

NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist

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Received February 11, 2010

Tables of ¹H and ¹³C NMR chemical shifts have been compiled for common organic compounds often used as reagents or found as products or contaminants in deuterated organic solvents. Building upon the work of Gottlieb, Kotlyar, and Nudelman in the *Journal of Organic Chemistry*, signals for common impurities are now reported in additional NMR solvents (tetrahydrofuran-*d*₈, toluene-*d*₈, dichloromethane-*d*₂, chlorobenzene-*d*₅, and 2,2,2-trifluoroethanol-*d*₃) which are frequently used in organometallic laboratories. Chemical shifts for other organics which are often used as reagents or internal standards or are found as products in organometallic chemistry are also reported for all the listed solvents.

Hanging above the desk of most every chemist whose work relies heavily on using NMR spectroscopy¹ is *NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities* by Gottlieb, Kotlyar, and Nudelman.² By compiling the chemical shifts of a large number of contaminants commonly encountered in synthetic chemistry, the publication has become an essential reference, allowing for easy identification of known impurities in a variety of deuterated organic solvents. However, despite the utility of Gottlieb et al.'s work,³ the chemical shifts of impurities in a number of NMR solvents often used by organometallic chemists were not included. Tetrahydrofuran-*d*₈ (THF-*d*₈), toluene-*d*₈, dichloromethane-*d*₂ (CD₂Cl₂), chlorobenzene-*d*₅ (C₆D₅Cl), and 2,2,2-trifluoroethanol-*d*₃ (TFE-*d*₃) are commonplace in laboratories practicing inorganic syntheses. Therefore, we have expanded the spectral data compilation with the inclusion of chemical shifts of common impurities recorded in the deuterated solvents heavily employed in our organometallic laboratories. The chemical shifts of various gases (hydrogen, methane, ethane, propane,

ethylene, propylene, and carbon dioxide) often encountered as reagents or products in organometallic reactions, along with organic compounds relevant to organometallic chemists (allyl acetate, benzaldehyde, carbon disulfide, carbon tetrachloride, 18-crown-6, cyclohexanone, diallyl carbonate, dimethyl carbonate, dimethyl malonate, furan, Apiezon H grease, hexamethylbenzene, hexamethyldisiloxane, imidazole, pyrrole, and pyrrolidine), have also been added to this expanded list.

Experimental Section

All deuterated solvents were obtained commercially through Cambridge Isotope Laboratories, Inc. NMR spectra were recorded at 298 K using 300, 500, or 600 MHz spectrometers (¹³C{¹H} NMR frequencies of 75.5, 126, or 151 MHz, respectively). Adopting the previously reported strategy,² standard solutions of mixtures of specific impurities were used to reduce the number of necessary individual NMR experiments. The combinations of organic compounds were chosen in a way in which intermolecular interactions and resonance convolution would be minimized. Unless otherwise stated, the standard solutions were prepared with qualitatively equal molar amounts of the following compounds: (solution 1) acetone, dimethylformamide, ethanol, toluene; (solution 2) benzene, dimethyl sulfide, ethyl acetate, methanol; (solution 3) acetic acid, chloroform, diethyl ether, 2-propanol, tetrahydrofuran; (solution 4) acetonitrile, dichloromethane, 1,4-dioxane, *n*-hexane, hexamethylphosphoramide (HMPA); (solution 5) 1,2-dichloroethane, *n*-pentane, pyridine, hexamethylbenzene; (solution 6) *tert*-butyl alcohol, 2,6-di-*tert*-butyl-4-methylphenol (BHT), cyclohexane,

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(1) For general information on ¹H and ¹³C{¹H} NMR spectroscopy, see: Balci, M. *Basic ¹H- and ¹³C-NMR Spectroscopy*; Elsevier: Amsterdam, 2005.

(2) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(3) According to ACS Publications as of December 2009 (<http://pubs.acs.org/>), Gottlieb et al.'s publication² is the most downloaded *Journal of Organic Chemistry* article over the preceding 12 months.

1,2-dimethoxyethane (DME), nitromethane, poly(dimethylsiloxane) (silicone grease), triethylamine; (solution 7) diglyme, dimethylacetamide, ethylene glycol, ethyl methyl ketone; (solution 8) allyl acetate, 2,6-di-*tert*-butyl-4-methoxyphenol (BHA), long-chain, linear aliphatic hydrocarbons from pump oil;⁴ (solution 9) benzaldehyde, carbon disulfide, carbon tetrachloride, cyclohexanone, dimethyl malonate, furan, Apiezon H grease (H grease); (solution 10) 18-crown-6, diallyl carbonate, dimethyl carbonate, hexamethyldisiloxane (HMDSO), imidazole, pyrrole, pyrrolidine.⁵ In the case of TFE-*d*₃, nitromethane was omitted from solution 6 and run separately, since the protons of nitromethane exchange with deuterium from TFE-*d*₃ in the presence of triethylamine. In the case of (CD₃)₂CO, pyrrolidine was omitted from solution 10, since the two compounds were observed to react with each other. The gases used in this study included hydrogen, methane, ethane, propane, ethylene, propylene, and carbon dioxide.

