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Acetoxymercuration of alkynes. ^{199}Hg NMR spectra of addition products from arylphenylethynes

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ABSTRACT: ^{199}Hg NMR spectra were measured in acetic acid, dichloromethane and chloroform for a series of mercurated arylphenylethenes derived from the acetoxymercuration of alkynes. Good linear correlations between ^{199}Hg chemical shifts and Hammett σ values, UV absorption maxima and calculated mercury atomic charge were obtained and are explained on the basis of electronic substituent effects. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{199}Hg chemical shifts, acetoxymercuration; alkynes; electronic effects

INTRODUCTION

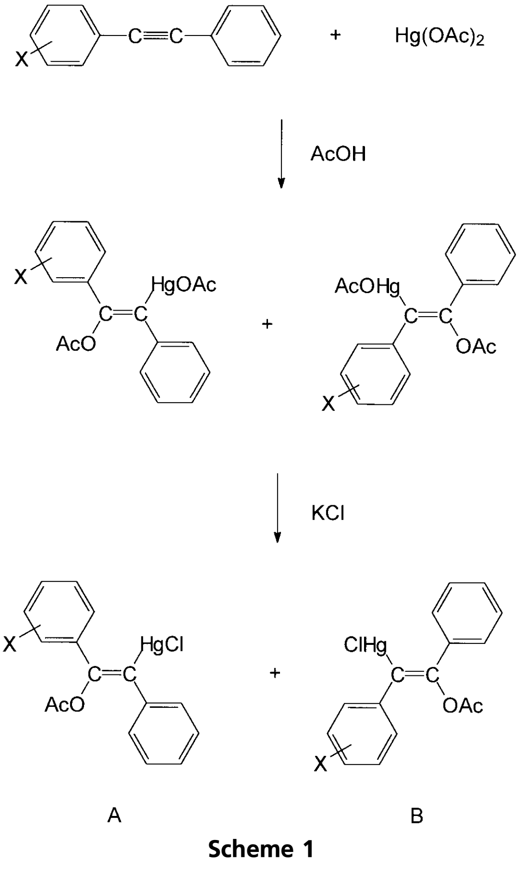
Among the several elements that have at least one nuclide suitable for NMR studies, mercury has two magnetically active isotopes, ^{201}Hg and ^{199}Hg. The latter has nuclear spin $I = 1/2$ and its natural abundance (16.84%) and receptivity (5.42 with respect to ^{13}C) make its direct detection by NMR relatively easy.[1–3] Following the pioneering work of Borzo and Maciel,[4] a wealth of data have been published on ^{199}Hg Fourier transform NMR spectra of inorganic and organometallic derivatives of mercury.[5,6] Also, magic angle spinning ^{199}Hg NMR has yielded valuable information for distinguishing different coordination environments in mercury complexes.[7]

In addition to the importance of accurately expanding the known ^{199}Hg shift data bank, our interest in organomercury compounds lies in the elucidation of the mechanism of the acetoxymercuration of alkynes (Scheme 1).[8,9] Kinetic studies carried out with different families of substituted alkynes demonstrated that the reaction occurs via an electrophilic attack in the rate-determining step. Linear free energy relationships together with the observed regiochemistry indicated that the cationic intermediate can shift from a bridged mercurinium species to a carbocation, depending on the substituent X of the phenyl ring.[8–10] The reaction is stereospecific, leading to the detection of mainly one structural isomer, generally the *E*-isomer from reactions carried out in acetic acid,[9–11] whereas the *Z*-isomer was obtained in alcohols.[12]

^{199}Hg chemical shifts are known to be very sensitive to the electronic environment and geometry at the mercury centre.[5] ^{199}Hg NMR could therefore be very useful in determining, by direct detection of the metal resonance, the structure of the reaction intermediate. It seems necessary, however, to define the ^{199}Hg NMR properties of the products of the acetoxymercuration of alkynes before attempting a spectroscopic study of the reaction mechanism. We have therefore carried out a systematic investigation of the NMR behaviour of a series of mercurated arylphenylethenes derived from the acetoxymercuration of alkynes.

