change the shape or relative positions of the curves in Figure 1 to any significant extent.

Effect of Each Solvent Component on the Rate of Radical Formation. 2-Propanol. To 10 mL of stock solution was added 0.33 mL of water. To 2-mL samples of this solution were added quantities of 2-propanol so that ratios of base to alcohol of 1:1 (0.015 mL of 2-propanol), 1:3 (0.045 mL), 1:5 (0.09 mL), and 1:10 (0.15 mL) were obtained. The results appear as curve A in Figure 1. The concentration of **1** varied between 0.097 and 0.090 M in this series.

H_2O. The effect of water concentration was determined with 10 mL of stock solution to which 0.75 mL of 2-propanol was added. Two-milliliter samples were taken and water added to each so that the molar concentrations of water were 0, 0.28 (0.01 mL of H_2O), 0.82 (0.03 mL), 1.35 (0.05 mL), and 1.86 (0.07 mL). The concentration of **1** varied between 0.093 and 0.090 over this range. The results are shown in Figure 1, curve B.

Hydrochloric Acid. The effect of hydrochloric acid was examined by first preparing a solution composed of 20 mL of stock solution, 1.5 mL of 2-propanol, and 0.66 mL of water. Two-milliliter samples were prepared with acid concentrations of 0.96×10^{-2}, 1.94×10^{-2}, 4.75×10^{-2}, 9.38×10^{-2}, 18.2×10^{-2}, 26.5×10^{-2}, and 37.1×10^{-2} M. The 2-propanol concentration was maintained at 0.87 ± 0.01 M, while the concentration of **1** varied between 0.090 and 0.087 M.

Piperylene. The effect of piperylene was determined with a 9.2×10^{-2} M solution of 2,4-pyridinedicarbonitrile in a solution composed of 30.8 mL of acetonitrile, 2.30 mL of 2-propanol, and 1.0 mL of water. Three solutions were prepared which contained 1.0×10^{-2}, 2.0×10^{-2}, and 9.9×10^{-2} M concentrations of piperylene. Samples were then run as described above. The highest concentration of piperylene which contained a 1:1 molar ratio of base to quencher showed essentially complete quenching of radical formation. Even the solution containing the lowest concentration of piperylene showed over 80% quenching.

Benzophenone. The effect of benzophenone was determined with a 0.047 M solution of **1** in 13/1 acetonitrile/2-propanol. Samples were prepared by taking 2-mL portions and adding aliquots of a 0.27 M solution of benzophenone in the same solvent. The molar ratio of **1**/benzophenone in each sample is as follows: 0.047:0.0041, 0.045:0.0080, 0.045:0.012, and 0.041:0.036. The results appear as curve D in Figure 1.[13]

Acknowledgment. We thank Dr. Nicholas Turro for the excitation spectra, Drs. Philip and Anne Rieger for their help with ESR and spin density measurements, Dr. Loris Grossi for his helpful discussions on ESR, Dr. Heinz Roth for the CIDNP experiments, Dr. George Kavarnos for his helpful discussions on electron transfer, and Donald Sears for his technical assistance.

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(13) When a $CuSO_4$ filter solution is used and most of the light is absorbed by benzophenone, the pyridinyl radical is observed immediately.

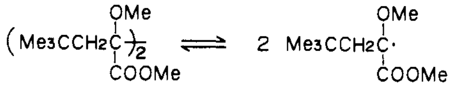
Observation by ESR of an Acrylate Radical Conformationally Locked by Complexation with $SnCl_4$

Hitoshi Tanaka,* Itsuo Sakai, and Tadatoshi Ota

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Tokushima University, Minamijosanjima, Tokushima 770, Japan. *Received June 26, 1985*

Abstract: The variation of conformational and electronic structures of 3,3-dimethyl-1-methoxy-1-(methoxycarbonyl)butyl radical by complexation with $SnCl_4$ was studied in chlorobenzene at various temperatures (5–130 °C) by means of ESR spectroscopy. The addition of equimolar amounts of $SnCl_4$ to the dimer reduced the standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) for the dimer $\rightleftharpoons$ radical equilibrium from 41.4 to 12.1 kcal/mol and from 49.2 to −6.7 cal/mol·deg at 25 °C, respectively. The ESR spectrum at 23 °C indicated a twisted conformation of the radical and trigonal bipyramid structure of $SnCl_4$ by complexation. These results were also supported by the ESR study on a deuterated compound.

