uda, A. Kazusaka, R. F. Howe, and G. W. Keulks, *J. Am. Chem. Soc.*, **101**, 2758 (1979).

(9) G. Parravano, H. G. Friedrick, and M. Boudart, *J. Phys. Chem.*, **63**, 1144 (1959).

(10) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).

(11) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772 (1969).

(12) D. Narayana, V. S. Subrahmanyan, J. Lal, M. Mahmood Ali, and V. Kesavulu, *J. Phys. Chem.*, **74**, 779 (1970).

(13) D. Narayana, J. Lal, and V. Kesavulu, *J. Phys. Chem.*, **74**, 4150 (1970).

(14) C. C. Chang and R. J. Kokes, *J. Am. Chem. Soc.*, **93**, 7107 (1971).

(15) S. Naito, H. Shimizu, E. Hagiwara, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 1519 (1971).

(16) R. J. Kokes and A. L. Dent, *Adv. Catal.*, **22**, 1 (1972).

(17) R. J. Kokes, A. L. Dent, C. C. Chang, and L. T. Dixon, *J. Am. Chem. Soc.*, **94**, 4429 (1972).

(18) A. L. Dent and R. J. Kokes, *J. Am. Chem. Soc.*, **92**, 6709 (1970).

(19) T. T. Nguyen and N. Sheppard, *J. Chem. Soc., Chem. Commun.*, 868 (1978).

(20) G. P. Lozos, B. M. Hoffman, and C. G. Franz, *QCPE*, **10**, 265 (1974).

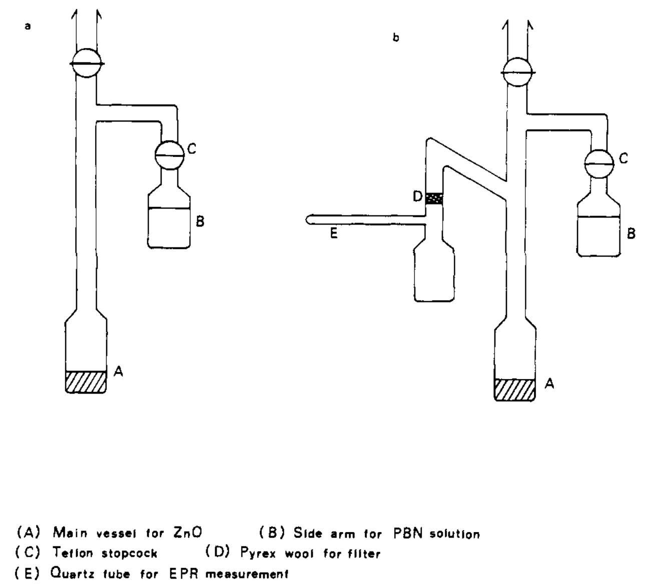


Figure 1. Apparatus used to prepare PBN adducts of adsorbed H_2 and propylene: (a) method A; (b) method B.

Table I. Hyperfine Coupling Constants (±0.1 G) of PBN Adducts[a]

R·	A_N	A_H	$A_H(A_D)$	ref
H	14.8	7.4	7.4	this work
H	15.0	7.5	7.5	22
H	14.8	7.0	7.0	23
D	14.7	7.3	(1.1)	this work
D	14.9	7.5	(1.1)	22
from C_3H_6	14.5	3.5		this work
$CH_2{=}CHCH_2$	14.5	3.5		this work
C_3H_7	14.1	3.9		24

[a] All radicals observed had $g = 2.0063 \pm 0.0001$.

