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ESR STUDY OF PHOSPHORANYL RADICALS OF PF_nH_{4-n} TYPE TRAPPED IN MATRICES

Kunihisa SOGABE, Akinori HASEGAWA, Tamikuni KOMATSU,
and Masaji MIURA
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Hiroshima 730

A series of phosphoranyl radicals of PF_nH_{4-n} type trapped in xenon and SF_6 matrices was investigated by ESR method. The isotropic hyperfine coupling of the phosphorus atom was found to decrease remarkably on the successive replacements of the ligand fluorine by hydrogen. This was interpreted in terms of the electronegativity difference between the fluorine and hydrogen atoms.

For the structure of phosphoranyl radicals, a distorted trigonal bipyramidal structure proposed by Higuchi[1) has so far been adopted. However, a regular trigonal bipyramidal structure, in which the unpaired electron occupied the Rundle three center nonbonding orbitals between the central phosphorus atom and the axial atoms, was reported to be suitable for the structure of phosphoranyl radicals in more recent ESR studies.[2-4) In such radicals, the isotropic hyperfine coupling of phosphorus atom tends to increase as the electronegativity of the ligand increases. However, no attempt has been made so far to observe a change in the isotropic hyperfine couplings of phosphorus atom produced by replacing systematically the ligands with ones having different electronegativity. The present authors intended to observe the ESR spectra of a series of phosphoranyl radicals of PF_nH_{4-n} type, which were brought about by the successive replacements of the most electronegative fluorine atom with a less electronegative hydrogen atom, and to discuss the ESR parameters in connection with the electronegativity of atoms.

Phosphine was prepared by the reaction of phosphorus trichloride and lithium aluminum hydride, while phosphine-d_3 was prepared by the use of lithium aluminum deuteride. Difluorophosphine and difluorophosphine-d_1 were produced by the reaction of difluoroiodophosphine, prepared by a conventional method, with hydrogen iodide and deuterium iodide, respectively. Trifluorophosphine was obtained from Stohler Isotope Chemicals. The matrices of xenon and SF_6 containing these specimens (ca. 1%) were frozen in Suprasil ESR sample tubes and irradiated at 77 K with γ-rays of ca. 6×10^5 R using a ^{60}Co source. ESR spectra measured at 77 K and/or 133 K.

ESR spectra observed with the γ-irradiated xenon matrices containing PH_3 and PD_3 are shown in Figs. 1 (a) and (b), respectively. The spectrum in Fig. 1 (a) was quite different from that assigned to PH_4 radical in a krypton matrix at 4.2 K by McDowell et al.$^{5)}$ and was reasonably assigned to a radical having a phosphorus nucleus with a coupling of 482 G and two equivalent hydrogen nuclei with couplings of 200 G. However, compared with results for the other radicals,$^{6-8)}$ the radical responsible for the spectrum was assigned not to phosphinyl radical,$^{8,9)}$ PH_2, but to phosphoranyl radical, PH_4^*, having two hydrogen atoms with large couplings in the axial positions and two hydrogen atoms with very small couplings in the equatorial positions of the trigonal bipyramidal structure. The value of 482 G evaluated for phosphorus atom is in fair agreement with that predicted by Ginns et al.$^{10)}$ The spin density in each of the axial hydrogen atoms was found to be ca. 0.39. This result positively proved that the unpaired electron occupies the Rundle three center nonbonding orbitals between the central phosphorus atom and the axial

