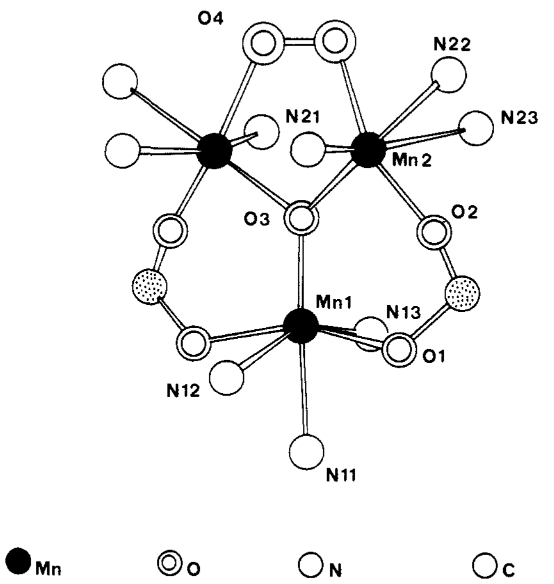

**Figure 2.** Structure of **2** showing the atomic numbering system used. Carbon atoms of the dien ligand and the methyl carbons of the acetato groups are not shown.

dien complex is apparently reversible as heating methanol solutions of **1** in a stream of nitrogen results in the disappearance of the brown color. Upon cooling the brown color of the solution is restored. This behavior could be due to oxidation of the methanol followed by regeneration of the complex in air and suggests that the complex may be a useful oxidation catalyst.[26]

Addition of small amounts of concentrated hydrochloric acid to a methanol solution of **1** results in the formation of deep red crystals formulated as $Mn_3(dien)_2(OAc)_2Cl(ClO_4)_2O_2 \cdot CH_3OH$.[27] The Raman spectrum of this complex shows no O–O stretching frequency, and the X-band EPR spectrum of the material is indicative of a complex containing Mn(II). The spectrum is very similar to the spectrum of a 2Mn(III)·Mn(II) complex described recently by Pecoraro.[11] The photosynthetic oxygen evolving complex has a chloride ion requirement so the structure of this material would be of considerable interest. We are attempting to obtain crystals suitable for structural analysis.

In summary, we have shown the polyamine dien can coordinate to Mn(III) without undergoing oxidation and that the complex isolated by using this ligand is a stable $\mu$-peroxy complex. This complex provides the first model for the binding of dioxygen to a manganese cluster in the photosynthetic oxygen evolving system, and the ease with which the peroxo group is oxidized in acidic solutions suggests a possible mechanism for oxygen release in photosynthesis.

The properties of these complexes and complexes produced by using the amines 2,3-tri, triethylenetriamine, 2,3,2-tet, 3,2,3-tet, and tren are under active investigation in this laboratory. It should be mentioned that the complex we have obtained by using the tren ligand is different from the complex described by Armstrong.[10]

**Acknowledgment.** The assistance of the Internal Research Committee of Victoria University is gratefully acknowledged. We are also grateful to Dr. E. Ainscough for assistance acquiring the EPR spectra, Joanne Rollo for assistance with the Raman spectra, and Dr. Ward T. Robinson for the collection of the X-ray data set.

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(27) Anal. Calcd for $C_{13}H_{36}N_6Cl_3O_{15}Mn_3$: C, 19.83; H, 4.58; N, 10.67; Cl, 13.51; Mn, 20.93. Found: C, 19.59; H, 4.71; N, 10.62; Cl, 13.67; Mn, 21.04.