Selectivity and rate are often influenced by the addition of a metal salt in reactions involving carbon-centered free radicals. Not only rate acceleration but also an increase in regioselectivity, higher regulation of polymer sequencies, and high retention of configuration have already been reported for metal-assisted Diels–Alder reactions[1] and radical polymerizations[2] as well as the formation of Grignard reagents.[3] These reactions have been explored as to mechanism as well as application, and the intermediacy of a complexed radical with restricted rotation has been assumed in certain cases. But as yet, little direct evidence has been obtained. In this paper we wish to report a twisted conformation for **2** coordinated with $SnCl_4$ in which $SnCl_4$ has a trigonal bipyramid structure.



$$(\mathrm{Me_3CCH_2}\overset{\mathrm{OMe}}{\underset{\mathrm{COOMe}}{\mathrm{C}}})_2 \rightleftharpoons 2\ \mathrm{Me_3CCH_2}\overset{\mathrm{OMe}}{\underset{\mathrm{COOMe}}{\mathrm{C}}}\cdot$$

1 2

Experimental Section

Materials. A mixture of methyl 2-methoxyacrylate[4] (3.00 g, 25.9 mmol) and 2,2′-azobis[2-methylpropane] (5.50 g, 38.7 mmol) in benzene (7.00 mL) was irradiated with a 100-W high-pressure mercury lamp for 1 day at ambient temperature. After removal of benzene, the mixture was diluted with methanol (10.0 mL) and cooled to 0 °C to afford a colorless solid. Recrystallization of the solid from methanol gave white needles (1.80 g, 40% yield based on methyl 2-methoxyacrylate) of **1**. Furthermore, liquid product (1.75 g, 39%) of **1** was also isolated from the residue by thin-layer chromatography. The needles and the liquid were assigned to the racemic and meso forms of **1**, respectively, on the

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(1) (a) Lutz, E. F.; Bailey, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 3899. (b) Bednarski, M.; Danishefsky, S. *Ibid.* **1983**, *105*, 3716. (c) Inukai, T.; Kojima, T. *J. Org. Chem.* **1971**, *36*, 924. (d) Belanger, J.; Landry, N. T.; Pare, R. J.; Jankowski, K. *Ibid.* **1982**, *47*, 3649.

(2) (a) Kavanov, V. A. *J. Polymn. Sci., Polym. Symp.* **1980**, *No. 67*, 17. (b) Hirooka, M. *Pure Appl. Chem.* **1981**, *53*, 681. (c) Hirai, H.; Takeuchi, K.; Komiyama, M. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 901.

(3) (a) Maruyama, K. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 897. (b) Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59. (c) Buske, G. R.; Ford, W. T. *J. Org. Chem.* **1976**, *41*, 1998.

(4) Ogata, N.; Nozakura, S.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2987.

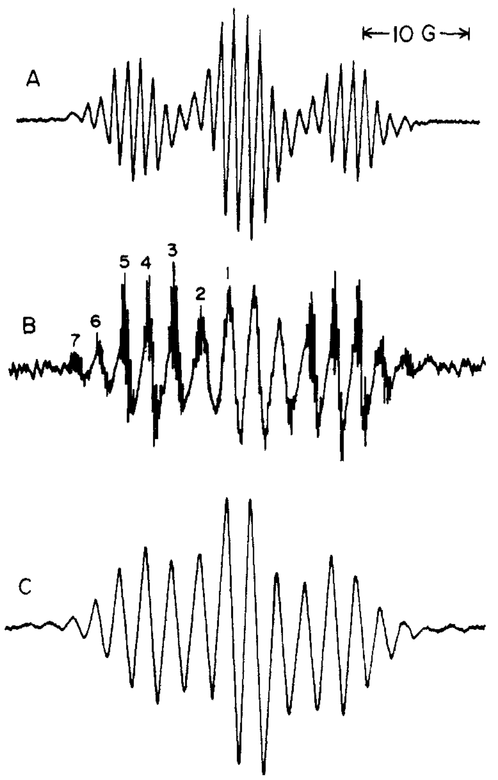

Figure 1. Experimental ESR spectra of **2** in the absence (A) and presence (B and C) of SnCl$_4$ in chlorobenzene at 23 °C. Microwave power 3 (A) and 0.2 mW (B and C); modulation amplitude 0.5 G (A), 0.1 G (B), and 1 G (C).

