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Ultrahigh Resolution in Proton NMR Spectra at 500 MHz: Two-Bond Intrinsic Chlorine and Silicon Isotope Effects

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"Heavy-atom" isotope effects on NMR ^1H chemical shifts have been reported in a few cases[1-3] but only for second-row elements. We now show that $^{37}Cl/^{35}Cl$ isotope effects on the ^1H chemical shifts in chlorinated methanes are about +0.2 ppb (ca. 0.1 Hz at 500 MHz) and that the $^{29}Si/^{28}Si$ isotope effect on the ^1H chemical shift in tetramethylsilane (TMS) is $+0.06 \pm 0.01$ ppb. It is likely that previously unreported splittings arising from heavy-atom isotope effects will be observable in the ^1H NMR spectra of other organic compounds, given the excellent resolution of modern high field NMR spectrometers.

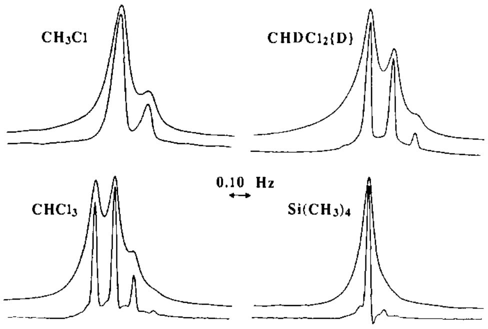

Figure 1. 500-MHz ^1H NMR spectra of CH_3Cl, $CHDCl_2$ (deuterium decoupled), and $CHCl_3$, showing $^{37}Cl/^{35}Cl$ isotope effects, and of $Si(CH_3)_4$ as a line shape and resolution reference (the ^{29}Si satellites lie outside the region shown). The upper trace in each spectrum has been obtained without any processing of the FID except for zero filling, and the lower trace represents the application of Lorentzian–Gaussian resolution enhancement, which is not the same for all the spectra.

Table I. Chlorine Isotope Effects on ^1H Chemical Shifts

compound	Δ^a (ppb)	fractional intensities calcd	fractional intensities obsd^b
$CH_3{}^{35}Cl$		0.755	0.78
$CH_3{}^{37}Cl$	0.25 ± 0.03	0.245	0.22
$CHD^{35}Cl_2$		0.570	0.56
$CHD^{35}Cl^{37}Cl$	0.21 ± 0.03	0.370	0.38
$CHD^{37}Cl_2$	0.42 ± 0.05	0.060	0.06
$CH^{35}Cl_3$		0.431	0.42
$CH^{35}Cl_2{}^{37}Cl$	0.17 ± 0.03	0.419	0.44
$CH^{35}Cl^{37}Cl_2$	0.35 ± 0.05	0.136	0.13
$CH^{37}Cl_3$	0.52 ± 0.08	0.015	0.01_5

[a] δ (molecule with no ^{37}Cl) − δ (molecule with one or more ^{37}Cl). [b] From peak heights of resolution enhanced spectra, normalized to 1 for each compound, error ca. ±0.01.

The ^1H spectra of methyl chloride (CH_3Cl), dichloromethane-d_1 ($CHDCl_2$, deuterium decoupled), and chloroform ($CHCl_3$) are shown in Figure 1 together with a line shape for the internal TMS reference line.[4] Since the natural abundances for ^{35}Cl and ^{37}Cl and 75.5 and 24.5%, respectively, the statistical intensity distributions in the multiplets for CH_3Cl, $CHDCl_2\{D\}$, and $CHCl_3$ are as shown in Table I. The observed multiplets, especially after some resolution enhancement, show intensities that are close to these values (Table I)[5] and require that these isotope effects be positive.[2] The sign of the chlorine isotope shift for ^1H in $CHCl_3$ is the same as for ^{19}F in $CFCl_3$.[6] The $^{37}Cl/^{35}Cl$ isotope effects in the chlorinated methanes decrease monotonically as the number of chlorine atoms is increased, and they are additive in $CHCl_3$ and $CHDCl_2$ (Table I). The $^{29}Si/^{28}Si$ two-bond isotope effect on the ^1H chemical shift in TMS is of the same order of magnitude as the above two-bond chlorine isotope effects when the different mass changes are taken into account. Measurement of this very small isotope effect (30 mHz at 500 MHz) is helped by the nonoverlapped spectrum [$^2J(^{29}Si-^1H) = 6.65$ Hz].[3] None of the molecules studied here give any indication of significant molecular alignment caused by the high magnetic field.[7]

We would like to make a few comments on the procedures required to obtain ultrahigh resolution spectra, especially for protons.[8] Careful sample preparation, temperature control of the probe, and magnetic field shimming are essential.[8,9] Furthermore, so-called "radiation damping" effects,[10,11] which are not

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[†] Graduate Fellow of the Division of Organic Chemistry, ACS, sponsored by the Proctor & Gamble Company, 1986–1987.

