^{18}O-Isotope Effect in ^{13}C Nuclear Magnetic Resonance Spectroscopy. 3. Additivity Effects and Steric Effects

John M. Risley and Robert L. Van Etten*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received April 18, 1980*

Abstract: An upfield shift was previously shown to occur in ^{13}C NMR spectroscopy upon replacement of ^{16}O by ^{18}O [Risley, J. M. and Van Etten, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 252-253]. The additivity of this effect is now demonstrated in two types of compounds. The multiple replacement of equivalent oxygen-16 atoms by oxygen-18 atoms results in a shift of the ^{13}C NMR signal of the oxygen-bearing carbon upfield by an equal amount upon each equivalent substitution. This direct additivity effect is demonstrated by a study of the mixed methyl *n*-[^{18}O]butyl orthocarbonates: the shift of the orthocarbonate carbon is 0.015 ppm/^{18}O. The individual contributions of the carbonyl oxygen and of the ether oxygen to the total shift of the carboxyl carbon in ^{18}O-labeled carboxylic esters are measured. The sum of the individual effects equals the shift observed for the totally labeled ester. The additivity observed for the effect of oxygen-18 on ^{13}C NMR signals is qualitatively similar to effects previously observed for analogous isotope shifts with other nuclei. The possible importance of steric effects in influencing the magnitude of the ^{18}O shift was explored by synthesizing ^{18}O-labeled, sterically hindered alcohols and a ketone. It is concluded that electronic substituent effects rather than steric effects are primarily responsible for the large ^{18}O-isotope shifts on the hydroxyl carbon of tertiary alcohols as compared to typical primary or secondary alcohols.

Introduction

In our initial report of the ^{18}O-isotope effect on ^{13}C NMR signals, we described the ^{18}O-induced upfield shift of the hydroxyl carbon ^{13}C resonance signal in *tert*-butyl alcohol compared to the normal ^{16}O analogue.[1] We also demonstrated a practical application of the isotope effect: the catalytic rate constant for the acid-catalyzed exchange of *tert*-[^{18}O]butyl alcohol in water as measured by ^{13}C NMR agreed with the rate constant measured by the more classical method of mass spectroscopy. Recently we[2] and others[3] have reported the effect of structure on the ^{18}O-isotope effect in ^{13}C NMR. We showed that the isotope effect is a general phenomenon; the magnitude of the isotope effect is significantly dependent on the structure of the carbon–oxygen functional group, while the hybridization of the oxygen-bearing carbon atom is of secondary importance.

To extend further our study of the ^{18}O-isotope effect on ^{13}C NMR signals, we have now examined additivity effects and steric effects. The additivity effect is the resultant of the individual isotope effects which are exerted on the nucleus being observed. Thus, upon heavy-atom isotopic substitution, an NMR signal will (usually) be shifted upfield[2] a specific amount for each equivalent isotopic substitution. The additivity effect was first demonstrated in ^{13}C NMR upon ^{2}H-isotopic substitution.[4-6] Most recently, the additivity effect upon oxygen-18 substitution was observed in ^{31}P, ^{55}Mn, and ^{95}Mo NMR.[7-12] The ^{18}O-isotope effect in ^{31}P NMR has provided enzymologists with an important new tool to study enzymes involved in phosphate reactions. In the present study, the additivity effect of oxygen-18 substitution in ^{13}C NMR spectroscopy is examined in detail by using two types of compounds, an orthocarbonic acid ester and carboxylic acid esters.

We have also studied the ^{13}C NMR spectra of highly ^{18}O-labeled, sterically hindered alcohols and a ketone. This study was carried out in order to see if steric effects contributed to the large ^{18}O-induced shifts observed in labeled *tert*-butyl alcohol[1] and 2-cyclohexylpropan-2-ol.[3]

Experimental Section

[^{18}O]Water (99 atom % excess ^{18}O, Norsk Hydro, Oslo) was used in the synthesis of the ^{18}O-labeled compounds. All other reagents were either analytical or spectrometric grade. Unlabeled water was glass-distilled. Mass spectral analyses were performed on a CEC-21-110B mass spectrometer.