bases of the NMR spectra and thermal interconversion from meso form to racemate. Racemate was employed in our experiment: mp 86.5–87.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.93 (s, 18 H), 1.88 (d, J = 15 Hz, 1 H), 2.28 (d, J = 15 Hz, 1 H), 3.64 (s, 6 H), 3.73 (s, 6 H); ^{13}C NMR (22.6 MHz, CDCl$_3$) δ 30.92 (q), 31.11 (s), 44.59 (t), 51.47 (q), 54.55 (q), 88.80 (s), 172.73 (s). Anal. Calcd for $C_{18}H_{34}O_6$: C, 62.40; H, 9.89. Found: C, 62.26; H, 9.78.

Deuterated **1** was prepared by using methyl-deuterated methyl 2-methoxyacrylate, which was synthesized according to the literature[4] except that CD_3OD was used instead of CH_3OH. The isotopic purity of this product was determined to be 95.1% by means of ^{1}H NMR spectroscopy. Anhydrous SnCl$_4$ (Wako Chemical Co.) was distilled on phosphorus pentoxide prior to use. ZnCl$_2$ (Alfa) was anhydrous ultrapure reagent grade, other Lewis acids (Aldrich) were also commercially available products, and they were used as supplied.

Measurements. The dimer (1.00 M) in chlorobenzene in an ESR cell was degassed by the freezing and thawing technique and finally filled with helium gas. When Lewis acid was used, it was introduced to the predegassed dimer solution in a drybox. ESR spectra were recorded on a JEOL JES-FE2XG spectrometer operating at X band (9.5 GHz) with a TE mode cavity. Integration and simulation of the ESR signal were carried out by using the JEOL ES-9835B computer data system. The temperatures of the ESR cavity were controlled by a JEOL ES-DVT1 controller, and they were corrected with a standard thermometer. Splitting constant a and g value were determined by comparison with those of Fremy's salt (a = 13.09 G, g = 2.0055)[5] in K$_2$CO$_3$ aqueous solution.

The equilibrium constants (K) were determined from the measurements of radical concentrations in chlorobenzene by means of ESR spectroscopy standardized with 1,3,5-triphenylverdazyl (purity 99.7% by UV spectroscopy) and Mn^{2+} at given temperatures. Calibration curves with verdazyl were obtained under the same conditions as used for the dimer solutions, i.e., same solvent, temperature, ESR cell, and instrument settings. Mn^{2+} was simultaneously employed with our samples or standard sample in the same ESR cavity to check the change of experimental conditions, such as Q value.

^{1}H and ^{13}C NMR spectra were obtained from a JEOL GX-400 (400 MHz) and Hitachi R-42FT (22.6 MHz) NMR spectrometers, respectively, in CDCl$_3$ at ambient temperature (23 ± 2 °C). The chemical shifts were referenced to internal tetramethylsilane.

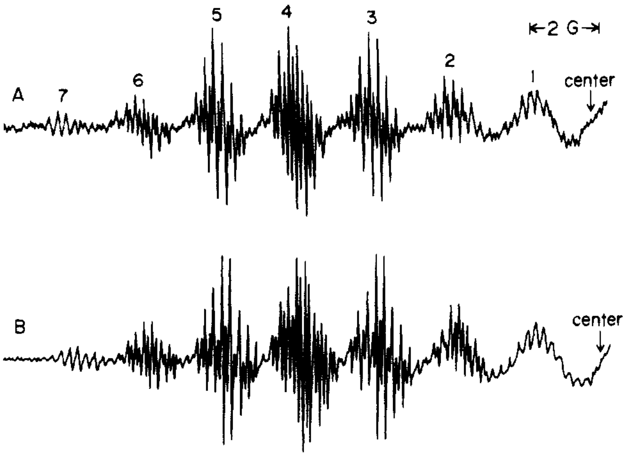

Figure 2. Expanded experimental (A) and simulated (B) ESR spectra of the seven lines numerically indicated in Figure 1B. Microwave power 0.2 mW; modulation amplitude 0.05 G.