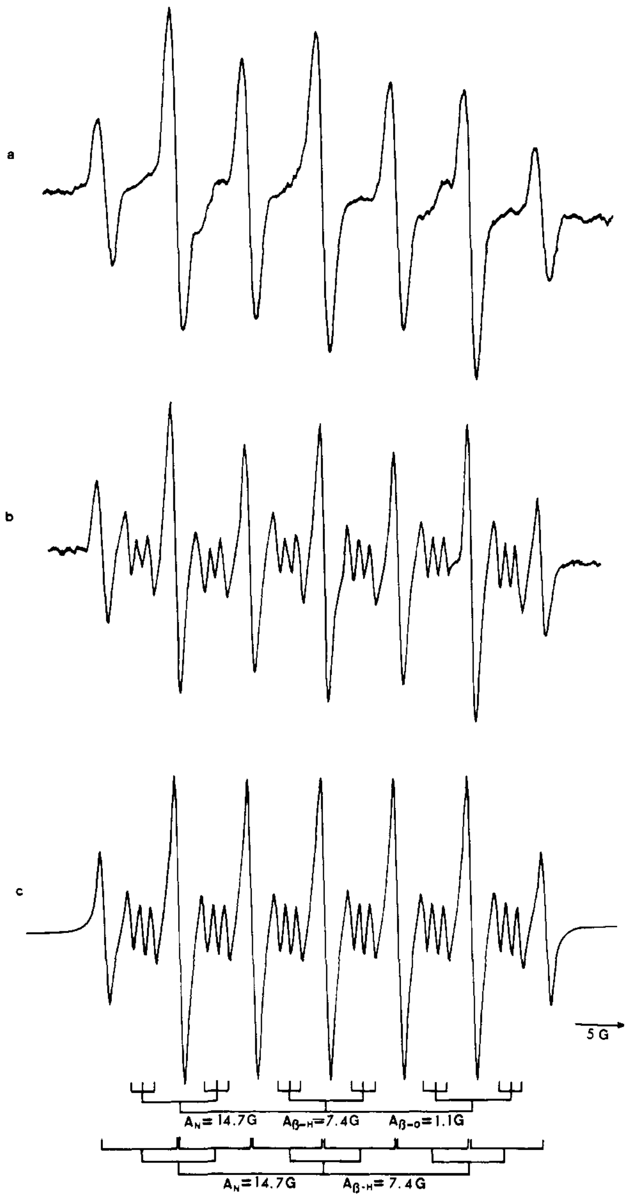


Figure 2. (a) EPR spectrum of reaction product of PBN and adsorbed H_2; (b) adsorbed HD; (c) simulation of (b) with a 2:1 ratio of PBN:H and PBN:D.

an 18-line signal previously[8] obtained from adsorbed D_2 (the additional lines due to hydrogen abstracted from the benzene solvent[8] were not observed in the present work with carbon tetrachloride as the solvent). The relative amounts of the H and D adducts could not be determined accurately from the overlapping signals. However, the observed spectrum could be satisfactorily computer simulated by summing the H and D adduct signals in a 2:1 ratio (Figure 2c).

Adsorption of propylene at room temperature and 100 torr onto ZnO followed by brief evacuation and reaction with PBN (method A) gave the spectrum shown in Figure 3a. The intensity of the 6-line signal corresponded to a spin concentration of about 1×10^{15} spins per g of ZnO. No trace of the 7-line H-atom-adduct signal was detected following propylene adsorption. No paramagnetic species at all were detected when the experiment was carried out by using method B.

An independent preparation of the allyl adduct of PBN was made following the procedure of Janzen and Blackburn.[21] This involved reaction of PBN with allyl magnesium bromide, followed by air oxidation of the hydroxylamine anion initially formed, as follows:

$$\mathrm{RMgBr} + \mathrm{T} \rightarrow \mathrm{RT}^- \xrightarrow{O_2} \mathrm{RT}\cdot \qquad (2)$$

Figure 3b shows the spectrum of the resulting nitroxide radical. The EPR parameters of the PBN adducts are summarized in Table I.

Discussion

The assignment of the signal in Figure 2a to the H-atom adduct of PBN follows from comparison of the hyperfine coupling constants with those of H-atom adducts formed during irradiation of gaseous CO/H_2 mixtures,[22] liquid hydrocarbons,[23] and alkyl cobalt complexes.[24] The experiments with HD and D_2 prove that the trapped H atom originates from adsorbed H_2. It remains to be considered which kind of adsorbed H_2 reacts with PBN.