Syntheses. The following ^{18}O-labeled compounds were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.

[^{18}O]Butan-1-ol. Butyraldehyde diethylacetal (50 mL, 0.29 mol, Pfaltz and Bauer), *p*-toluenesulfonic acid (0.12 g, dried over NaOH), and $H_2{}^{18}O$ (2.50 mL, 0.14 mol) were refluxed for 2 h; the solution was protected with a $CaCl_2$ drying tube. After the solution was cooled for 15 min at room temperature, [^{18}O]butyraldehyde and ethanol were distilled with no attempt made to separate the two compounds. The [^{18}O]butyraldehyde was reduced with aqueous sodium borohydride as described by Chaikin and Brown.[13] The solution was fractionally distilled, and the fraction containing the [^{18}O]butan-1-ol was dried over anhydrous potassium carbonate. The [^{18}O]butan-1-ol was distilled, again dried over anhydrous potassium carbonate, and redistilled. The yield of anhydrous [^{18}O]butan-1-ol was 60% (6.12 g, 7.5 mL) and contained 47 atom % excess ^{18}O.

Methyl *n*-[^{18}O]Butyl Orthocarbonates. The four mixed orthocarbonates were prepared after the procedure given by Smith and Delin.[14] Trimethyl *n*-[^{18}O]butyl orthocarbonate was synthesized by refluxing a 1:1 mole ratio of tetramethyl orthocarbonate and [^{18}O]butan-1-ol in the presence of dried *p*-toluenesulfonic acid for 30 min. Upon fractional distillation a 28% yield of the ester was obtained. The other three esters—dimethyl di-*n*-[^{18}O]butyl, methyl tri-*n*-[^{18}O]butyl, and tetra-*n*-[^{18}O]butyl—were synthesized by refluxing a 3:1 mole ratio of [^{18}O]butan-1-ol and tetramethyl orthocarbonate, respectively, for 1 h in the presence of dried *p*-toluenesulfonic acid. Upon fractional distillation the esters were obtained in yields of 29% dimethyl di-*n*-[^{18}O]butyl, 31% methyl tri-*n*-[^{18}O]butyl, and 13% tetra-*n*-[^{18}O]butyl orthocarbonate. The ^{18}O-isotopic enrichment for each ester was identical with that of [^{18}O]butan-1-ol, 47%.

***n*-[*ether*-^{18}O]Butyl Acetate.** Acetyl chloride (0.38 mL, 5.3 mmol) was added dropwise to [^{18}O]-butan-1-ol (0.50 mL, 5.4 mmol) with stirring in an ice bath. Ether was added, and the solution was dried over anhydrous sodium sulfate. Distillation of the solution gave *n*-[*ether*-

(1) Part 1: Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 252-253.
(2) Part 2: Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.*, **1980**, *102*, 4609-4614.
(3) Vederas, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 374-376.
(4) Alei, M., Jr.; Wageman, W. E. *J. Chem. Phys.* **1978**, *68*, 783-784.
(5) Bell, R. A.; Chan, C. L.; Sayer, B. G. *J. Chem. Soc., Chem. Commun.* **1972**, 67-68.
(6) Colli, H. N.; Gold, V.; Pearson, J. E. *J. Chem. Soc., Chem. Commun.* **1973**, 408-409.
(7) Cohn, M.; Hu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 200-203.
(8) Lutz, O.; Nolle, A.; Staschewski, D. *Z. Naturforsch., A* **1978**, *33A*, 380-382.
(9) Cohn, M.; Hu, A. *J. Am. Chem. Soc.* **1980**, *102*, 913-916.
(10) Webb, M. R.; Trentham, D. R. *J. Biol. Chem.* **1980**, *255*, 1775-1778.
(11) Haase, A. R.; Lutz, O.; Müller, M.; Nolle, A. *Z. Naturforsch., A* **1976**, *31A*, 1427-1428.
(12) Buckler, K. U.; Haase, A. R.; Lutz, O.; Müller, M.; Nolle, A. *Z. Naturforsch., A* **1977**, *32A*, 126-130.
(13) Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 122-125.
(14) Smith, B.; Delin, S. *Sven. Kem. Tidskr.* **1953**, *65*, 10-16.