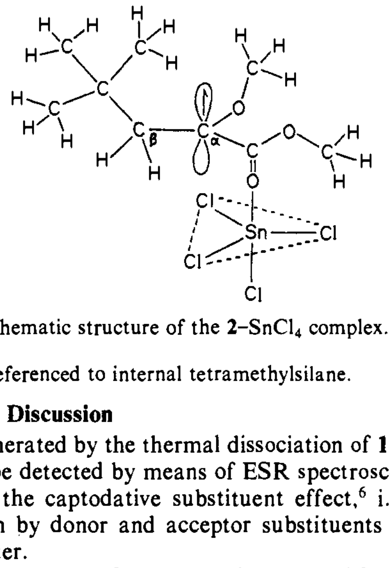

Figure 3. Schematic structure of the **2**–SnCl$_4$ complex.

Results and Discussion

2 was generated by the thermal dissociation of **1** and is stable enough to be detected by means of ESR spectroscopy, possibly because of the captodative substituent effect,[6] i.e., enhanced stabilization by donor and acceptor substituents on the same radical center.

Figure 1 shows the ESR spectra of the radical **2** in the presence and absence of SnCl$_4$, [**1**] = [SnCl$_4$] = 1.00 M. The ESR spectrum of the uncomplexed radical **2** (Figure 1A) exhibits splitting by two equivalent β-H's (CH$_2$), $a_{\beta\text{-H}}$ = 9.31 G, three equivalent γ-H's (OMe), $a_{\gamma\text{-H}}$ = 2.65 G, and three equivalent δ-H's (COOMe), $a_{\delta\text{-H}}$ = 1.20 G, g = 2.0037.[7] When SnCl$_4$ is added to the dimer solution, the spectrum of radical **2** changes greatly, as can be seen in Figure 1B. It is clear that the complexed radical mainly consists of 18 lines (Figure 1C) and the wings of the spectrum split further into a number of sharp lines (Figure 1B). An expanded spectrum of the seven lines numerically indicated in Figure 1B is shown in Figure 2A. For the complexed radical **2**, ESR parameters that are supported by the spectrum simulation (Figure 2B) are $a_{\beta\text{-H}}$ = 7.46 and 10.30 G, $a_{\gamma\text{-H}}$ = 2.39 G, $a_{\delta\text{-H}}$ = 2.27 G, and a_{Sn} = 8.16 G[8] and a couple of decuplet splitting by three equivalent ^{35}Cl and ^{37}Cl nuclei, $a_{^{35}\text{Cl}}$ = 0.25 and $a_{^{37}\text{Cl}}$ = 0.21 G.[9]

The large a_{Sn} value indicates significant spin density on the Sn atom in spite of its δ position with respect to the radical center,

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[5] Fischer, H., Hellwege, K.-H., Ed. *Landholt—Boernstein New Series*; Springer-Verlag: Berlin, 1977–1979; Group II, Vol. 9.

[6] Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

[7] At 23 °C, **1** does not dissociate to **2** in the absence of SnCl$_4$, so uncomplexed radical **2** was generated by the photoreaction of methyl 2-methoxyacrylate (2 M) and 2,2′-azobis[2-methylpropane] (1.2 M). Thus obtained ESR spectrum is close to that obtained by the dissociation of **1** at 127 °C.

[8] Natural abundances of ^{115}Sn, ^{117}Sn, and ^{119}Sn are 0.35, 7.67, and 8.68% (I = $^1/_2$), respectively, and the ^{117}Sn/^{119}Sn ratio of magnetic moments is 0.9558. Thus the observed a_{Sn} is an apparent value since the splittings by the Sn nuclei are indistinguishable in the broad line spectrum.

[9] Natural abundances of ^{35}Cl and ^{37}Cl are 75.4 and 24.6% (I = $^3/_2$), respectively and the ^{35}Cl/^{37}Cl ratio of magnetic moments is 1.201.