Dent and Kokes[11] have shown that the rapidly chemisorbed H_2 (type I) can be completely removed from ZnO by evacuation at room temperature for 20 min, whereas the slowly chemisorbed type II H_2 is more strongly held. Our inability to form the H-atom adduct of PBN with samples which had been outgassed for 1 h following H_2 adsorption suggests that the trapped H atoms originate from type I chemisorbed H_2. The infrared data[10,11] indicate that this consists of ZnH and OH species. Kokes et al.[17] have pointed out the existence of an equilibrium isotope effect in the room temperature type I adsorption of HD, with ZnHOD being favored over ZnDOH by a factor of at least 2.2 to 1. A similar ratio is found here for the relative amounts of PBN H- and D-atom adducts obtained from adsorbed HD, suggesting that it is the H (or D) atom from ZnH (or ZnD) that reacts with PBN.

---

(21) E. G. Janzen and B. J. Blackburn, J. Am. Chem. Soc., **91**, 4481 (1969).

(22) S. Nagai, K. Matsuda, and M. Hatada, J. Phys. Chem., **82**, 322 (1978).

(23) S. W. Mao and L. Kevan, J. Phys. Chem., **78**, 91 (1974).

(24) G. Roewer and D. Rehorek, J. Prakt. Chem., **320**, 566 (1978).

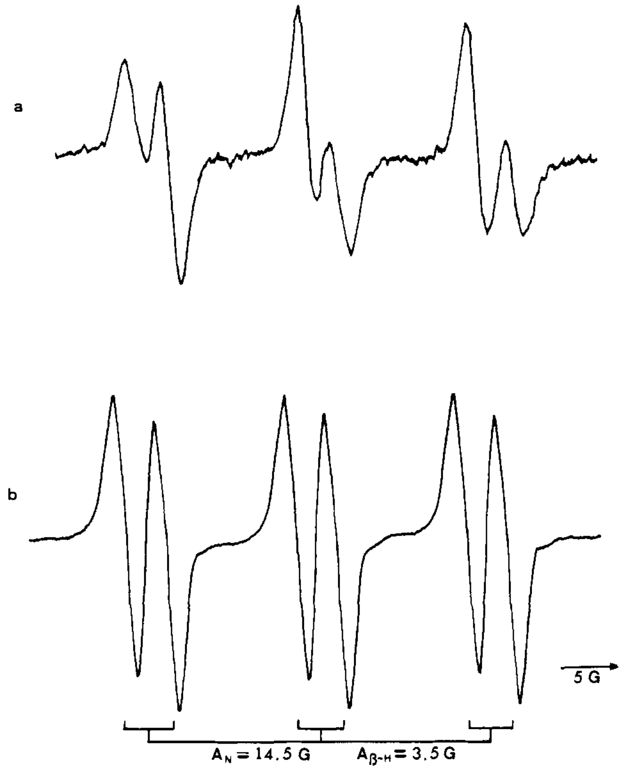


Figure 3. (a) EPR spectrum of reaction product of PBN and adsorbed propylene; (b) reaction product of PBN and allyl magnesium bromide.

The maximum amount of type I H_2 adsorption on Kadox 25 ZnO is about 0.1 $cm^3\ g^{-1}$.[11] Assuming formation of equal quantities of ZnH and OH species, we estimated the maximum possible spin concentration of PBN H-atom adduct to be about 2.6×10^{18} spins per g of ZnO. The observed spin concentrations are typically 0.5% of this value. There are several reasons why less than the expected amount of the PBN H-atom adduct is detected. Firstly, the yield of the H-atom adduct may be limited by the occurrence of at least two other competing reactions:

$$RT\cdot + R\cdot \rightarrow \text{products} \qquad (3)$$

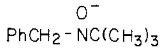
$$RT\cdot + RT\cdot \rightarrow \text{products} \qquad (4)$$

Reaction 3 represents trapping of a further H atom by the PBN adduct formed initially, and reaction 4 involves a bimolecular self-reaction. Schmid and Ingold[25] have recently measured rate constants for the trapping of alkyl radicals by a variety of spin traps, including PBN. For the case R = 1-hexyl and T = PBN, they report that the rate constant for reaction 3 exceeds that for reaction 1 by 3 orders of magnitude. No comparable data are available for the H-atom adduct of PBN, but the steady state concentration of HT· is likely to be similarly restricted by the tendency of the adduct to undergo further reactions, particularly reaction 3.