0002-7863/80/1502-6699$01.00/0

Table I. Shifts in the ^{13}C Nuclear Magnetic Resonance Positions of Carbon Atoms Bound to Oxygen upon Replacement of ^{16}O by ^{18}O

compd	^{18}O-isotope shift,[a] ppm (upfield from the corresponding ^{16}O compound)
butan-1-ol	0.020
trimethyl *n*-[^{18}O]butyl orthocarbonate carbonate carbon	0.015
ether carbon of *n*-butyl	0.025
dimethyl di-*n*-[^{18}O]butyl orthocarbonate carbonate carbon	0.015 (per ^{18}O)
methyl tri-*n*-[^{18}O]butyl orthocarbonate carbonate carbon	0.015 (per ^{18}O)
tetra-*n*-[^{18}O]butyl orthocarbonate carbon carbon	0.015 (per ^{18}O)
n-butyl acetate-*ether*-^{18}O carboxyl carbon	0.015
ether carbon	0.029
ethyl acetate-*carbonyl*-^{18}O carboxyl carbon	0.038
p-bromophenacyl formate carboxyl carbon	0.054[b] (per two ^{18}O's)
triphenylcarbinol	0.025
tri-*tert*-butylcarbinol[c]	0.030
tert-butyl alcohol	0.035[d]
2-cyclohexylpropan-2-ol	0.032[e]
acetone	0.050[b]
di-*tert*-butyl ketone	0.054

[a] Solvent $CDCl_3$/1% Me_4Si except as noted. [b] From ref 2. [c] Acetone was the solvent for the tri-*tert*-butylcarbinol because the hydroxyl carbon resonance signal has the same chemical shift as $CDCl_3$. The fact that acetone was the solvent should not affect the result because it has been demonstrated that the isotope shifts are independent of solvent.[2,3] [d] From ref 1. [e] From ref 3.

^{18}O]butyl acetate in nearly quantitative yield (0.7 mL), 47% ^{18}O-enriched in the ether oxygen.

[*carbonyl*-^{18}O]Ethyl Acetate. Triethyl orthoacetate (2.0 mL, 10.9 mmol) and $H_2{}^{18}O$ (0.10 mL, 5.6 mmol) were stirred together at room temperature. A catalytic amount of dried *p*-toluenesulfonic acid was added and [*carbonyl*-^{18}O]ethyl acetate was formed immediately. The solution was stirred an additional 5 min and fractionally distilled. The yield was nearly quantitative (0.5 mL), and the ester was 71% ^{18}O isotopically enriched.

[^{18}O]Triphenylcarbinol. This compound was prepared by the Grignard reaction of phenylmagnesium bromide with [^{18}O]benzophenone.[15] The isotopic enrichment was 75 atom % ^{18}O.

Di-*tert*-[^{18}O]butyl Ketone. This compound was a gift from Professor Robert Benkeser and Dr. Charles Muth. It was prepared by the reverse addition of *tert*-butyllithium and ethyl pivaloate in ether (unpublished results). The labeled compound was prepared by the base-catalyzed exchange of di-*tert*-butyl ketone (1 mL) and $H_2{}^{18}O$ (0.4 mL) in THF (1 mL) and sodium hydroxide (one pellet) for 23 h. The water and THF were distilled. Ether was added to the ketone, the ethereal solution was dried over anhydrous sodium sulfate, and the ether was distilled. The isotope enrichment was 33 atom %.