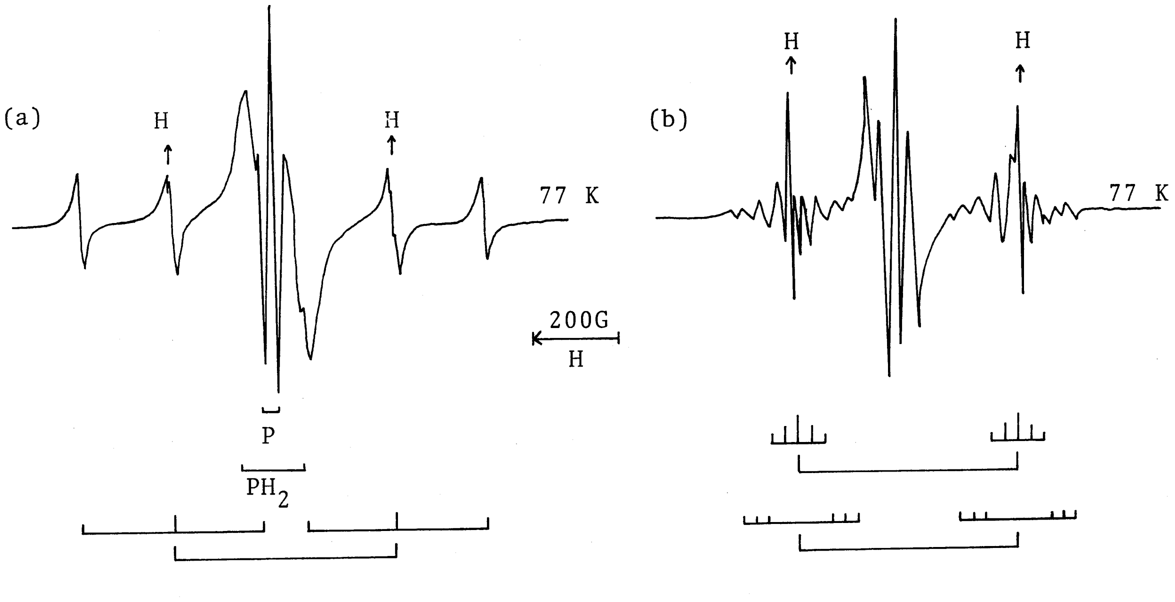

Fig. 1. ESR spectra of the γ-irradiated xenon matrices containing (a) PH_3 and (b) PD_3.

hydrogen atoms.

In this manner, PH_4, PF_2H_2, and PF_4 radicals were produced by γ-irradiation of xenon matrices containing PH_3, PF_2H, and PF_3, respectively, while PFH_3, PF_3H, and PF_4 radicals were also obtained for SF_6 matrices containing PH_3, PF_2H, and PF_3, respectively. All the radicals, except for the PF_4 radical, were identified for the first time in this study and their assignments were confirmed by using deuterated specimens. In these radicals, the atom once detached and then bound was found to occupy the axial position in the trigonal bipyramidal structure.

To discuss the correlation among the ESR parameters precisely, the isotropic hyperfine couplings of the central phosphorus atom and the axial fluorine and hydrogen atoms were plotted against the number of the hydrogen atoms in the phosphoranyl radicals. The regular relations were obtained, except for the PF_2H_2 radical, as shown in Fig. 2. The successive replacements of a fluorine atom in PF_4 radical by a hydrogen atom, irrespective of the axial or equatorial positions,

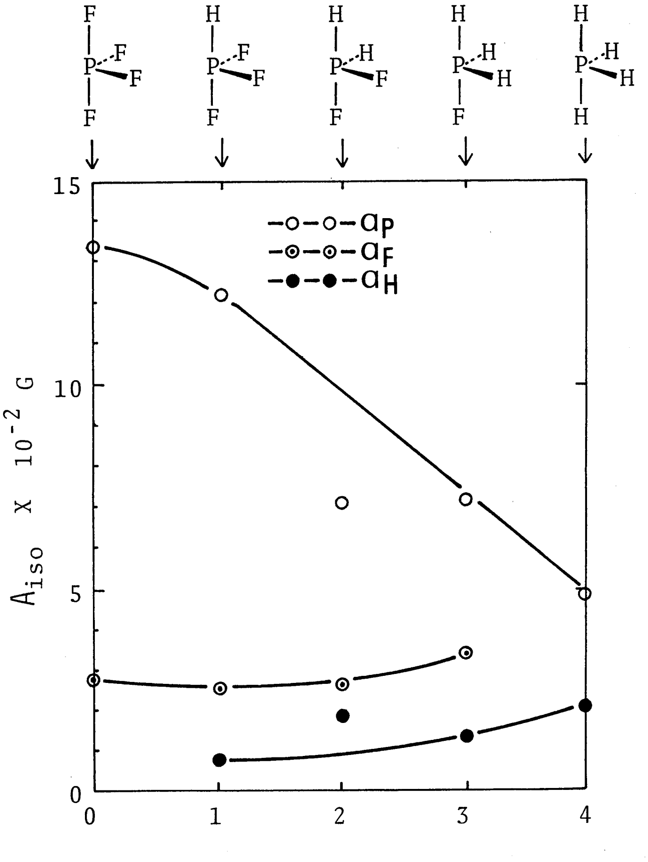

Fig. 2. The structure of phosphoranyl radicals of PF_nH_{4-n} type and the isotropic hyperfine couplings of the central phosphorus, the axial fluorine and the axial hydrogen atoms in these radicals.

cause a remarkable decrease in the coupling of the phosphorus atom. This change may be connected with the electronegativity difference between fluorine and hydrogen atoms.

The curve plotted for the isotropic hyperfine couplings of the phosphorus atom allows us to expect a value of ca. 950 G for the PF_2H_2 radical, whereas the value evaluated is 701 G. Any electronic interaction between the equatorial fluorine and hydrogen atoms expected from large difference in their electronegativities may weaken the bondings between the central phosphorus atom and the equatorial atoms, which results in an access of the axial atoms to the central phosphorus atom. Thus, a transfer of spin density occurs from the central phosphorus atom to the axial atoms. This accumulation of spin density in the axial atoms is proved by the observed hyperfine coupling of the axial hydrogen atom, which is superior to the value expected from the curve of the axial hydrogen couplings.

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* In more recently, the ESR spectra of PH_nD_{4-n} radicals were reported A. J. Colussi, J. R. Morton, and K. F. Preston, J. Chem. Phys., 62, 2004 (1975).

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