Before examining the various standard contaminant solutions by ¹H NMR spectroscopy, solvent residual signals⁶ and chemical shifts for H₂O⁷ for each NMR solvent were referenced against tetramethylsilane (TMS, δ 0 ppm) and reported. Before collecting ¹³C{¹H} NMR spectral data, solvent signals⁶ were recorded with reference to the signal of a TMS internal standard. For D₂O, ¹H NMR spectra were referenced to the methyl signal (δ 0 ppm) of sodium 3-(trimethylsilyl)propane-sulfonate,^{8,9} and ¹³C{¹H} NMR spectra were referenced to the signal for the methyl group of methanol (one drop, added as an internal standard), which was set to 49.50 ppm.²

In a typical experiment for collecting ¹H NMR spectral data, a 3 μL sample of a standard contaminant solution was added to an NMR tube containing approximately 0.4 mL of a deuterated solvent. For ¹³C{¹H} NMR spectral data collection, an approximately 50 μL sample of the standard contaminant solution was added. When there was any uncertainty in the assignment of a resonance, the solution was spiked with an additional 1–2 μL of the impurity in question to accurately identify its chemical shift. In cases where the chemical shifts of resonances were highly dependent on the concentration of the impurities present, ambiguous resonances were instead resolved via gradient-

(4) VWR brand vacuum pump oil #19.

(5) The components of solution 10 were stable together in dilute solution but unstable when neat mixtures were prepared. In general, it was observed that the nitrogen-containing compounds and possibly 18-crown-6 catalyzed the hydrolysis of the carbonates, reacted directly with them, or both. Therefore, for the purpose of storage, the solution was partitioned into two subsolutions: (solution 10A) 18-crown-6, imidazole, pyrrole, pyrrolidine; (solution 10B) diallyl carbonate, dimethyl carbonate, hexamethyldisiloxane. These subsolutions were stable for long periods as neat mixtures and were combined to form solution 10 by adding equal portions to an NMR tube containing the desired deuterated solvent.

(6) For ¹H NMR spectra, the solvent residual signals arise from the proton of isotopomers containing one less deuterium atom than the perdeuterated solvent: e.g., CDHCl₂ in CD₂Cl₂. For ¹³C NMR spectra, the solvent signals arise from the ¹³C atoms at natural abundance in the perdeuterated solvent.

(7) The chemical shift for H₂O can vary depending on the temperature, [H₂O], and the solutes present: e.g., a downfield shift may be observed in the presence of any hydrogen bond acceptors. For more information see page 75 of ref 1.

(8) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Granger, P.; Hoffman, R. E.; Zilm, K. W. *Pure Appl. Chem.* **2008**, *80*, 59.

(9) For information on the temperature dependence of HDO chemical shifts in D₂O, see ref 2.

selected heteronuclear single-quantum coherence (gs-HSQC) and gradient-selected heteronuclear multiple-quantum coherence (gs-HMQC) NMR spectroscopies. For the experiments involving gases, a J. Young NMR tube containing approximately 0.4 mL of NMR solvent was first degassed with three freeze–pump–thaw cycles. Using a vacuum line equipped with a gas manifold, 1 atm of the desired gas was added to the tube. Each gas was run separately, degassing between each gas sample.

Results and Discussion

Chemical shifts for each of the impurities are reported in the tables: ¹H and ¹³C{¹H} NMR spectral data of all substrates are presented in Tables 1 and 2, respectively. Notably, physically larger tables, containing all the data from Tables 1 and 2 as well as the chemical shifts of additional organic compounds, are provided in the Supporting Information. Unless noted otherwise, coupling constants (reported in Hz) and resonance multiplicities (abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, m = multiplet, br = broad) were observed to be solvent-independent.

It was noted that the amount of gas dissolved in solution gave ¹H NMR signal integrations that were qualitatively comparable to those for the solutions made with the 3 μL additions of the liquid or solid contaminants. However, typically in order to observe signals for the gas samples by ¹³C{¹H} NMR spectroscopy, additional time for data collection was required. The solubility of each gas in D₂O was extremely limited, making ¹³C detection impractical. Of all the gases, methane required the most number of transients in order to obtain an observable signal by ¹³C{¹H} NMR spectroscopy. In most cases, the ¹³C chemical shift of methane was acquired through the use of gs-HMQC NMR spectroscopy to provide enhanced sensitivity. In order to reflect what would be observed in typical NMR-scale experiments, ¹³C detection was not pursued with isotopically enriched gases. A number of misreported values were discovered in the years since the original publication¹⁰ and in the preparation of this paper. These are detailed in the Supporting Information, and the values are now correctly listed in Tables 1 and 2.

Acknowledgment. G.R.F. and K.I.G. thank the Department of Energy (Contract No. DE-FG02-06ER15765) for support. A.J.M.M. and J.E.B. thank the Moore Foundation for support. N.H.S. and B.M.S. thank Abbott Laboratories, Amgen, Merck, Bristol-Myers Squibb, Boehringer Ingelheim, the Gordon and Betty Moore Foundation, and Caltech for financial support.

Supporting Information Available: Large-format tables of the all the NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(10) The misreported value for acetonitrile in C₆D₆ from the original paper² was also pointed out by Dr. Jongwook Choi, to whom we are grateful.