Tri-*tert*-[^{18}O]butylcarbinol. The procedure of Bartlett and Lefferts[16] was followed. Di-*tert*-[^{18}O]butyl ketone (0.8 mL) in ether was added to *tert*-butyllithium (3.2 mL, 2 M in pentane, Aldrich) over 10 min at −70 °C and stirred for 1 h. The solution was allowed to come to room temperature during the hydrolysis. The organic layer was separated, and the solvent was removed by using a rotary evaporator. The resultant solid was recrystallized by dissolving the solid in 3 mL of ethanol and adding the solution to 3 mL of cold water. The crystals were collected and dried; mp 113 °C (lit.[16] 113–117 °C). The isotopic enrichment was 33 atom %.

NMR Spectra. The ^{18}O-isotope effects on natural abundance ^{13}C NMR signals were measured by using a Varian CFT-20 spectrometer. The instrument was fitted with an 8-mm probe and a 5-mm insert containing the sample was used. A 300-Hz sweep width, a 45° pulse angle, and an 8K data block were used. A line-broadening factor was applied to the accumulated FID such that the resolution of the orthocarbonate carbon was 0.12 Hz. Protons were broad band decoupled. ^1H NMR spectra were recorded on a Varian A-60A spectrometer. Deuteriochloroform (99.8 atom % D containing 1% Me_4Si Aldrich) was the solvent except as noted. Because the ^{18}O-isotopic enrichment of each compound was established by mass spectrometry and agreed with the isotopic contents subsequently estimated by ^{13}C NMR spectroscopy, a single ^{13}C NMR spectrum was sufficient to measure the isotope-induced shift. The error in the measured isotope effect was ±0.002 ppm.

Results

Table I lists the magnitudes of the upfield shift of the ^{13}C NMR signal upon ^{18}O incorporation into the different compounds. In addition, the shifts observed for the totally labeled carboxylate *p*-bromophenacyl [$^{18}O_2$]formate,[2] *tert*-butyl alcohol,[1] 2-cyclohexylpropan-2-ol,[3] and acetone[2] have been included for comparison. Figure 1 shows a portion of the ^{13}C NMR spectra of the four mixed methyl *n*-[^{18}O]butyl orthocarbonates. The resonance position of the unlabeled (^{16}O) species has arbitrarily been assigned the value of 0.000 ppm. The theoretical distribution expected for each ^{18}O-labeled orthocarbonate is noted in the legend for Figure 1.

Discussion

The additivity effect of ^{18}O on ^{13}C NMR signals was briefly mentioned in our previous paper.[2] We showed that the carboxyl carbon resonance signal in benzoic acid was shifted upfield 0.031 ppm upon substitution with one oxygen-18 atom and 0.062 ppm upon substitution with two oxygen-18 atoms. Although we did not directly observe the same effect for sodium formate, we did observe that the shift for two oxygen-18 atoms was 0.050 ppm and therefore the shift per ^{18}O would be 0.025 ppm–identical with the isotope shift we observed for the mono-^{18}O-substituted 7-carboxynorbornene epimers.

The additivity effect of multiple oxygen-18 substitution upon ^{13}C NMR signals is elegantly illustrated by the mixed methyl *n*-[^{18}O]butyl orthocarbonates (Figure 1). The relative peak heights observed for each species are in agreement with the statistical distribution calculated from the initial ^{18}O content of the butan-1-ol. The result nicely shows the effect of the substitution of ^{18}O for ^{16}O as each of the five unlabeled and labeled esters can be easily recognized. The magnitude of the isotope effect on the orthocarbonate signal, 0.015 ppm/^{18}O, is much smaller than that which would be expected on the basis of observations[2,3] for alcohols, ether carbons in carboxylates, and ethers (Table I). In fact, the shift of the sp^3-hybridized orthocarbonate carbon atom closely approximates the isotope shift observed for the sp^2-hybridized carbon in a carbon–oxygen single bond—as seen in vinyl esters, phenol, and carboxylates (Table I). The reason for the relatively small shift of 0.015 ppm in these types of compounds is not obvious and will require further investigation.

