BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1643—1644 (1975)

An ESR Study of Diborane Anion Radicals in the Adsorbed State

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(Received January 16, 1975)

Synopsis. The ESR spectra were examined for diborane anion radicals, $B_2H_6^-$, formed when diborane adsorbed on several kinds of adsorbents was irradiated with γ-rays at 77 K or diborane adsorbed at 77 K on adsorbents pre-irradiated with γ-rays at 77 K. The radicals in the adsorbed state were compared with those in an argon matrix, previously reported.

The ESR spectra of two kinds of radicals have been investigated in connection with diborane. When the solid of diborane was irradiated with γ-rays, the ESR spectrum of neutral diboranyl radicals formed by extracting one of the two bridging hydrogens of diborane was observed. The radical was investigated in detail by means of both ESR measurements with an irradiated single crystal of diborane[1] and theoretical calculations.[1,2] On the other hand, when an argon matrix containing diborane and sodium was irradiated with UV light at 4.2 K, an electron on the sodium atom was transferred to diborane and the ESR spectrum of diborane anion radicals was observed.[3] Kasai *et al.*[3] interpreted the anion radical as having a bridging structure with an unpaired electron in a b_{3g}orbital given by an antibonding combination of the 2p orbitals of the two borons perpendicular to the plane defined by the four terminal hydrogen atoms. However, Claxton *et al.*[4] recently proposed, on the basis of the results of *ab initio* UHF calculations, that the anion radical favors a staggered structure rather than the bridged D_{2h} structure of the parent molecule. They also said that the neutral diboranyl radical is presumably formed by proton loss from the cation radical of diborane,$B_2H_6^+$.

Several kinds of radicals have been revealed by ESR spectroscopy to be produced upon the irradiation of specimens adsorbed on the surfaces of solids; for example, cation radicals of benzene[5] and toluene,[6] anion radicals of O_2, CO_2, SO_2 and TCNE,[7] and neutral radicals from methane[8] and ethane[9] were observed on the surface of silica gel.

Thus, it may be of interest to investigate what kind of radical species is produced by the irradiation of diborane in such an adsorbed state.

Diborane, B_2H_6, and deuterodiborane, B_2D_6, were prepared by a method described elsewhere.[1] The silica gel, alumina, magnesium oxide, mordenite (HZ type), and zeolite (MgY type) used as the adsorbents for diborane were outgassed in a vaccum of 10^{-5} Torr at 550 °C for *ca.* 30 hr, while the adamantane was evacuated at room temperature for 1 hr. Diborane gas was introduced into ESR sample tubes containing these adsorbents through breakable seals at room temperature, except for the case of pre-irradiation, where the gas was introduced at 77 K. The irradiation with γ-rays was carried out at 77 K for 2 hr at a does rate of *ca.* 6×10^5 rad/hr from a ^{60}Co source, and the ESR spectra were measured at 77 K with an ESR spectrometer described elsewhere.[1]

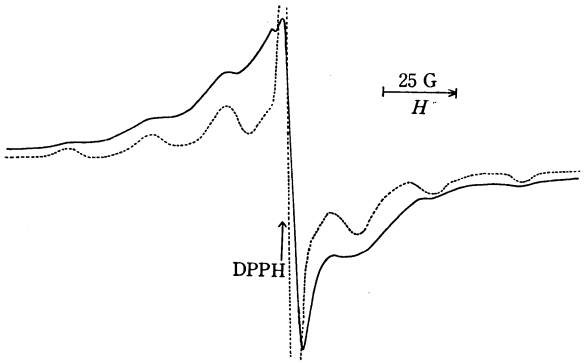

Fig. 1. ESR spectra of anion radicals of B_2H_6 (solid line) and B_2D_6 (dotted line) adsorbed on silica gel.

The ESR spectrum observed after the irradiation of diborane adsorbed on silica gel is shown in Fig. 1. The spectrum consists of a broad spectrum with seven peaks attributable to two equivalent boron atoms ($I=^3/_2$) and a spectrum of trapped electrons in the central region of the spectrum. These seven peaks could be explicitly distinguished when deuterodiborane was used, as is shown by a dotted line in Fig. 1. These observed spectra, except for that of the trapped electron, are very similar to those of the diborane anion radical, $B_2H_6^-$, and the deuterated anion radical, $B_2D_6^-$, observed in an argon matrix at 4.2 K,[3] while they are quite different from those of diboranyl radicals observed in the polycrystalline states of diborane and deuterodiborane.[1] No transformation of the observed spectrum to that of diboranyl radicals was detected during storage at 77 K under room light for several days.