RESULTS AND DISCUSSION

The general formula of the compounds investigated is shown is Scheme 1. Chloromercurio derivatives, characterized as described previously,[13] were used instead of



Scheme 1

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Table 1. ^{199}Hg chemical shifts for 1-acetoxy-2-chloromercuriodiarylethenes

Compound	X	X′	$-\delta$ AcOD [$\Delta\nu_{1/2}$ (Hz)]	$-\delta$ (CD_2Cl_2) [$\Delta\nu_{1/2}$ (Hz)]	$-\delta$ ($CDCl_3$) [$\Delta\nu_{1/2}$ (Hz)]
1	*p*-OMe	H	1201.0 [85]	1148.7 [140]	1149.2 [110]
2	*p*-Me	H	1203.1 [100]	1151.1 [85]	1154.6 [85]
3	H	H	1207.5 [75]	1155.2 [85]	1154.9 [85]
4	*p*-F	H	1212.6 [–][a]	1157.0 [–][a]	1155.4 [100]
5	H	*p*′-F	1214.3 [–][a]	1157.7 [–][a]	
6	H	*p*′-I	1215.1 [75]	1157.3 [100]	1155.3 [75]
7	H	*p*′-Cl	1215.9 [100]	1161.5 [70]	1157.6 [85]
8	*m*-F	H	1216.3 [–][a]	1159.9 [90]	1158.9 [100]
9	H	*m*′-F	1218.4 [–][a]		
10	H	*m*′-Cl	1219.3 [75]	1159.0 [100]	1157.4 [100]
11	H	*m*′-Br	1219.5 [95]	1158.7 [125]	1156.8 [120]
12	H	*p*′-Br	1219.6 [80]	1161.5 [85]	1160.7 [85]
13	H	*m*′-NO_2	1226.7 [85]	1160.9 [90]	1167.5 [90]
14	H	*p*′-NO_2	1231.8 [75]	1167.7 [100]	1168.1 [85]

[a] Not determined.

the acetoxymercurio species originating from the reaction because they are more suitable for crystallization.[11–13]

Data obtained for the series investigated are reported in Table 1. In many cases the interpretation of ^{199}Hg chemical shifts reported in the literature for mercury derivatives is confused by the uncertainty on the species to which they refer and by the different temperatures at which data were recorded. All the data reported here are referred to the resonance of $HgMe_2$ ($\delta = 0.0$) and were collected at a constant temperature of 298 K.

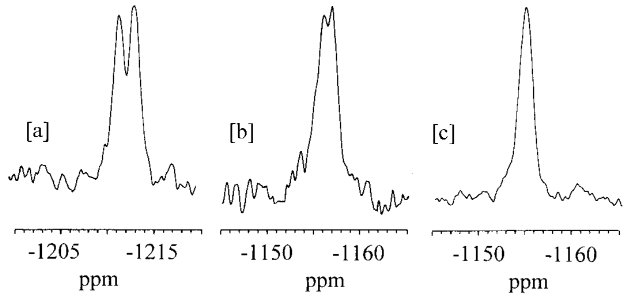

Figure 1. ^{199}Hg NMR spectra of a 1 : 1 mixture of (*E*)-1-acetoxy-2-chloromercurio-1-(*p*-fluorophenyl)-2-phenylethene (**4**) and (*E*)-1-acetoxy-2-chloromercurio-2-(*p*-fluorophenyl)-1-phenylethene (**5**) in (a) acetic acid, (b) dichloromethane and (c) chloroform.

Three different solvents were used: acetic acid because it is the solvent of the acetoxymercuration reaction and chloroform and dichloromethane for comparison with the data published in these solvents for numerous organomercurio derivatives.[6,14]

The δ ^{199}Hg values in chlorinated solvents fall within a 20 ppm range, whereas those in acetic acid are slightly more sensitive to the effect of substituents ($\Delta\delta_{max} = 30$ ppm). There is a general pattern of higher shielding when acetic acid is used as a solvent, the difference between the shifts in dichloromethane and those in the acetic acid being *ca* 60 ppm, indicating, as expected a stronger electrostatic interaction in the more polar solvent, in agreement with previously reported data.[6]

Variation of the solvent also affects the spin–lattice relaxation times that were determined from the unsubstituted chloromercuriodiphenylethene (**3**) in acetic acid and dichloromethane ($T_1 = 19$ and 46 ms, respectively). Introducing a substituent on one of the phenyl rings does not alter significantly the relaxation time ($T_1 = 43$ ms for **7** in dichloromethane), nor does the substitution of AcO for Cl at the metal centre ($T_1 =$ 19 ms for acetoxymercuriodiphenylethene in acetic acid). Relaxation arising from chemical shift anisotropy is the dominant mechanism at field strengths $B_0 \geqslant 4.7$ T for mercury compounds and produces broad resonances.[6] The measured half-height linewidths in the