The additivity effect is demonstrated in another way by the carboxylates. Recognizing that the carbonyl-labeled ester should be an intermediate in the hydrolysis of the ortho ester to ^{18}O-acetic acid,[17] we developed a convenient synthesis for the carbonyl-labeled ester starting with ^{18}O-water and an ortho ester. The isotope-induced shift of the ^{13}C NMR signal of the carboxylate ester carbon when ^{18}O occupies the carbonyl position is 0.038 ppm. When the ^{18}O is located in the ether position the isotope effect is 0.015 ppm (Table I). The sum of these two effects (0.053 ppm) is nearly equal to the isotope effect observed for the totally labeled

(15) Vogel, A. "Textbook of Practical Organic Chemistry"; Longman: London, 1978; pp 371–372.

(16) Bartlett, P. D.; Lefferts, E. B. *J. Am. Chem. Soc.* **1955**, *77*, 2804–2805.

(17) Hutchinson, C. R.; Mabuni, C. T. *J. Labelled Compd. Radiopharm.* **1977**, *13*, 571–574.

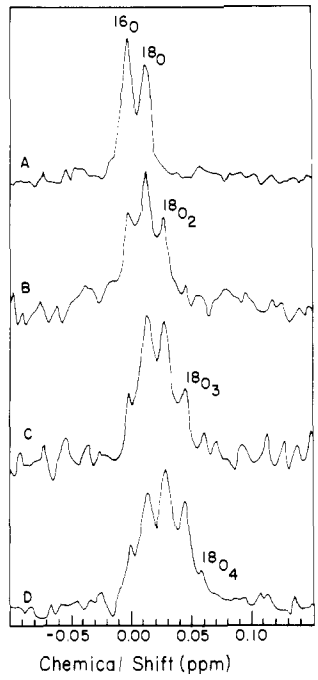

Figure 1. Four mixed methyl *n*-[^{18}O]butyl orthocarbonates illustrate the additivity of the ^{18}O-isotope effect on ^{13}C NMR signals. The upfield shift in the ^{13}C NMR signal of the orthocarbonate carbon is 0.015 ppm/^{18}O (47 atom % ^{18}O in $CDCl_3$/1% Me_4Si). (A) Trimethyl *n*-butyl orthocarbonate. (B) Dimethyl di-*n*-butyl orthocarbonate. (C) Methyl tri-*n*-butyl orthocarbonate. (D) Tetra-*n*-butyl orthocarbonate. On the basis of the ^{18}O content of the *n*-butyl alcohol starting material, the expected distribution of each ^{18}O-labeled orthocarbonate would be as follows:

	statistical distribution, %				
ester	$^{18}O_0$	$^{18}O_1$	$^{18}O_2$	$^{18}O_3$	$^{18}O_4$
butyl trimethyl	53	47			
dibutyl dimethyl	28	50	22		
tributyl methyl	15	40	35	10	
tetrabutyl	8	28	37	22	5

carboxylate—0.054 ppm. The ^{18}O-isotope effect on the carbonyl portion of the carboxylate signal (0.038 ppm) approaches, but remains significantly less than, that observed for aldehydes and ketones ($\simeq$0.050 ppm),[2,3] indicating that it does not behave as an isolated carbonyl group.

There is of course a resonance interaction between the π bond in the carbonyl bond and the p orbitals of the ether-bond oxygen. This resonance interaction appears to be an important factor in affecting the magnitude of the isotope-induced shift, since the resultant carbonyl isotope effect is significantly smaller than the isotope effect observed for the aldehydes and ketones. A similar explanation may be advanced to explain the relatively small isotope shifts observed in the case of the amides.[3] The carbonyl π bond/ether oxygen p orbital interaction appears to be even more important than carbonyl π bond/conjugated double-bond systems, for the change in the isotope effect is much larger in the carboxylate (π bond/p orbital) than in the aldehyde or ketone (conjugated carbonyl π bond/π bond interaction). One might expect that this resonance interaction of the carbonyl π bond/ether oxygen p orbital would significantly affect the magnitude of the ^{18}O-isotope effect on the ether (σ) bond of the carboxylate. The resultant partial double-bond character of the ether bond might lead to an increase in the isotope effect which could approach the isotope effect observed for a carbonyl group. Yet no increase in the ^{18}O-isotope effect on the ether (σ) bond of the carboxylate is observed. The isotope effect is the same as that observed for the other sp^2-hybridized carbon–oxygen single bonds such as phenol or phenyl vinyl ether.[2] The relative magnitudes of the latter isotope effects were explained[2] primarily on the basis of changes in the hybridization of the carbon atom from sp^3 to sp^2. A further possible significance of resonance interactions is not yet clear. The resolution of these points will require more theoretical work.