In order to determine whether the cation radical or the anion radical was produced, the effect of the pre-irradiation on the radical production was investigated. The ESR spectrum of electrons trapped by defects in silica gel was observed with silica gel irradiated with γ-rays at 77 K. When diborane gas was adsorbed on the pre-irradiated silica gel, the intensity of the ESR spectral line of the trapped electrons was reduced; the same spectrum with seven peaks as that observed in the case of the post-irradiation appeared simultaneously. This observation may mean that the trapped electron on the surface silica gel is transferred to the diborane, which is well-known to be an electron-deficient molecule. The formation of the anion radical in the adsorbed state may be interpreted as arising from the electron transfer from the adsorbent to the diborane, as in the cases of the anion radicals of O_2, CO_2, SO_2, and TCNE adsorbed on silica gel.[7] Accordingly, it may be concluded that the anion radical was produced by the irradiation of diborane adsorbed on silica gel and by the adsorption of diborane

on pre-irradiated silica gel.

The ESR spectra of the anion radical of diborane in the adsorbed state were examined not only with adsorbents of metal oxides, alumina, magnesium oxide, mordenite, and zeolite, but also with the recently discovered organic adsorbent, adamantane.[10] All of the observed spectra of the anion radicals were interpreted by analogy with the analysis of the spectrum by Kasai and Mclood.[3] The parallel components of the hyperfine couling of the two boron atoms were easily determined from the spectra observed with deuterodiborane, whereas the perpendicular components for the two boron atoms and the proton coupling were not explicitly evaluated from the observed spectra. Accordingly, the parallel components for the boron atoms, $A_{//}(^{11}B)$, observed with different kinds of adsorbents were evaluated to be as follows:

Silica gel	25.0 *G*	Mordenite	25.4 *G*
Alumina	25.4 *G*	Zeolite	24.6 *G*
Magnesium oxide	24.7 *G*	Adamantane	19.0 *G*

Except for the case of adamantane, the parameters are in close agreement with that reported previously.[3] The value observed with adamantane is considerably smaller than those with the other adsorbents. For the anion radical in the argon matrix at 4.2 K, Kasai and Mclood.[3] gave these ESR parameters: $A_{//}$ (^{11}B) $=24.5\pm0.5$ *G*, $A_{\perp}$ (^{11}B) $=2.5$ *G* and $A(H)\leq 15$ *G*. Claxton *et al.*,[4] however, estimated the coupling of six hydrogens to be $A_{//}(H)=A_{\perp}(H)=7$ *G* by the use of a curve resolver. On the basis of a comparison between the estimated values of $a(^{11}B)$ and $a(H)$ and the results of their *ab initio* calculation, Claxton *et al.*[4] concluded that the anion radical of diborane has not a bridge structure, but a staggered conformation. Thus, the present authors attempted to observe the proton coupling directly by means of ENDOR.

The ENDOR spectra of the anion radical adsorbed on silica gel and adamantane were measured at 77 K with a JEOL type ES-EDX-1 spectrometer. Unfortunately, no ENDOR signal except for the ENDOR signals due to the electron trapped in the cavity of adamantane[11] was observed, in spite of careful measurements. Therefore, the attempt to check experimentally the proposed staggered conformation of the diborane anion radicals from proton couplings was unsuccessful, and the discussion of the structure of the anion radicals in the adsorbed state could not be advanced beyond the staggered conformation discussed by Claxton *et al.*[4] However, the small coupling of $A_{//}(^{11}B)$ observed with adamantane may suggest that some distortion of the staggered conformation arises from the existence of the radical in the cavity of a molecule of adamantane.

It may be mentioned that the method using an adsorbent is very much more convenient for producing the anion radicals of diborane compared with that using an inert gas matrix containing sodium at 4.2 K.[3]

The authors would like to express their gratitude to Professor Kazuhiko Ishizu of Ehime University for measuring the ENDOR spectra and to Professor Junkichi Sohma of Hokkaido University for his valuable discussions.

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