(1) "Heavy" refers to atoms of higher atomic number than hydrogen.

(2) For recent reviews, see: (a) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105–234. (b) Jameson, C. L. In *Specialist Periodical Reports*; The Royal Society of Chemistry: London, 1986; NMR Spectroscopy, Vol. 15, pp 1–27. (c) Hawkes, C. E. In *Specialist Periodical Reports*; The Royal Society of Chemistry: London, 1986; NMR Spectroscopy, Vol. 15, pp 28–80. A positive isotope effect corresponds to a greater shielding for the heavier isotope.

(3) $^{13}C/^{12}C$ isotope effects give rise to *nonoverlapped sharp* ^1H lines whose frequencies can be accurately measured. One-bond and two-bond $^{13}C/^{12}C$ isotope effects on ^1H chemical shifts are typically 1–5 and 0.5–1.5 ppb, respectively.[2a] The few known analogous $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotope effects have similar magnitudes.[2a]

(4) The CH_3Cl sample contained about 5% of CH_3Cl in CD_2Cl_2. The $CHDCl_2$ was observed as the isotopic impurity in CD_2Cl_2. These solutions were filtered into high quality 5-mm NMR tubes (Wilmad 535), and oxygen was removed by bubbling argon into the solution for a short time. The $CHCl_3$ was in a sealed degassed Bruker "line shape" sample (10% $CHCl_3$ in acetone-d_6). All samples contained about 1% TMS. A Bruker AM500 equipped with an Oxford Instrument 11.7 T solenoid was used with the spectrometer locked on deuterium, except for the $CHDCl_2$ sample, where C_6F_6 was used as an ^{19}F lock. Shimming was done manually on the TMS free induction decay (FID), finishing with an acquisition time of about 20 s. Data acquisition times were between 30 and 60 s, and a spectral resolution of 2 mHz per point was achieved by using small spectral windows set to either TMS or to the chlorinated methane and by zero filling of the FID's. The TMS line shown in Figure 1 has a full line width at half height of 60 mHz before resolution enhancement.

(5) The protons in the chloromethanes are expected to have small coupling constants to chlorine, but strong quadrupole relaxation leads to almost complete decoupling. The T_2 in $CHCl_3$ has been reported to be 10 s, corresponding to a line width of 0.03 Hz; the two chlorine isotopes have broadening effects that differ by only 10% because of cancelling differences in gyromagnetic ratios and quadrupole moments (Abragam, A. *The Principles of Nuclear Magnetism*; Oxford: London, **1961**: p 332).

(6) Carey, P. R.; Kroto, H. W.; Turpin, M. A. *J. Chem. Soc., Chem. Commun.* **1969**, 188. Brey, W. S., Jr.; Ladner, K. H.; Block, R. E.; Tallon, W. A. *J. Magn. Reson.* **1972**, *8*, 406–409. The $^{37}Cl/^{35}Cl$ isotope effect in $CFCl_3$ is temperature dependent and about two orders of magnitude larger than that in $CHCl_3$.

(7) For a review of molecular alignment at high magnetic fields in isotropic solvents, see: (a) van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Acc. Chem. Res.* **1974**, *17*, 172–180. See, also: (b) Anet, F. A. L. *J. Am. Chem. Soc.* **1986**, *108*, 1354–1355. (c) Bastiaan, E. W.; Bulthuis, J.; MacLean, C. *Magn. Reson. Chem.* **1986**, *24*, 723–728.

(8) For "ultrahigh" resolution in 50-MHz ^{13}C NMR spectroscopy, see: (a) Allerhand, A.; Addleman, R. E.; Osman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5809–5810. (b) Allerhand, A.; Dohrenwend, M. *J. Am. Chem. Soc.* **1985**, *107*, 6684–6688. (c) Allerhand, A.; Addleman, R. E.; Osman, D.; Dohrenwend, M. *J. Magn. Reson.* **1985**, *65*, 361–363. (d) Maple, S. R.; Allerhand, A. *J. Magn. Reson.* **1986**, *66*, 168–171. (e) Allerhand, A.; Bradley, C. H. *J. Magn. Reson.* **1986**, *67*, 173–176. (f) Maple, S. R.; Allerhand, A. *J. Am. Chem. Soc.* **1987**, *109*, 56–61. For ultrahigh resolution in ^1H spectroscopy, see ref 7b and references therein.