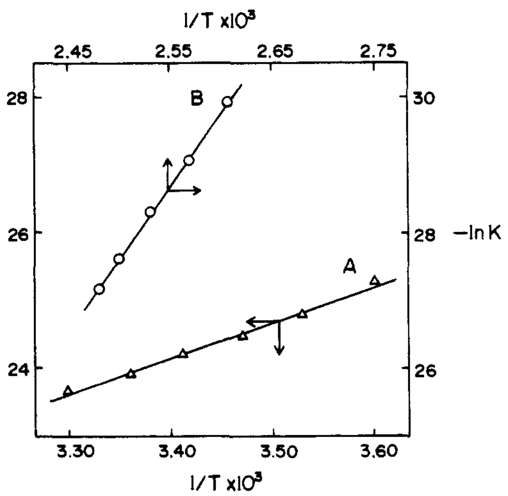

Figure 4. Plots of ln K vs. $1/T$ for the **1** $\rightleftharpoons$ **2** equilibrium in the presence (A) and absence (B) of $SnCl_4$.

which implies the formation of a tight complex. This is in contrast to complexed radicals such as $Me_2(CN)CCH_2\dot{C}(CN)SEt-SnCl_4$,[10] $Me_3CCH_2\dot{C}(CN)SEt-SnCl_4$,[11] $Me_2\dot{C}CN-AlMe_3$,[12] and $Me_2\dot{C}COOMe-AlMe_3$,[12] which possess either a negligible splitting by the Sn nuclei or a very small splitting by the Al nucleus of 0.49 and 1.70 G. Moreover, the participation of three equivalent Cl nuclei in the complex formation strongly suggests that the structure of $SnCl_4$ should be trigonal bipyramid, not octahedron. Its structure is represented in Figure 3.

It is worth noting that the δ proton hyperfine splitting is markedly influenced by complexation in contrast with the γ proton. Accordingly, $SnCl_4$ brings about a spin polarization rather than a spin delocalization of the radical, which may also lead to an electronic repulsion between complexed radicals and results in the increase in the equilibrium constant, as will be mentioned later.

Also noteworthy is the observation that at 23 °C the β proton hyperfine splitting constant of **2** becomes unequivalent by complexation with $SnCl_4$ while that of the uncomplexed radical **2** showed splitting by two equivalent hydrogen atoms. A doublet of doublets was also observed for the *tert*-butyl substituted radical $Me_3CCH_2\dot{C}(OCMe_3)COOCMe_3$ in chlorobenzene at 23 °C.[13] Therefore, steric hindrance seems to be the most important factor governing the rotation of the C_α–C_β bond.

The addition of equimolar amounts of $SnCl_4$ to **1**, [**1**] = [$SnCl_4$] = 1.00 M, reduced the dissociation temperature from about 100 °C to near 0 °C. The equilibrium constants (K) for the dimer $\rightleftharpoons$ radical equilibria, $K = [\text{radical}]^2/[\text{dimer}]$, were determined in chlorobenzene in the temperature range 5–30 °C and 110–130 °C in the presence and absence of $SnCl_4$, respectively. Plots of ln K vs. $1/T$ are depicted in Figure 4. The standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were calculated from the equation $-RT \ln K = \Delta H° - T\Delta S°$, where R is the gas constant and T is the absolute temperature. From Figure 4, it was found that the addition of $SnCl_4$ reduced $\Delta H°$ from 41.4 to 12.1 kcal/mol and $\Delta S°$ from 49.2 to −6.7 cal/mol·deg at 25 °C, suggesting a pronounced decrease in bond dissociation energy of **1** by complexation and a stronger interaction of $SnCl_4$ with **2** rather than **1**. Weaker Lewis acids such as $AlEt_3$ and $ZnCl_2$ resulted in a negligible or small effect, and side reactions occurred in the presence of BCl_3 even at ambient temperature. The addition of $EtAlCl_2$ reduced the dissociation temperature to near ambient temperature and enhanced the concentration of the radical but did not control the conformation of the radical. When smaller amounts of $SnCl_4$ were employed as the complexing reagent, the decrease in the thermodynamic parameters were suppressed and splitting constants showed little change even with a 1:10 $SnCl_4$ to **1** molar ratio, which