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# Effect of Pressure on the Proton–Proton Vicinal Coupling Constants in 1,1,2-Trichloroethane and 1,1,2,2-Tetrachloroethane-*1*-$^{13}C$. A New Approach to High-Pressure Study of Molecular Conformations

H. Yamada,* T. Kazuoka, and A. Sera

*Department of Chemistry, Faculty of Science*
*Kobe University, Nada-ku, Kobe 657, Japan*

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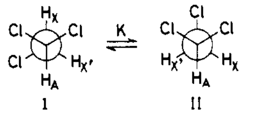
We report here the first observation of a pressure-induced change in $J_{vic}$ and demonstrate that the experiment possibly provides a new, straightforward approach to conformation studies at high pressure.[1]

Our choice of title compounds[2] was governed by the availability of quantitative information of the NMR parameters characteristic of the trans and gauche conformers,[3,4] as well as by the simplicity of the proton spectra. Use of $J_{vic}$ in the conformational study requires extremely precise measurement of doublet separations.[5] We employed a linear sweep rate of 108 Hz/250 s in a continuous wave mode ($\nu_0$ = 100 MHz), while the field control was effected by means of an internal NMR lock.[6]

Figure 1 shows the pressure dependence of $J_{vic}$ in trichloroethane, which exhibits a small but steady decrease upon increase in pressure.[7] The observed coupling constant, $J_{vic}$, can be expressed in terms of the weighted mean of the coupling constants in the trans and gauche isomers,[8] i.e.



$$J_{vic} = n_I J_I + (1 - n_I) J_{II} \qquad (1)^9$$

Since $J_I > J_{II}$ holds generally,[5] the decrease in $J_{vic}$ demonstrates that the population of the gauche conformer II increases at high pressure. This agrees qualitatively with the observation of Christian et al. based on a high-pressure IR experiment.[12] This is also in accord with the general view that high pressure favors more polar conformers.

In order to provide quantitative understanding, it is necessary to use in eq 1 a reasonably consistent set of $J_I$ and $J_{II}$ values. Employing the Karplus-type eq 2,[13] with $A$ = 11.1 Hz and $B$ =

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(1) For reviews of high-pressure high-resolution NMR, see: Ando, I.; Webb, G. A. *Magn. Reson. Chem.* **1986**, *24*, 557. For the experimental technique employed, see: Yamada, H. *Rev. Sci. Instrum.* **1974**, *45*, 640.

(2) $^{13}C$-Enriched sample was prepared by chlorination of ethyne-*1*-$^{13}C$, which was synthesized from $Ba^{13}CO_3$ via ethene-*1*-$^{13}C$.

(3) Chen, J. S.; Shirts, R. B.; Lin, W. C. *J. Phys. Chem.* **1986**, *90*, 4970.

(4) Gutowsky, H. S.; Belford, G. G.; McMahon, P. E. *J. Chem. Phys.* **1962**, *36*, 3353.

(5) For example, see ref 4.

(6) At least 10 measurements were made at a given pressure. Reproducibility better than ±0.03 Hz was generally attained.

(7) A 50 mol % solution gave a smaller pressure dependence, i.e., −0.13–0.16 Hz/300 MPa.

(8) Theoretically, conformers with any dihedral angle should be taken into account and weighted statistically.[3] In the present discussion, however, only the discrete stable conformers have been postulated as a first approximation.

(9) A basic assumption of this type of treatment is that $J_I$ and $J_{II}$ are pressure-independent. Evidence in support of this assumption can be obtained from an examination of $J_{vic}$ in the "rigid" molecule such as 1,1-dichloroethane, for which the pressure-induced change in $J_{vic}$ proved to be less than ±0.03 Hz. An observed constancy (±0.02 Hz) of $J_{vic}$ in a "rigid" system,[10,11] upon changing the solvents ($\epsilon$ = 2–35), may be taken as further confirmation for the assumption.

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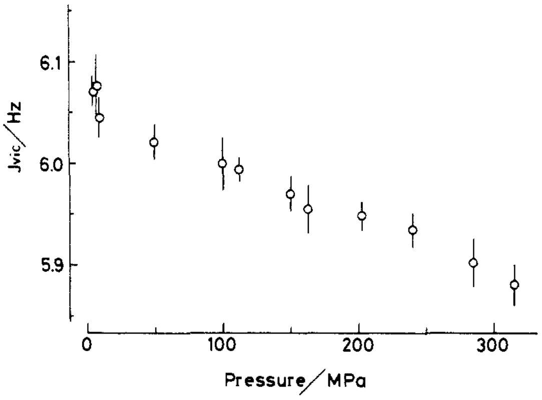

**Figure 1.** Pressure effect on $J_{vic}$ in 1,1,2-trichloroethane containing 10 mol % cyclopentane as an internal reference, at 45 °C.