(9) Temperature homogeneity in the sample for ^1H appears to be less important than for ^{13}C.[8a] However, temperature stability is required for proper shimming.

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important for ^{13}C NMR, can lead to line broadening, even for fairly dilute proton samples, because of the high-Q and large filling factors of probe coils in modern high field NMR spectrometers. Additionally, even a small amount of radiation damping, which leads to only a slight line broadening, can give rise to major spacing and intensity artifacts in *partially overlapped resonances.* This second effect of radiation damping is not removed by line narrowing techniques, and it is strongly pulse angle dependent. Analogous effects have been investigated previously in sweep NMR with a special feedback spectrometer,[12] but the "multiplet" effect in radiation damping does not seem to have been described previously in ordinary FT NMR. Radiation damping can be reduced by decreasing the filling factor (e.g., by using a smaller diameter tube for a given coil), by decreasing the concentration of the compound, or by detuning the probe. Multiplets whose partially overlapped lines are independent of the pulse angle are free from radiation damping effects.[13]

We plan to investigate other heavy-atom isotope effects on protons by ultrahigh resolution ^1H NMR. Such data are of value in understanding vibrational effects on chemical shifts and to provide comparisons with quantum mechanical calculations.[2]

Acknowledgment. The 500-MHz spectrometer was purchased through funds provided in part by the National Science Foundation.

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(10) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford: London, 1961; pp 73–74.

(11) (a) Bloembergen, N.; Pound, R. V. *Phys. Rev.* **1954**, *95*, 8–12. (b) Bruce, C. R.; Norberg, R. E.; Pake, G. E. *Phys. Rev.* **1956**, *104*, 419–420.

(12) Hobson, R. F.; Kaiser, R. *J. Magn. Reson.* **1975**, *20*, 458–474.

(13) We plan to investigate further the radiation damping effects in overlapped multiplets. In CH_3Cl, radiation damping can change the 3:1 doublet into, for example, an apparent 1:1 doublet.

Carbon–Hydrogen Bond Activation and Carbon–Carbon Bond Formation in the Reaction between Ethylene and Hexaisopropoxyditungsten

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Ethylene reacts with certain metal surfaces to give a capping (μ_3) ethylidyne ligand.[1] In triosmium carbonyl chemistry ethylene has been shown to undergo successive C–H activation to give a μ-σ,π-vinyl and a μ-vinylidene ligand.[2] A similar reaction sequence has been reported by Puddephatt and co-workers in the addition of ethyne to a hydrido triangulo platinum complex.[3] We have repeatedly emphasized the relationships, both structural and chemical, between reduced metal oxides of molybdenum and tungsten and smaller alkoxide clusters and their larger (closo) counterparts.[4] For example, the square-$Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ and butterfly-$Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ molecules[5] are *arachno* subunits of the $M_6(\mu_3\text{-}X)_8$ cluster unit, and $W_4(O\text{-}i\text{-}Pr)_{12}$[6] represents a fragment of the $M_6(\mu_2\text{-}X)_{12}$ unit.[7] Furthermore the M_4–alkoxide clusters are formed from the coupling of M_2 alkoxides by steric control in the choice of the OR group. Indeed we have established that an equilibrium exists between $W_4(O\text{-}i\text{-}Pr)_{12}$ and $W_2(O\text{-}i\text{-}Pr)_6$.[6,8] One of our hypotheses is that these small unsaturated alkoxide cluster units may provide models for active sites on reduced metal oxide surfaces. We describe here the observation of the activation of ethylene by $W_2(O\text{-}i\text{-}Pr)_6$ under extremely mild conditions.

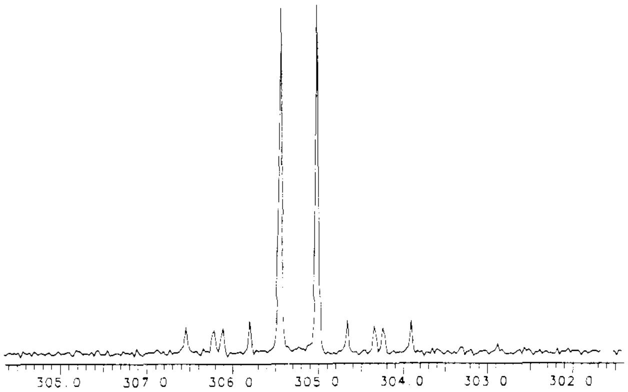

Figure 1. $^{13}C\{^1H\}$ spectrum of the alkylidyne carbon in the ^{13}C labeled compound $W_2(\mu\text{-}{}^*C^*CH_2{}^*CH_2{}^*CH_2)(O\text{-}i\text{-}Pr)_6$ where *C represents 99 mol % ^{13}C. The spectrum is interpretable in terms of $^1J_{CC} = 30$ Hz and a satellite spectrum arising from coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance $^1J_{WC} = 117$ and 165 Hz. The proton-coupled spectrum reveals that the alkylidyne carbon is coupled to two equivalent hydrogen atoms, consistent with the connectivity μ-$^*C^*CH_2$, $^2J_{CH} = 6$ Hz. The spectrum was recorded at 22 °C, 75.4 MHz in benzene-d_6. Chemical shifts were referenced to the central carbon signal of benzene-d_6 at 128.0 ppm.