A second factor which may influence the yield of the H-atom adduct is that the ZnO surface is not energetically uniform, and only a small fraction of the type I adsorbed H_2 may be able to react with PBN. The accepted explanation[16] for the formation of ZnH and OH species in type I chemisorption is that the H–H bond is heterolytically cleaved on ZnO pair sites, forming a hydride species on the zinc and a protonic species on the oxide:

$$Zn^{2+}\ O^{2-} + H_2 \rightarrow Zn^{2+}\ H^- + O^{2-}\ \ H^+$$

If this is the case, attack of the hydride ion on PBN would produce the hydroxylamine anion (III), which must be oxidized to produce

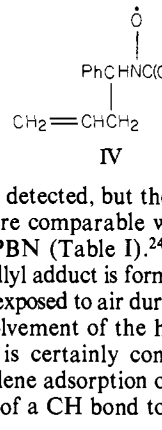


$$\overset{O^-}{PhCH_2\text{-}NC(CH_3)_3}$$

III

the nitroxide radical (II). The fact that both experimental methods produced comparable concentrations of the nitroxide suggests that an oxidation step is not involved (unlike the situation with adsorbed propylene, discussed below). The total amount of type I chemisorption corresponds to about 5% of the monolayer capacity of ZnO,[11] which certainly implies that special sites are involved. Kokes and Dent[16] have concluded that the amount of type I chemisorption is not a function of the nonstoichiometry of ZnO, in contrast to earlier suggestions[13] that surface defects in the form of excess Zn or Zn^+ are responsible for H_2 chemisorption. Our spin trapping experiments do not permit identification of the adsorption site, but it appears that at least part if not all of the ZnH species formed in type I chemisorption involve largely covalent bonding with the surface. This may be confined to certain edge or edge-type defect sites. Abstraction of H atoms by PBN from hydrogen-donating solvents such as tetrahydrofuran during photolysis is known[1] and has also been observed for benzene.[8] We envisage a similar abstraction of H atoms from the ZnH species in type I chemisorption of H_2, although photolysis is not involved in this case.

The EPR spectrum obtained by trapping adsorbed propylene with PBN is identical with that of the radical produced by reacting PBN with allyl magnesium bromide, leaving little doubt that the allyl adduct of PBN (IV) is formed. No hyperfine splitting from



$$\begin{array}{l} \quad\ \ \dot{O} \\ \quad\ \ | \\ PhCHNC(CH_3)_3 \\ \quad | \\ CH_2{=}CHCH_2 \end{array}$$

IV

the allyl side chain is detected, but the proton and ^{14}N hyperfine coupling constants are comparable with those reported for the *n*-propyl adduct of PBN (Table I).[24]

The fact that the allyl adduct is formed from propylene on ZnO only if the solution is exposed to air during the preparation (method A) suggests the involvement of the hydroxylamine anion as an intermediate. This is certainly consistent with the proposed mechanism of propylene adsorption on ZnO,[18,19] which involves heterolytic cleavage of a CH bond to produce a proton and the allyl anion:

$$Zn^{2+}\ O^{2-} + C_3H_6 \rightarrow Zn^{2+}\ [C_3H_5]^-\ O^{2-}\ H^+$$

The fraction of adsorbed propylene trapped by PBN is less than 1% of the total, for reasons similar to those discussed above for H_2 adsorption.

It is noteworthy that no trace of a PBN H-atom adduct could be detected following propylene adsorption. This supports the suggestion made above from the HD experiment that the H or H^+ adsorbed on oxide ion sites does not react with PBN. In comparing the behavior of adsorbed H_2 and propylene toward PBN, the difference in frequency between the OH species produced from H_2 (3489 cm^{-1}) and propylene (3593 cm^{-1}) is significant. Dent and Kokes[18] proposed that the 104-cm^{-1} shift was due to the perturbing influence of an adjacent propylene. The spin-trapping experiments however suggest that there may be a marked difference in polarity between the ZnH and $Zn(C_3H_5)$ bonds and therefore in the corresponding OH bonds as well. This is consistent with the fact that propylene is much more strongly adsorbed than type I H_2.[18] The major limitation of the spin-trapping technique as applied to ZnO is that only a small fraction of the adsorbed species are detected, which are not necessarily typical of the entire surface.

---

(25) P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, **100**, 2493 (1978).