A relationship between carbon–oxygen bond length and the ^{18}O-isotope effect was discussed previously.[2] The results presented here reinforce the conclusion that there is no general correlation between carbon–oxygen bond length and the magnitude of the ^{18}O-isotope effect, although such a correlation may exist within a specific class of compound. Carbon–oxygen bond lengths are usually longer in amide carbonyls than in esters and shortest in aldehydes and ketones. However, the carbonyl group in the ester shows a greater isotope shift than the amide,[3] but both isotope effects are significantly less than that for the aldehydes or ketones.

Thus the additivity effect of ^{18}O-isotopic substitution upon ^{13}C NMR signals may be added to previously defined additivity effects. For example, the effect of ^{2}H substitution in ^{13}C NMR was nicely illustrated in the cases of multiple substitution in methane and benzene.[4,6] For the case of ^{18}O, the additivity effect was previously illustrated in phosphate (0.020 ppm/^{18}O), permanganate (0.59 ppm/^{18}O), and molybdate (0.25 ppm/^{18}O).[7,8,11,12] In comparison to these latter three tetrahedrally coordinated species, the ^{18}O shift for the orthocarbonate studied here is 0.015 ppm/^{18}O.

The relatively large ^{18}O-isotope effects obtained for the two *tertiary* alcohols reported to date—*tert*-butyl alcohol, 0.035 ppm,[1] and 2-cyclohexylpropan-2-ol, 0.032 ppm[3]—are surprisingly high when compared to the ^{18}O-induced shifts observed for *primary* and *secondary* alcohols,[2,3] which are much smaller. The magnitudes of the isotope effect on the *tertiary* alcohols could conceivably result from the steric constraints of the substituent groups attached to the hydroxyl carbon. If this were the case, then a highly sterically substituted *tertiary* alcohol might be expected to show an even larger isotope effect than those previously observed. We first tested the possibility of steric effects on the ^{18}O-isotope effect in the hindered alcohol triphenylcarbinol (Table I). An ^{18}O-isotope effect of only 0.025 ppm was observed. At first glance this seems small, since one might expect to observe an isotope effect of a magnitude at least similar to that observed with *tert*-butyl alcohol. However, upon closer analysis of the isotope effect in triphenylcarbinol, the smaller shift is quite plausible. It has been observed that the substituent-group effect[2] of the substitution of an aryl group for an alkyl group on the ^{18}O-isotope effect is approximately −0.003 ppm and that effect is largely independent of the structure of the carbon–oxygen functional group.[2,3] Thus, upon substitution of three phenyl groups for the three methyl groups in *tert*-butyl alcohol, for which the isotope effect is 0.035 ppm, a decrease of approximately 0.009 ppm in the isotope effect (to 0.026 ppm) might be expected for triphenylcarbinol as compared to that for *tert*-butyl alcohol. The latter empirically predicted result is very close to the isotope effect which is experimentally observed.

The above argument leads to the conclusion that, although the magnitudes of the isotope effect differ substantially between the two compounds, the two compounds (*tert*-butyl alcohol and triphenylcarbinol) behave similarly and exert the same isotope effect on the hydroxyl carbon. It is only the substituent group which affects the magnitudes of the isotope effect. If steric factors are important in affecting the magnitude of the isotopic shift, then one might conclude that triphenylcarbinol is as sterically hindered as *tert*-butyl alcohol.

