amount of ionic character in the Fe–C bond is at this time undetermined.

The magnetic susceptibility of powder samples of **1**, in contrast to the 1-D polymorph, obeys the Curie expression, i.e., $\chi T = 0.81$ BM. This is in accord with values obtained for other ferrocenium salts[13] and suggests very little magnetic coupling between the intradimer $S = \frac{1}{2}$Fe(III)'s separated by ~14 Å. The $(TCNQ)_2^{2-}$ dimer is strongly antiferromagnetically coupled. For single crystals of **1**, $\chi_{\parallel} = 2\chi_{\perp}$ where $\chi_{\parallel}$ is measured parallel to the dimer axis. In **1** the structural arrangement consists only of isolated dimers. Within an isolated dimer the $S = \frac{1}{2}Fe^{III}$ sites are 13.993 (2) Å apart and the separation between $DMeFc^{+\cdot}$ and $TCNQ^{-\cdot}$ (3.554 Å) and $TCNQ^{-\cdot}$–$TCNQ^{-\cdot}$ (3.147 Å) suggest that b_{2g}–b_{2g} electronic interactions exist within the dimer to form a filled a_u bonding orbital (Figure 4b). Coupling between parallel and perpendicular dimers appears to be minimal owing to a lack of direct orbital interactions; however, cyano interactions with the $DMeFc^{+\cdot}$ ion where N(4) has a close approach of 3.271 Å to C(8)′ and 3.354 Å to C(2)′ suggest some interactions. Also, there are numerous Fe^{III}–Fe^{III} distances (Table I), which are significantly shorter than the intradimer Fe–Fe distance.

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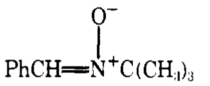
Spin Trapping of Adsorbed Hydrogen

Sir:

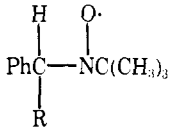
The spin trapping technique has been widely used to identify radical species produced in solution or the gas phase.[1] The method has not hitherto been applied to species adsorbed from the gas phase on solid catalyst surfaces. We report in this communication the scavenging of hydrogen adsorbed on zinc oxide by the spin trap *N-tert*-butyl-α-phenylnitrone (PBN, I).



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

I

PBN has been used to trap radicals produced during radiolysis of liquid hydrocarbons,[2] irradiation of gaseous CO–H_2 mixtures,[3] and electrolysis of water.[4] A radical R· will attack the α carbon of I to produce the stable radical II, and the nature of R· may be deduced from the EPR spectrum of II.



$$Ph\underset{\displaystyle \underset{R}{|}}{\overset{\displaystyle \overset{H}{|}}{C}}{-}\overset{\displaystyle \overset{O\cdot}{|}}{N}C(CH_3)_3$$

II

Zinc oxide samples (Kadox, 5 $m^2\ g^{-1}$) were outgassed in vacuo at 400 °C and then exposed to H_2 or D_2 at room temperature for 10 min. After brief evacuation, a solution of PBN in benzene (4×10^{-3} N) was added to the sample through a grease-free stopcock. In order to examine the adsorbed phase, the benzene was removed by evaporation and the solid sample transferred to an EPR tube. Alternatively, the solid sample was rinsed with benzene, and the filtrate collected and concentrated by partial evaporation of the solvent. Spectra were recorded at room temperature on a Varian E4 or E115 spectrometer at 9 GHz.

Figure 1 shows spectra obtained when PBN was adsorbed on ZnO containing preadsorbed H_2 (trace a) and D_2 (trace b). The spectra are poorly resolved, but show seven lines in the case of H_2 and six for D_2. Examination of the solution spectra ob-

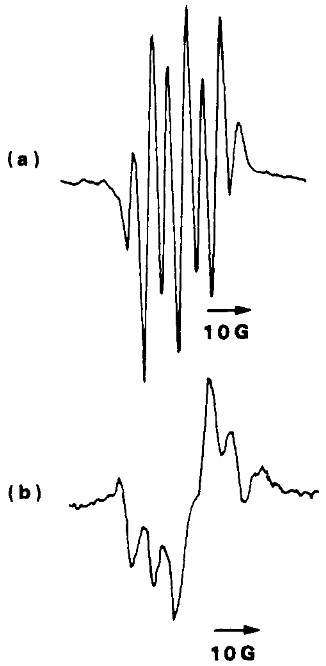


Figure 1. EPR spectra of ZnO containing (a) adsorbed H_2 and (b) adsorbed D_2 after adsorption of PBN from benzene solution.

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Table I. Hyperfine Coupling Constants for PBN Adducts (in gauss)

	A_N	A_H	A_D
H_2 or D_2 on ZnO	14.8	7.41	1.08
CO/H_2 irradiation[a]	15.0	7.5	
irradiation of liquid alkanes[b]	14.8	7.0	

[a] Reference 3. [b] Reference 2.

tained with the desorbed material permits the radical species to be identified (Figure 2). The spectrum obtained with adsorbed H_2 (trace a) is attributed to the addition of $H^{\cdot}$ to I; the hyperfine pattern consists of a 1:1:1 triplet due to ^{14}N, further split into 1:2:1 triplets due to two equivalent β protons. With D_2 (trace b), the addition product of $D^{\cdot}$ to I gives a triplet-doublet-triplet splitting pattern, with the smaller triplet due to the β deuteron.