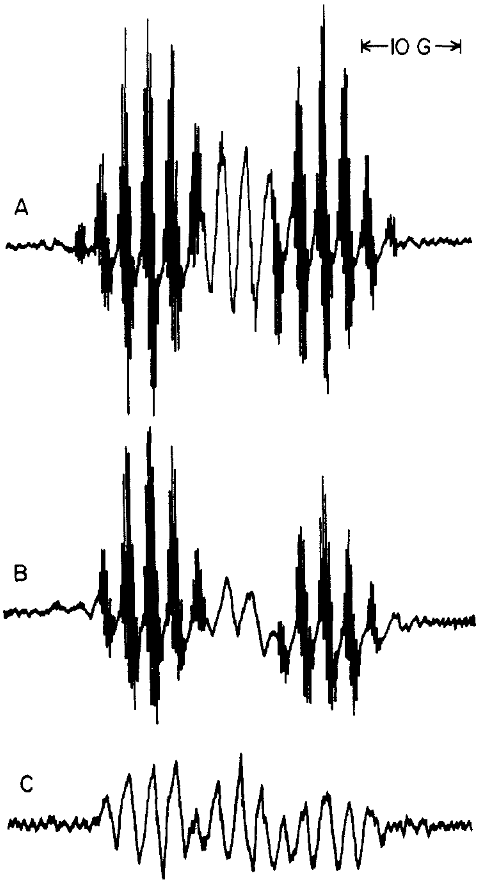

Figure 5. Experimental ESR spectra of the **2**–$SnCl_4$ complex in chlorobenzene at 40 °C (A), 60 °C (B), and 94 °C (C). Microwave power 0.2 mW; modulation amplitude 0.1 G.

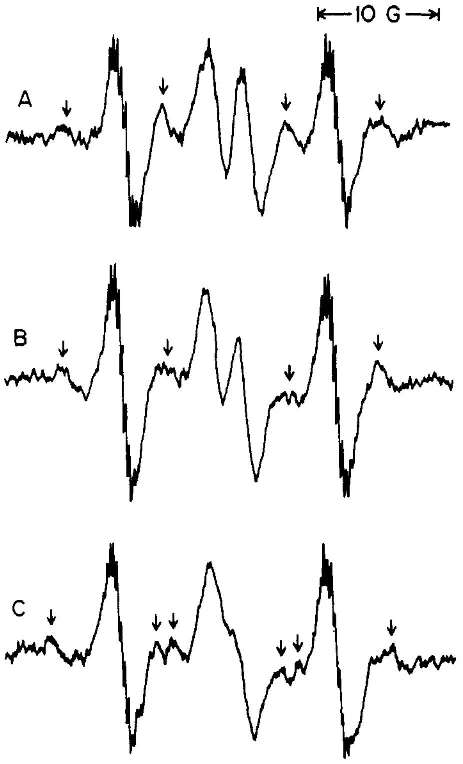

Figure 6. Experimental ESR spectra of the $(CH_3)_3CCH_2\dot{C}(OCD_3)COOCD_3-SnCl_4$ complex in chlorobenzene at 23 °C (A), 40 °C (B), and 60 °C (C). Arrows indicate splittings due to the Sn nuclei. Microwave power 0.2 mW; modulation amplitude 0.1 G.

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(12) Brumby, S. *J. Chem. Soc., Chem. Commun.* **1982**, 677.

(13) Photoreaction of *tert*-butyl 2-*tert*-butoxyacrylate and 2,2′-azobis[2-methylpropane] afforded this radical, $a_{\beta\text{-H}}$ = 11.16 and 14.25 G in chlorobenzene at 23 °C.

suggests a strong interaction between the radical and $SnCl_4$.

Figure 5 represents the variation of the ESR spectra of the complexed radical **2** with temperature; [**1**] = [$SnCl_4$] = 1.00 M. Such variation of the spectra is completely reversible except that the radical decays at high temperature (over about 60 °C). Therefore, the variation is not due to another new radical produced by the reaction of the complexed radical. It is clear that the change of the central absorption lines is much larger than that of the wings of the spectrum. Analyses of the signals reveal that it is due to the larger variation of the $a_{\beta\text{-H}}$ value than the $a_{\gamma\text{-H}}$, $a_{\delta\text{-H}}$, and a_{Cl} values; e.g., $a_{\beta\text{-H}} = 7.96$ and 9.91 G, $a_{\gamma\text{-H}} = 2.36$ G, $a_{\delta\text{-H}} = 2.30$ G, $a_{^{35}Cl} = 0.25$ G, and $a_{^{37}Cl} = 0.21$ G at 60 °C.

It is well-known that the $a_{\beta\text{-H}}$ value is dependent on both the spin density ρ on the radical carbon and the time-average dihedral angle θ between the β hydrogen and the $2p_z$ orbital on the carbon.[14] Although it is now difficult to determine the exact θ value since the ρ value is expected to be reduced by complexation,[11] it seems that $SnCl_4$ regulates the rotation between β hydrogen and the carbon p_z orbital to some extent, $\theta = 54$–57° at 23 °C, based on the $a_{\beta\text{-H}}$ value of 17.6 G for 1-methoxy-1-(methoxycarbonyl)ethyl radical,[15] in which the methyl group rotates freely, $\langle\theta\rangle = 45$ °.