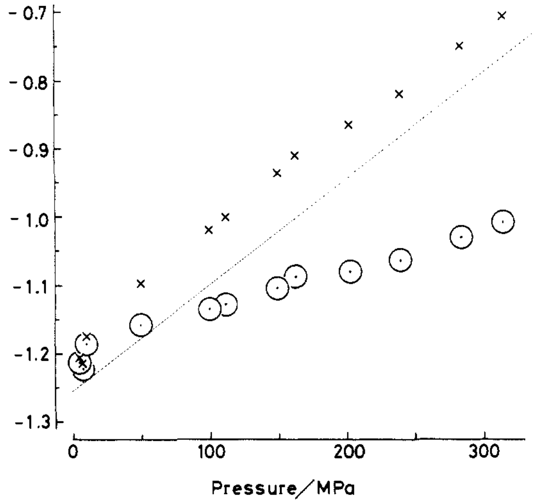

**Figure 2.** Pressure effect on ln $K$ for 1,1,2-trichloroethane at 45 °C. Open circles refer to uncorrected data. Crosses refer to "distortion"-corrected data, calculated by using $K = (J_I + (1.5 \times 10^{-3})P - J_{vic})/(J_{vic} - J_{II})$. The dotted line depicts the result of a high-pressure IR experiment at 45 °C.[12]

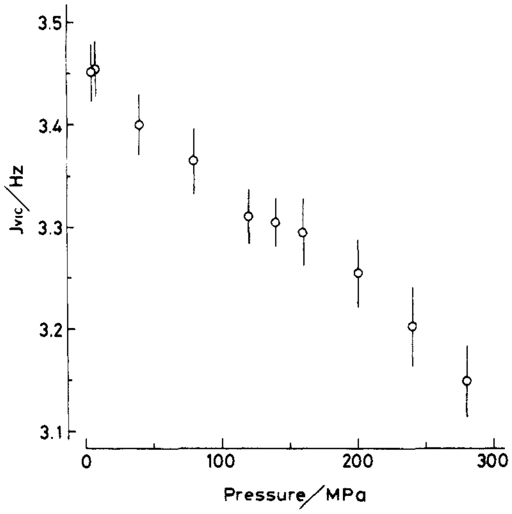

**Figure 3.** Pressure effect on $J_{vic}$ in 1,1,2,2-tetrachloroethane-*1*-$^{13}C$ containing 50 mol % cyclopentane, at 45 °C.

0.1,[3] we obtain $J_I$ = 7.22 Hz and $J_{II}$ = 2.22 Hz, thereby the equilibrium constant is given by (3).