Figure 2 (b) also shows small amounts of the hydrogen addition product and another unidentified radical which was not present if a non-hydrogen-containing solvent such as carbon tetrachloride was used. A sample of ZnO was exchanged with D_2O and then outgassed in the usual way. Adsorption of hydrogen on this sample gave a spectrum showing the hydrogen addition product with a very small contribution from the deuterium addition product.

Table I compares the hyperfine splitting constants that we have observed with those reported in the literature for the addition products of $H^{\cdot}$ and $D^{\cdot}$ to I. The solution spectra are certainly those of II with R = $H^{\cdot}$ or $D^{\cdot}$. The similarity of the adsorbed phase spectra to those from solution indicates that the addition products are formed on the ZnO surface by reaction of I with adsorbed hydrogen or deuterium.

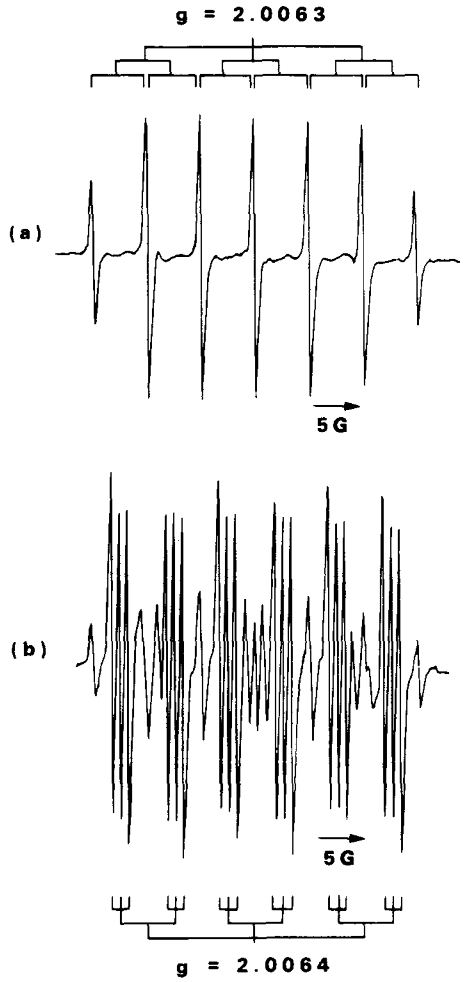

Figure 2. EPR solution spectra of PBN adducts desorbed from ZnO containing (a) adsorbed H_2 and (b) adsorbed D_2.

It has been shown by infrared spectroscopy that adsorption of H_2 on ZnO at room temperature involves a reversible dissociative chemisorption to form Zn-H and O-H species.[5,6] Our experiments indicate that hydrogen adsorbed on ZnO can be abstracted by PBN. Further experiments are needed to determine which hydrogen is abstracted and to determine the mechanism of abstraction. Trapping of the adsorbed hydrogen by PBN does not necessarily imply the presence of free hydrogen atoms on the ZnO surface, but does indicate that the reactivity of adsorbed hydrogen resembles that of hydrogen atoms produced in radiolysis[2] or electrolysis[4] experiments. The question of the extent of the radical character of hydrogen adsorbed on ZnO has still to be answered. Nevertheless, PBN is clearly a valuable spin trap to use in studying surface species having radical character. We envisage many systems of catalytic importance in which the presence of radical intermediates may be investigated by this technique.

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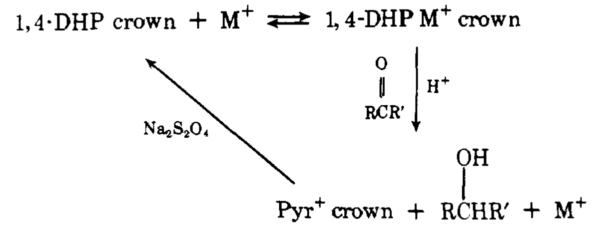
Asymmetric Reductions with a Chiral 1,4-Dihydropyridine Crown Ether[1]

Sir:

We are interested in the catalytic cycle shown in eq 1. A 1,4-dihydropyridine (DHP) is contained in a segment (for example a crown ether) capable of complexing a metal ion, M^+. The encapsulated M^+ then complexes with a carbonyl compound, forming a ternary complex in which the carbonyl group is activated toward hydride acceptance through its complexation to M^+.[2,3] The pyridinium salt (Pyr^+) formed on reduction of the carbonyl group is reduced back to 1,4-DHP with $Na_2S_2O_4$.[4] Such a cycle has attractive synthetic and biomimetic aspects,[5] especially if the 1,4-DHP-crown combination is chiral and is capable of carrying out reductions with a significant degree of asymmetric induction.[6] We report here the preliminary results of work intended toward the achievement of the above goals.[7]



(1)

The synthetic route to the desired 1,4-DHP-crown compounds is shown in Scheme I. Chiral starting materials were the *tert*-butyl esters of optically pure L-alanine (**2a**) and L-