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Characterization of organic iodides with iodine-127 nuclear magnetic resonance spectroscopy

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ABSTRACT

The spectra of the Iodine-127 nucleus could not be readily obtained since it has a spin number, *I*, of 5/2 and a nonspherical charge distribution. When we applied ^{127}I NMR to organic iodides, the I^- and IO_4^- signals of organic molecules provided a clear singlet in solutions of $(CD_3)_2S(O)$ or $(CD_3)_2NC(O)D$. The spectra of ^{127}I NMR revealed the oxidation state of iodine atoms in the organic molecule, which would not have been evident in the ^{1}H and ^{13}C NMR spectra. Here, we report the practical examples of the characterization of organic iodides via solution-^{127}I NMR spectroscopy.

Introduction

Organic iodides are important synthetic moieties that exist in many chemical reagents and intermediates for molecular transformation.[1] They are widely used in organometallic synthesis as a halogenated substrate in coupling reactions.[2] Organic iodides are unique since they are also used as oxidizing agents.[3] Generally, organic compounds are identified by the combination of ^{1}H and ^{13}C NMR, infrared (IR), mass (MS), and ultraviolet–visible (UV–vis) spectra.[4] In particular, ^{1}H and ^{13}C NMR are dominant data in the characterization of the structure of organic molecules.[5] Because ^{1}H and ^{13}C nuclei have $I = 1/2$, the resonances for H and C nuclides can be readily observable. Such sensitivities of NMR chemical shifts and coupling constants to different electronic environments at the nuclei have been employed for the identification of organic molecules. In contrast, the ^{127}I nucleus had an $I = 5/2$ ($I \neq 1/2$) and a 100% of a natural abundance, meaning that organic iodides can be magnetically active and examined by ^{127}I NMR. Some pioneering reports in inorganic chemistry, however, have indicated that ^{127}I NMR properties are quadrupolar ($I > 1/2$), and that the resonances of the iodine nuclides are observable only in symmetrical environments, such as those that are spherical or those at the center of a cubic array of ligands in a tetrahedron or octahedron.[6] While there are many reports of ^{127}I NMR chemical shifts (δ) for iodide (I^-) ions in D_2O, ^{127}I chemical shifts in solution are restricted to those of I^- for inorganic iodides and water-soluble organic iodides in D_2O (ca. δ 0 ppm),[6,7] and to those of IO_4^- ions for inorganic metaperiodates (ca. δ 4100 ppm).[6] Solid-state measurements for iodine materials are numerous.[8] To the best of our knowledge, there are few examples in which the spectra of ^{127}I NMR from an organic iodide have been investigated under dissolved conditions in a non-aqueous solution.[6b] In addition, the spectra of ^{127}I NMR might reveal the oxidative state of iodine and the molecular structure of organic iodides, which would not be evident in the ^{1}H and ^{13}C NMR spectra. Hence, we attempted to record the ^{127}I NMR spectra for organic iodides in various solutions. Herein, we report the first use of ^{127}I NMR experiments to compare and characterize organic iodides in solution for the sake of identifying the iodine itself.

Results and discussion

First, we conducted ^{127}I NMR measurements for I^- ions and IO_4^- ions in inorganic salts. Most iodine salts, for which ^{127}I shifts in aqueous media have been reported, have been classified as inorganic salts: the metallic iodide in D_2O with a shift of ca. δ 0 and the metallic metaperiodate, ca. δ 4100.[6,7] On the basis of known examples of inorganic salts, the differences in ^{127}I shift values should be considered as occurring as the cation (metal) species is

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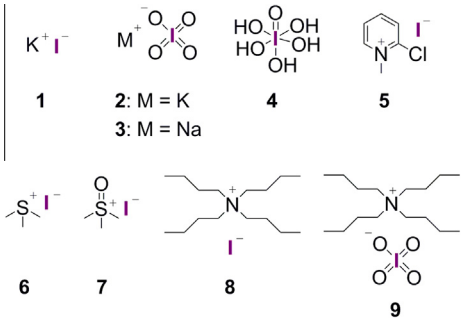

Figure 1. Inorganic iodides **1**–**4** and organic iodides **5**–**9** explored by ^{127}I NMR.

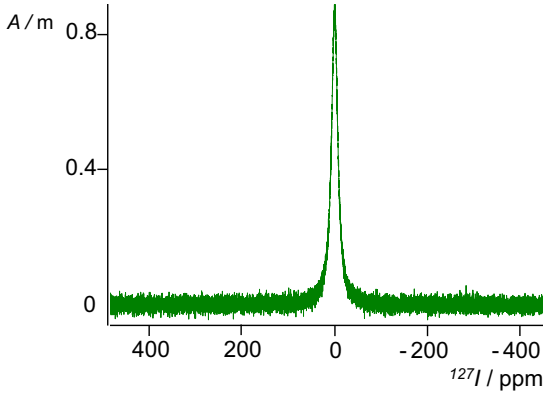

Figure 2. The ^{127}I NMR spectrum of a solution of iodide **1** in D_2O (0.2 M). ^{127}I shift: δ 0 ppm; $W_{1/2}$: 1830 Hz; S/N ratio = 34:1; *A*/m = abundance/millions.

changed against the iodine anions. Although few experimental values have been reported for organic salts, the position of these ^{127}I shifts could be expected to accompany downfield shifts of similar magnitude upon oxidation of the I^- ion (δ 0) to form the IO_4^- ion (δ 4100). The ^{127}I NMR chemical shift of a variety of iodine salts in solution was measured at natural abundance on a JEOL JNM-ECA 600 NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{127}I, 120 MHz) in a 5 mm broadband probe at ambient probe temperature. The 90° pulse was set 13.75 μs, since a 2.4 M potassium iodide (**1**) solution measured in D_2O resulted in a 2300 Hz broad-band peak. The chemical structures of iodine salts are shown in Figure 1.