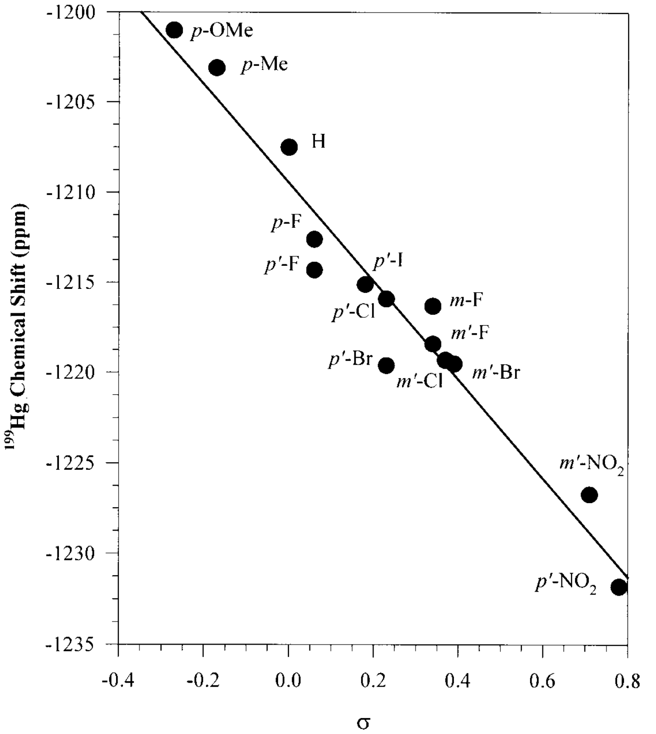

Figure 2. Least-squares fit of ^{199}Hg chemical shifts measured in AcOH *vs.* Hammett σ ($r^2 = 0.954$).

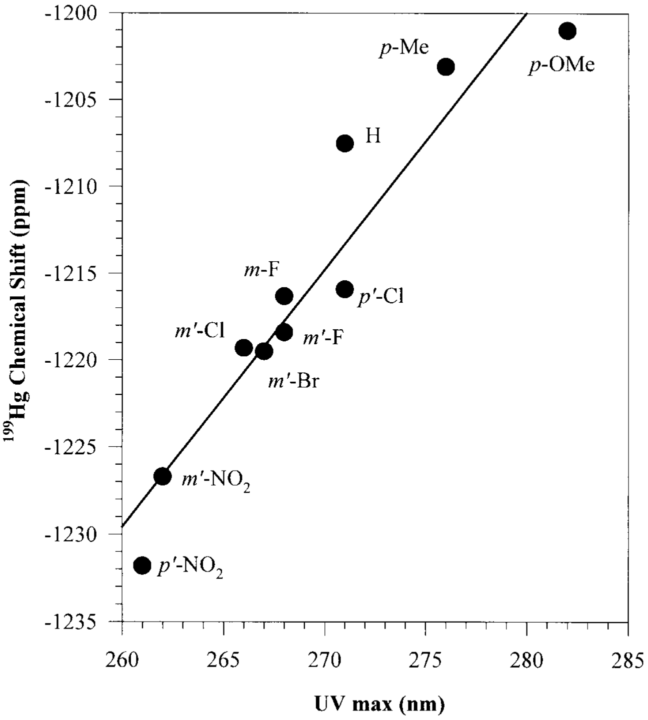

Figure 3. Least-squares fit of ^{199}Hg chemical shift *vs.* UV absorption of arylphenylethenes in AcOH ($r^2 = 0.899$).

series of investigated compounds vary from 75 to 140 Hz and their values do not show any significant correlation with structural isomerism or solvent variation (Table 1).

When acetic acid is used as a solvent two distinct resonances were observed in the cases when the products of acetoxymercuration are a *ca* 1:1 mixture of regioisomers. [*p*-F (**4**)–*p*′-F (**5**) and *m*-F (**8**)–*m*′-F (**9**)] [Fig. 1(a)]. In dichloromethane two resonances for regioisomers were observed only for the **4**–**5** mixture [Fig. 1(b)], while the spectrum consists of a single resonance when the solvent is chloroform [Fig. 1(c)]. We have tentatively attributed the most upfield shifted resonance to the species where fluorine is closer to mercury since electron-withdrawing substituents on organomercurio compounds are known to increase shielding and the effect would be the stronger the closer the substituent is to the metal centre.[5]

Exchange with chloride ions, present in deuterochloroform as hydrogen chloride impurity, was also observed: the δ value measured for 1-acetoxy-2-acetoxymercurio-1,2-diphenylethene in chloroform ($\delta = -1154.9$) is in fact a value typical of RHgCl species. The spectrum of the same compound dissolved in acetic acid shows a resonance at $\delta = -1525.7$, consistent with its formulation as an acetoxymercurio species. Therefore, it seems advisable not to use chlorinated solvents for the study of RHgX derivatives.