Addition of ethylene (2 equiv) to a hydrocarbon solution of $W_2(O\text{-}i\text{-}Pr)_6$ leads to a reaction at −20 °C. The initially formed complex is possibly a dissociatively labile adduct $W_2(O\text{-}i\text{-}Pr)_6(C_2H_4)_x$ which reacts at 22 °C, $t_\infty = 24$ h, to give a new compound both quantitatively and irreversibly.[9] The new compound is highly fluxional on the NMR time scale, and even at −90 °C the alkoxide signals are not completely frozen out in toluene-d_8. However, it appears that the alkoxide methyne signals fall into a 3:2:1 integral ratio. Thoughout the temperature range +22 °C to −90 °C the ^1H signals derived from ethylene appear as triplets $\delta = 4.70$ and 2.75 ppm and a quintet $\delta = 3.58$ with $J_{HH} = 6.0$ and 6.5 Hz, respectively. On single frequency decoupling the quintet resonance at 3.58 ppm, *both* triplets collapse to singlets, which establishes the connectivity $X\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Y$ (the apparent quintet is really a triplet of triplets). In the ^{13}C spectrum there are resonances at δ 56.3 with $J_{^{183}W-^{13}C} = 99$ Hz and $\delta = 42.6$ and 54.2. There is no discernible coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance to the latter two resonances, but in the proton-coupled ^{13}C spectrum all of the above carbon signals show one bond coupling to two hydrogen atoms. This reliably establishes the connectivity $WCH_2CH_2CH_2Y$. There is in addition a fourth carbon resonance at δ 305.3. Reactions employing $^*C_2H_4$, where *C respresents 99 mol % ^{13}C identify the connectivity depicted diagrammatically in I below, in which the alkylidyne carbon bridges two inequivalent W atoms. The proton-decoupled spectrum of the alkylidyne carbon δ 305.3 ppm is shown in Figure 1 for the product derived from the use of $^*C_2H_4$. Note the appearance of two significantly different couplings to ^{183}W, 117

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(1) (a) Eg. on Pt surfaces, see: Somorjai, G. A. In *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: 1981; p 278. (b) See, also for μ-vinylidyne and μ-ethylidyne interconversions: Hills, M. M.; Parmeter, J. E. Weinberger, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597. Hatzikus, G. H.; Loxton, C. M.; Masel, R. I. *J. Vac. Sci. Technol.*, in press (Proc. 1986 Am. Vac. Soc. Natnl. Symp.).

(2) Deeming. A. J. In *Transition Metal Clusters*; Wiley-Interscience: Johnson, G. F. G., Ed.; 1980; Chapter 6, p 428 Figure 12, and references therein.

(3) Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111.

(4) Chisholm, M. H. In *Inorganic Chemistry Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symp. Ser.; American Chemical Society: Washington, DC, 1983, Chapter 16, p 243. Chisholm, M. H. *J. Solid State Chem.* **1985**, *57*, 120.

(5) Chisholm, M. H.; Errington, R. J.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2025. Chisholm, M. H.; Clark, D. L.; Errington, R. J.; Folting, K.; Huffman, J. C. *Inorg. Chem.*, submitted for publication.

(6) Chisholm, M. H.; Clark, D. L.; Folting, K.; Huffman, J. C. *Angew. Chem.* **1986**, *25*, 1014.

(7) For drawings of the so-called 6–8 and 6–12 clusters, see the following: Raithby, P. R. in ref 2., Chapter 1, pp 118–121, Figures 2, 3, 5, and 6 or Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 4th eds; Wiley: 1980; p 57.

(8) For $W_4(O\text{-}i\text{-}Pr)_{12} \rightarrow 2W_2(O\text{-}i\text{-}Pr)_6$, $\Delta H° = +23$ kcal mol^{-1} and $\Delta S° = +61$ eu. Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. *J. Am. Chem. Soc.*, submitted for publication.

(9) We have recently characterized the bisethylene adduct $W_2(ONp)_6(C_2H_4)_2$ formed by the addition of ethylene to hydrocarbon solutions of $W_2(ONp)_6$ where Np = neopentyl.

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