A 0.2 M potassium iodide (**1**) solution in D_2O was measured in 100 scans with a spectral width of 1000 ppm, resulting in a 1830 Hz broad peak with S/N = 34:1 (Fig. 2), which was used to set the chemical shift scale reference at 0 ppm (Table 1). A 0.1 M solution of potassium periodate (**2**) in D_2O gave a singlet at 4113 ppm with a very low S/N ratio (6:1). A 0.1 M sodium periodate (**3**) in D_2O came in at 4111 ppm with an acceptable value (δ 4121;[6a] δ 4090[9]). The peak of the I^- for **1** appeared at δ 273 in $(CD_3)_2S(O)$, and at δ 179 in $(CD_3)_2NC(O)D$, with a narrower peak width than the aqueous I^- (δ 0 in D_2O). This large solvent effect on the ^{127}I shift had not ever been reported. The ^{127}I NMR spectra of inorganic periodates **2**–**3** in $(CD_3)_2S(O)$ and $(CD_3)_2NC(O)D$ demonstrated dramatic improvements in resolution obtained by using organic solvents instead of D_2O. Accordingly, the spectra of the inorganic IO_4^- exhibited a singlet at 4133 ppm in $(CD_3)_2S(O)$, and at 4138 ppm in $(CD_3)_2NC(O)D$, with a narrower peak width ($W_{1/2}$ < 240 Hz) and a better S/N ratio (>98:1).

A broad peak ($W_{1/2}$ = 7090 Hz) at 4112 ppm was detected in a solution of metal-free orthoperiodic acid (**4**) in D_2O. The peak of orthoperiodate **4** in solutions presented the same ^{127}I shifts as those of periodates **2**–**3**. This observation suggested that solutions of **4** contained the form of tetrahedral IO_4^- ion, which was produced in part by the hydration and solvolysis of the octahedral H_5IO_6.[6c,10] The ^{127}I resonance for the forms of octahedral $[H_{5-n}IO_6]^{n-}$ had not appeared at 2800–3100 ppm, wherein a very broad and weak signal had been reported.[6c] We thought that chemical exchange effects between different forms of $[H_{5-n}IO_6]^{n-}$ ions in metal-free solutions could have possibly led to the failure in observing such spectra.[10] It should be noted that a potassium iodate (KIO_3) solution gave no detectable signal because of the asymmetric structure of the IO_3^- ion. The inorganic iodides **1**–**3** showed a singlet in its spectra in $(CD_3)_2S(O)$ and $(CD_3)_2NC(O)D$, which were also good solvents for the dissolution of organic iodides. In fact, 2-chloro-1-methylpyridinium iodide (**5**), trimethylsulfonium iodide (**6**), trimethylsulfoxonium iodide (**7**), tetrabutylammonium iodide (**8**), and tetrabutylammonium metaperiodate (**9**) were soluble in $(CD_3)_2S(O)$ and $(CD_3)_2NC(O)D$ compared with a limited dissolution to D_2O. The salts **5**–**6** were soluble in water, but the salts **7**–**9** were not soluble. The salts **5**–**9** are important organic reagents for synthetic methods that include Mukaiyama esterification[11] and Corey–Chaycovsky reaction.[12] We thought that the ^{127}I NMR in a solution should be measured for salts **5**–**9**, because these can be

Table 1
Chemical shifts, peak widths and S/N ratios for **1**–**9** in a spectrum

	Chemical shift [δ ppm]/$W_{1/2}$ [Hz]; S/N ratio[a]						
#[b]	D_2O	$CDCl_3$	CD_3OD	$CD_3S(O)CD_3$	CD_3CN	$CD_3C(O)CD_3$	$(CD_3)_2NC(O)D$
1	0/1830; 34:1	ND[c]	ND[c]	273.3/1780; 17:1	ND[c]	ND[c]	179.4/1010; 24:1
2	4113[d]/442; 6:1	ND[c]	ND[c]	4133/217; 127:1	ND[c]	ND[c]	4138/167; 98:1
3	4111/920; 9:1	ND[c]	ND[c]	4133/239; 148:1	ND[c]	ND[c]	4138/193; 157:1
4	4112/7090; 3:1	ND[c]	4128/2800; 2:1	4133/302; 184:1	4133/11,200; 2:1	ND[c,e]	4138/157; 299:1
5	8.2[f]/4300; 6:1	ND	ND	ND	ND	ND[c]	ND
6	11.1/2710; 7:1	ND[c]	ND	279.6/1620; 12:1	131.4[g]/737; 13:1	ND[c]	202.7/1770; 17:1
7	ND[c]	ND[c]	ND[c]	265.8/3080; 5:1	ND[c]	ND[c]	187.2/2880; 5:1
8	ND[c]	ND	ND	255.5/1630; 13:1	132.0[h]/1010; 33:1	129.8/2300; 13:1	182.4/1700; 22:1
9	ND[c]	4132/782; 53:1	4129/1740; 11:1	4135/168; 219:1	4138/96; 187:1	4140/149; 179:1	4138/134; 170:1

[a] The spectra are shown in Figures S1–S31 of the Supplementary data.
[b] Compounds are shown in Figure 1.
[c] The solubility in a solvent was too low to give visible peaks.
[d] The concentration of the solution was <0.1 M.
[e] Insoluble precipitation was formed in the solution.
[f] The number of scans was 700.
[g] The concentration of the solution was <0.1 M. The temperature was set at 50 °C.
[h] The concentration of the solution was 0.24 M.; $W_{1/2}$: the peak width at half-height; S/N ratio: the signal/noise ratio; ND: not detected.