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Pressure Effect on the P-H and ^{13}C-H Spin-Spin Coupling Constants in Diphenylphosphine and Diphenylmethane-α-^{13}C in Chloroform

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Upon pressurization, $^{1}J_{P-H}$ in Ph_2HP has been found to increase notably, while $^{1}J_{^{13}C-H}$ in $Ph_2{}^{13}CH_2$ has been observed to remain nearly unaffected. An increased hydrogen bonding interaction between phosphorus lone pair electrons and chloroform is considered to be responsible to the pressure induced change in $^{1}J_{P-H}$.

Recent developments on the high-pressure high-resolution NMR technique have aroused an increasing interest as a new tool in high pressure chemistry.$^{1)}$ Main application of this technique have included studies of the effect of pressure on chemical exchange processes, relaxation of chemically shifted nuclei, and chemical shifts. It is surprising, however, that only few works have so far been done on the effect of pressure on the spin-spin coupling constant.$^{2,3)}$ This letter describes our findings in the pressure induced change in the coupling constants, $^{1}J_{P-H}$ and $^{1}J_{^{13}C-H}$, observed by use of a thermal expansion type high pressure NMR technique.$^{4)}$

A solution consisting of 16 mol% diphenylphosphine and 84 mol% chloroform was introduced into a high pressure cell. To avoid line broadening due to P-H proton exchange, very small amount of triethylamine was added. At present, we are unable to perform the sample instillment$^{4)}$ under an inert atmosphere, so that considerable amount (ca. 8 mol%) of diphenylphosphine was oxidized during this process and the solution was contaminated with diphenylphosphine oxide. However, contamination with the oxide proved to have only negligibly small effect on the magnitude of $^{1}J_{P-H}$. We thus decided to undergo the experiment using this same solution throughout the experiment. Diphenylmethane-α-^{13}C (90 atom%) was used as a 5 mol% solution in chloroform. The experimental procedure for the high-pressure NMR (ν_0=100 MHz, 35 °C) was the same as that described earlier.$^{4)}$ Since the pressure effect on the coupling constant is small, precise measurement of line positions was of primary importance. Line positions of P-H and ^{13}C-H doublet were measured with respect to side bands of the solvent chloroform produced by audio-frequency modulation of the oscillator. The precision of ±0.07 Hz was generally achieved.

Figure 1 shows the pressure dependence of $^{1}J_{P-H}$, which is evidently increased by the application of hydrostatic pressure. This result stands in contrast to the observation in diphenylmethane, in which $^{1}J_{^{13}C-H}$ is found to be almost unaffected,

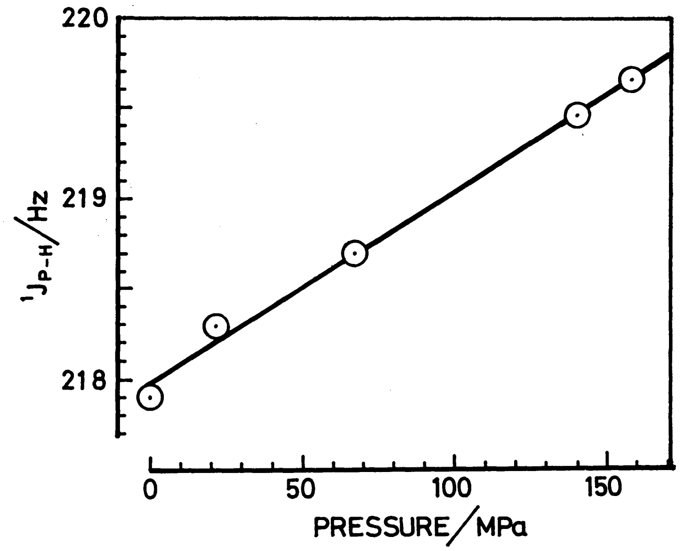

Fig. 1. Pressure induced change in the P-H spin-spin coupling constant.

i.e., an increase by 0.1 Hz upon pressurization up to 150 MPa. Pressure effect on the coupling constant is considered to arise from a pressure induced variation of solvent effect, which can be divided into three main contributions;[5)] (i) density dependence, (ii) electrostatic interaction, and (iii) specific association effect such as hydrogen bonding. Observed insensitivity of $^1J_{^{13}C-H}$ to the pressurization, however, suggests that the effect (i) should be very small.[2)] Thus, the pronounced pressure dependence of $^1J_{P-H}$ has to be mainly interpreted on the basis of effects (ii) and (iii). In particular, an important contribution is considered to arise from a hydrogen bonding of the type (II),

$$\underset{\text{(I)}}{Ph_2HP\text{:}} + HCl_3 \rightleftharpoons \underset{\text{(II)}}{Ph_2HP\text{:}\cdots\cdots HCCl_3} \qquad (1)$$

which, being intensified by pressurization, leads to an increase in s-character in the P-H bonding orbital,[6)] thereby gives rise to the increased $^1J_{P-H}$. Pressure induced displacement, (I)$\rightarrow$(II), of the rapid equilibrium (1) may also produce an increase in the time averaged $^1J_{P-H}$. Some evidence for these interpretations may be provided by studies on the solvent dependence of $^1J_{P-H}$. For example, phosphine was shown to give a high $^1J_{P-H}$ value[7)] in chloroform, which was interpreted as being caused by the hydrogen bonding effect.[6)] A high pressure experiment using aprotic solvents, as well as a study on the concentration dependence at high pressure is required to provide a better understanding of the present observation.

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7) It was found that $^1J_{P-H}$ in diphenylphosphine and $^1J_{^{13}C-H}$ in diphenylmethane increased by 2.3 Hz and by 0.3 Hz, respectively, upon changing the solvent from benzene to chloroform.

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