Restriction of such free rotation was clearly demonstrated by using $(CH_3)_3CCH_2\dot{C}(OCD_3)COOCD_3$, as shown in Figure 6, where [deuterated **1**] = [$SnCl_4$] = 1.00 M. The doublet of doublets at 23 °C, consistent with a conformationally locked structure, was converted to a triplet with increasing temperature. Small absorptions denoted in this figure by downward arrows are assigned to doublet splitting by ^{115}Sn, ^{117}Sn, and ^{119}Sn nuclei, $a_{Sn} = 8.85$ and 9.63 G at 40 and 60 °C,[8] which clearly supports the spectral analysis previously mentioned.

Acknowledgment. We express our cordial thanks to Dr. Y. Miura (Osaka City University, Japan) for his helpful discussion.

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(14) Heller, C.; McConnell, M. H. *J. Chem. Phys.* **1960**, *32*, 1535.

(15) This radical was produced by the hydrogen abstraction from methyl 2-methoxypropionate by *tert*-butoxy radical in chlorobenzene under UV light irradiation at 23 °C.

Origin of Deuterium Isotope Effects on Carbon-13 Chemical Shifts

Kenneth L. Servis* and Robert L. Domenick

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90089-1062.

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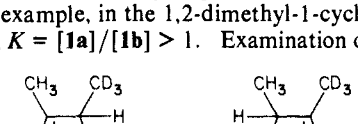
Abstract: In an attempt to model deuterium isotope effects on carbon-13 chemical shifts in the NMR spectra of aliphatic molecules and carbocations, ab initio calculations have been performed at the STO-3G level. The total charge and the gross orbital charges on the nuclei in these compounds were calculated as a function of the C–H bond lengths. The gross atomic charge and the gross orbital charges vary linearly with the bond length for small displacements around the equilibrium bond length. Assuming a charge shift relationship and reasonable values of the isotope effect on bond displacement, the magnitude and directions of the variations of electron density with C–H bond length were found to be sufficiently large to account for the magnitude and sign of the chemical shift isotope effects in acetone and the 2-propyl cation. The sign of β-deuterium isotope effects in cations with two-electron three-center bonds is not adequately accounted for.

The substitution of deuterium for hydrogen in organic compounds can alter the carbon-13 chemical shift of carbon atoms as many as six bonds removed from the site of substitution.[1] Saunders et al.[2] have shown that when deuterium is substituted for hydrogen at positions β to the cationic carbon in equilibrating carbenium ions, the equilibrium is shifted toward the carbenium ion isotopomer which has hydrogen β to the formally charged carbon. For example, in the 1,2-dimethyl-1-cyclopentyl cation, **1a** is favored, $K = [\mathbf{1a}]/[\mathbf{1b}] > 1$. Examination of the two-bond deuterium isotope effect on the carbon-13 chemical shift in nonequilibrating β-deuterated carbocations has shown the sign and magnitude of the effect at the positively charged carbon to depend upon the electron-demand and -delocalization mechanism at the cationic center. Servis and Shue[3] reported that β-deuterium substitution in classical static carbenium ions produces a downfield shift of the cationic carbon-13 resonance. In addition, Servis and Shue reported that the positively charged carbons in allylic and benzylic conjugated cations are unaffected by β-deuterium substitution. The β effect for such ions was related to the demand for hyperconjugative stabilization. Forsyth et al.[4] recently provided additional evidence for the hyperconjugative origin of the isotope effect arising from β-deuterium substitution in classical carbocations.



1a 1b

In three cases where the carbocations are believed to be σ-delocalized, β-deuterium substitution produces a shielding of the cationic carbon. The β effect in these ions arises from an isotopic perturbation of resonance. The electron distribution in the bridging three-center two-electron bond is perturbed by the replacement of hydrogen by deuterium.

The chemical shielding of a nucleus in a molecule is a function of the internuclear separations.[5] In principle, chemical shifts could be calculated by integrating the chemical shielding of the nucleus as a function of distance over the vibrational potential surface. Since vibrations are in general anharmonic, bonds are more or

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(5) Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4977.

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