To test further the possible importance of steric effects, we synthesized ^{18}O-labeled tri-*tert*-butylcarbinol. The ^{18}O-isotope effect observed in tri-*tert*-butylcarbinol was 0.030 ppm upfield, which is a significant decrease from *tert*-butyl alcohol. If steric effects were contributing to the isotope shift, then at least a comparable isotope shift would be expected in tri-*tert*-butylcarbinol as that observed in *tert*-butyl alcohol. In fact a smaller shift is observed. Thus, substituent electronic effects[2] on the hydroxyl carbon are more likely responsible for the large isotope shifts in *tert*-butyl alcohol and 2-cyclohexylpropan-2-ol.

The possible importance of steric effects in ketones was tested by the synthesis of ^{18}O-labeled di-*tert*-butyl ketone. Di-*tert*-butyl ketone did show an increase of 0.004 ppm in the ^{18}O-isotope effect as compared with acetone.[2] However, the isotope effect is of the same magnitude as that observed for cyclohexanone and cyclohexyl methyl ketone.[3] We conclude that steric effects have little direct

importance in affecting the magnitude of the ^{18}O-induced shift in ^{13}C NMR spectroscopy, at least in these symmetrically substituted examples. The primary factor affecting the magnitude of this isotope effect is the structure of the carbon–oxygen functional group.

Acknowledgment. This investigation was supported by Research Grant GM 27003-10 from the National Institute of General Medical Sciences. We thank Professor Robert Benkeser and Dr. Charles Muth for aiding us in obtaining two of the compounds used in this study.

Chemical, Spectral, Structural, and Charge Transport Properties of the "Molecular Metals" Produced by Iodination of Nickel Phthalocyanine

Charles J. Schramm, Raymond P. Scaringe, Djordje R. Stojakovic, Brian M. Hoffman,* James A. Ibers,* and Tobin J. Marks*[1]

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received February 11, 1980*

Abstract: This paper presents a detailed study of the solid-state chemical, spectral, structural, and charge transport properties of the materials which result from treating nickel phthalocyanine (NiPc) with elemental iodine. A range of $NiPcI_x$ stoichiometries is obtained where $x = 0$ to ca. 3.0; electrical conductivities of compressed polycrystalline samples are comparable with those of other "molecular metals". Single crystals were obtained for $NiPcI_{1.0}$. These crystallize in the space group D_{4h}^2-$P4/mcc$, with two formula units in a unit cell having dimensions $a = 13.936$ (6), $c = 6.488$ (3) Å. Full-matrix least-squares refinement of 65 variables gave a final value of the conventional R index (on F) of 0.042 for 375 reflections having $F_o^2 > 3\sigma(F_o^2)$. The crystal structure consists of stacked, planar NiPc units (staggered by 39.5°) and disordered chains of iodine atoms extending in the c direction. The NiPc units have crystallographically imposed symmetry $4/m$. The interplanar Ni–Ni separation is 3.244 (2) Å, and the intramolecular Ni–N distance, 1.887 (6) Å. Analysis of the diffuse scattering pattern arising from disordered iodine chains reveals that iodine is present as I_3^-. An I–I distance of 3.00 Å and a I···I distance of 3.72 Å are derived from the diffuse scattering. Resonance Raman and iodine-129 Mössbauer spectroscopic measurements indicate that iodine is present predominantly if not exclusively as I_3^- for all $NiPcI_x$ where $x \leq 3$. Optical spectroscopic and X-ray powder diffraction studies of the $x \neq 1.0$ phases suggest that mixtures of several discrete phases are present. Single-crystal electron spin resonance studies (ESR) of $NiPcI_{1.0}$ reveal that the iodine oxidation is ligand centered yielding π radical cations. The charge distribution thus can best be represented as $[Ni^{II}Pc]^{0.33+}(I_3^-)_{0.33}$, although there is ca. 0.002 unit of charge back-transferred from each I_3^- unit to the metallomacrocycle stack. Susceptibility measurements by ESR and static techniques can be interpreted in terms of a narrow bandwidth metal (ca. 0.37 eV) and a significant contribution from van Vleck paramagnetism. The electrical conductivity of $NiPcI_{1.0}$ crystals has been investigated by four-probe techniques. Room-temperature conductivities along the crystallographic stacking direction are in the range 260–750 Ω^{-1} cm^{-1} and carrier mean free paths are in the range 3.3–8.2 Å. The temperature dependence of the conductivity is metallic ($\rho \sim T^{1.9\pm0.2}$) down to ca. 55 K, at which point there occurs an abrupt reduction in conductivity. Neither the resonance Raman of the I_3^-, the ESR line width, nor the magnetic susceptibility is sensitive to this transition.