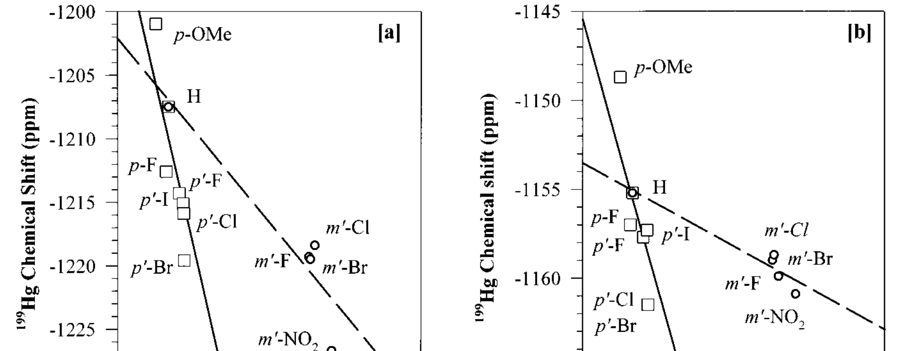

Figure 4. Least-squares fits of ^{199}Hg chemical shift measured in (a) AcOH and (b) CH_2Cl_2 *vs.* calculated Hg atomic charge. For the series of *para*-substituted compounds $r^2 = 0.889$ in AcOH and $r^2 = 0.797$ in CH_2Cl_2.

The electronic effect of the substituents is clearly expressed by the graph shown in Fig. 2, where ^{199}Hg chemical shifts are plotted against Hammett σ values. The correlation is good with the δ values measured in acetic acid, with a higher shielding shown by the species with electron-withdrawing substituents. Data in dichloromethane give a poorer correlation but the trend is still present.

Figure 3 reports is graphical form the correlation between δ ^{199}Hg and the wavelength of the highest UV absorption in the optical spectra of the series of mercurated arylphenylethenes. The correlation is fairly good and can be explained by the dependence of ^{199}Hg chemical shifts on the paramagnetic term of the nuclear screening constant σ_p. This is in fact a function of ΔE^{-1}, where ΔE is the mean excitation energy of the magnetic dipole-allowed electronic transitions. In the case of heavy nuclei, such as mercury, variations in nuclear shielding are in fact dominated by σ_p.[6] A similar trend has been reported previously for silyl mercury derivatives.[15]

The good correlation observed between δ ^{199}Hg and Hammett σ values can be explained as an effect of the electron density at mercury, since variation of the shielding with atomic charge is a well known property of all nuclei and σ_p is a function of the effective nuclear charge.[15] A theoretical approach based on *ab initio* calculation with the RHF/LanL2Dz[16] basis set was used to determine the mercury atom charge, which was calculated by Mulliken population analysis (MPA). Atomic charges are not quantum mechanical observables and methods for their calculation are necessarily arbitrary. Therefore, it is not the absolute values obtained that should be considered, but only their variation within the series. Figure 4(a) shows the correlation obtained between the ^{199}Hg chemical shifts measured in acetic acid and the calculated charges. When the δ values measured in dichloromethane are considered, the correlation is not as good for the *para*-substituted compounds but it is better for the series of *meta*-substituted compounds [Fig. 4(b)].

In the case of organomercurio derivatives, a decrease in the mercury atomic charge parallels the decrease in ΔE and is expected to cause an increase in shielding, as reflected by our results.[5,6] The data show the great sensitivity of δ ^{199}Hg to changes in charge density that is >1000 ppm e^{-1} for the *para*-substituted derivatives and *ca* 300 ppm e^{-1} for the *meta*-substituted compounds.

EXPERIMENTAL

Mercury derivatives of arylphenylethenes were prepared and characterized as reported previously.[13]

Electronic spectra were recorded with a Cary 1E spectrophotometer. A Bruker AM 400 NMR spectrometer operating at a frequency of 71.64 MHz was used to obtain ^{199}Hg NMR spectra. All chemical shifts are given in ppm from neat $HgMe_2$ used as an external standard. The temperature was maintained at 298 K by means of a variable-temperature controller. Typical spectra consist of 512 transients of 4096 data points over an 8 kHz bandwidth with a 90° pulse of 12.5 μs. Non-selective spin–lattice relaxation times were obtained by using the standard (180°–τ–90°) inversion–recovery method with a repetition rate of 2 s^{-1}. T_1 relaxation times were calculated from semilogarithmic plots derived from spectra consisting of 256 scans. The mean square errors did not exceed 10%. The concentration of the samples was in the range 5×10^{-2}–5×10^{-3} M. A 1 : 2 mixture of deuterated and non-deuterated solvents was used. No variation of chemical shifts was observed in such a concentration range.

Starting from crystallographic data,[11] geometry optimization and MPA analysis were performed using the Gaussian 94 system of programs.[17]

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