$$J_\phi = A(\cos^2 \phi - B \cos \phi) \qquad (2)$$

$$K = (J_I - J_{vic})/(J_{vic} - J_{II}) \qquad (3)$$

In Figure 2, the pressure dependence of ln $K$ is depicted by open circles. The data can be fitted to the equation $\Delta V = -RT \ln (K/K_0)/(P - P_0)$, where $\Delta V$ represents the volume change for conversion of I into II, $\Delta V \equiv V_{II} - V_I$. The linear approximation gives $\Delta V = -1.7$ cm$^3$ mol$^{-1}$. The result demonstrates that the partial volume of II is indeed smaller than that of I. However, it is noted that our $\Delta V$ value is too small (less negative) as compared with those obtained by high-pressure IR and Raman studies. For example, Christian et al.[12] obtained $\Delta V = -3.8$ cm$^3$ mol$^{-1}$ for 1,1,2-trichloroethane (neat sample) and Taniguchi et al.[14] reported $\Delta V = -3.8$ cm$^3$ mol$^{-1}$ for 1,2-dichloroethane (20 mol % in hexane). One possible explanation for the disagreement is that the structure of the **individual** conformer may distort upon pressurization. This possibility has been pointed out by Taniguchi et al. in their high-pressure Raman studies on the trans-gauche equilibrium of 1,2-dichloroethane.[15] It is proposed that the distortion in the direction of the eclipsed structure takes place at the rate of ca. 2 deg/100 MPa. Higher polarity of the eclipsed structure, as well as the overlap of Cl atoms, and the packing of the molecule in the solution are thought to be responsible for the distortion. It seems likely that a similar distortion takes place for I upon pressurization, so that the molecule attains a higher polarity and a smaller molar volume. Thereby a decrease in the dihedral angles, $\phi(H_A\text{-}C\text{-}C\text{-}H_X)$ and $\phi(H_A\text{-}C\text{-}C\text{-}H_{X'})$ should give rise to some change in $J_I$. Using (2), we obtain $(\partial/\partial\phi)J_{\phi\approx60°} \approx -0.15$ Hz deg$^{-1}$ and $(\partial/\partial\phi)J_{\phi\approx180°} \approx 0$ Hz deg$^{-1}$. Assuming a distortion rate of $-2$ deg/100 MPa[16] for I, we calculate $(\partial/\partial P)J_I \approx +0.15$ Hz/100 MPa, a positive increment in $J_I$ caused by pressurization. For II, the distortion is considered to be smaller since the accompanying polarity change is smaller. The distortion, if any, produces the increments in $J_{II}$ with opposite signs, which should cancel each other. On the basis of the above consideration, a correction for the pressure-induced distortion has been made and the equilibrium constants have been re-calculated. The result is shown by crosses in Figure 2, which gives $\Delta V = -3.8$ to 4.0 cm$^3$ mol$^{-1}$. The agreement with the high-pressure IR data (dotted line in Figure 2) is quite satisfactory. However, in view of the approximations employed in the present discussion, this agreement may be *partly* coincidental.

1,1,2,2-Tetrachloroethane-*1*-$^{13}C$ was examined in cyclopentane in 50 mol % concentration.[17] Since trans (III) → gauche (IV) transformation accompanies a polarity change greater than for I → II, the pressure dependence of $K$ was expected to be more pronounced. Figure 3 shows the pressure-induced change in $J_{vic}$, where a noticeable pressure effect can be seen, as expected. Employing an equation similar to (3), with $J_{III}$ = 16.35 Hz and $J_{IV}$ = 2.01 Hz,[4] we obtain $\Delta V = -2.4$ cm$^3$ mol$^{-1}$, where the calculation has been made without correcting for the pressure-induced distortion. For III, the distortion effect on $J_{III}$ can be neglected since $(\partial/\partial\phi)J_{\phi\approx180°} \approx 0$. In VI, the distortion would be more restricted than in trichloroethane because of overcrowding by four Cl atoms. Furthermore, an increase in polarity brought about by distorting IV would be smaller. In this respect, it seems improbable that as much distortion takes place in IV as in trichloroethane. While lack of adequate knowledge about the distortion thus prevents us from obtaining an accurate reading of $\Delta V$ for tetrachloroethane, there can be little doubt about the qualitative conclusion that $\Delta V$ cannot be less negative than $-2.4$ cm$^3$ mol$^{-1}$ for a 50 mol % solution. This is because the distortion of IV produces a positive increment in $J_{IV}$, which always leads to a negative increment in $\Delta V$.

**Acknowledgment.** Financial support for this study was provided by the Itoh Science Foundation and by Grant-in-Aid for Scientific Research (No. 56550572) from the Ministry of Education, Japan.

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[14] Taniguchi, Y.; Takaya, H.; Wong, P. T. T.; Whalley, E. *J. Chem. Phys.* **1981**, *75*, 4815.

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[16] Because of a similarity between the gauche Cl–C–C–Cl moiety of I and that of gauche dichloroethane, the same magnitude of the distortion rate is postulated.

[17] Higher concentration leads to broadened spectra because of the increase in viscosity at high pressure. The 50 mol % represents the effective limit of sensitivity in our high-pressure cell in order to attain a sufficient S/N in the satellite signal.