Present experience indicates that for a coordination compound to form an electrically conductive molecular crystal two criteria are highly desirable, if not essential. First, the metal–ligand molecules must be arrayed in close communication and in crystallographically similar environments. Second, the metal–ligand complex must adopt a nonintegral formal oxidation state.[2] The latter characteristic has been referred to as "partial oxidation", "mixed valence", or "incomplete charge transfer", and, although this state has generally been effected with oxidizing agents, in principle it could equally well be achieved by a partial reduction. The highly conductive coordination compounds studied to date, as exemplified by the tetracyanoplatinate materials, represent a class of materials in which transport properties can be understood almost completely in terms of the charge carriers being confined to a conducting spine of metal atoms.[2] The coordinated ligands (e.g., CN^-) are essential in dictating the structural and electronic properties of the metal-atom chain, but appear to play little or no direct role in the charge-transport process.

Mixed-valent coordination complexes of an entirely different variety are represented by a growing number of partially oxidized materials containing metal complexes of planar, conjugated organic ligands.[3-5] Especially in the case of iodine oxidants, it is possible to synthesize broad classes of nonintegral oxidation state materials,

(1) Camille and Henry Dreyfus Teacher-Scholar.

(2) (a) Miller, J. S.; Epstein, A. J., Eds. *Ann. N.Y. Acad. Sci.* **1978**, 313. (b) Keller, H. J., Ed. "Chemistry and Physics of One Dimensional Metals", Plenum Press: New York, 1977. (c) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1–151. (d) Keller, H. J., Ed. "Low Dimensional Cooperative Phenomena"; Plenum Press: New York, 1975.

(3) (a) Petersen, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286–288. (b) Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Science* **1978**, *200*, 47–48.

(4) (a) Phillips, T. E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 7734–7736. (b) Hoffman, B. M.; Phillips, T. E.; Schramm, C. J.; Wright, S. K. In "Molecular Metals", Hatfield, W. E., Ed.; Plenum Press: New York, 1979; pp 393–398. (c) Wright, S. K.; Schramm, C. J.; Phillips, T. E.; Scholler, D. M.; Hoffman, B. M. *Synth. Met.* **1979/80**, *1*, 43–51. (d) Phillips, T. E.; Scaringe, R. P.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3435–3444.

(5) (a) Marks, T. J. In ref 2a, pp 594–616. (b) Cowie, M.; Gleizes, A.; Grynkewich, G. W.; Kalina, D. W.; McClure, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2921–2936. (c) Brown, L. D.; Kalina, D. W.; McClure, M. S.; Ruby, S. L.; Schultz, S.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *ibid.* **1979**, *101*, 2937–2947. (d) Kalina, D. W.; Lyding, J. W.; McClure, M. S.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.*, in press. (e) Lin, L.-S.; Marks, T. J.; Kannewurf, C. R.; Lyding, J. W.; McClure, M. S.; Ratajack, M. T.; Whang, T.-C. *J. Chem. Soc., Chem. Commun.*, in press. (f) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7071–7073. (g) Marks, T. J.; Schoch, K. F., Jr.; Kundalkar, B. R. *Synth. Met.* **1980**, 1, 337–347.

0002-7863/80/1502-6702$01.00/0