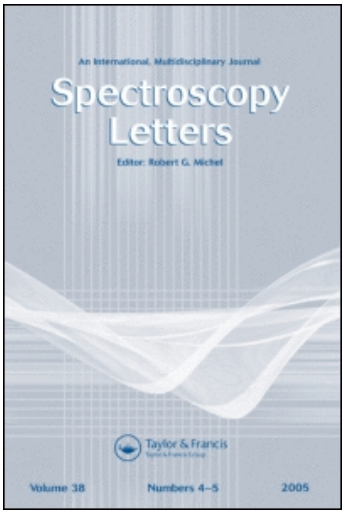

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Haloacetylated Compounds: Solvent Effects on the ^{17}O Nmr Chemical Shifts of 1,1,1-Trichloro-4-Methoxy-3-Alken-2-Ones

Marcos A. P. Martins[a]; Geonir M. Siqueira[a]; Alex F. C. Flores[a]; Nilo Zanatta[a]; Helio G. Bonacorso[a]
[a] Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, Brazil

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HALOACETYLATED COMPOUNDS: SOLVENT EFFECTS ON THE ^{17}O NMR CHEMICAL SHIFTS OF 1,1,1-TRICHLORO-4-METHOXY-3-ALKEN-2-ONES

Key Words: ^{17}O NMR, solvent effect, vinyl ketone, MO Calculations

Marcos A. P. Martins*, Geonir M. Siqueira, Alex F.C. Flores, Nilo Zanatta and Helio G. Bonacorso

Departamento de Química, Universidade Federal de Santa Maria
97.105-900 Santa Maria, RS, Brazil
e-mail: *mmartins@base.ufsm.br*
http://*www.ufsm.br/nuquimhe*

ABSTRACT

A multi-linear-regression analysis using the Kamlet-Abboud-Taft (KAT) solvatochromic parameters in order to elucidate and quantify the solvent effects on the ^{17}O chemical shifts of *(E)*-1,1,1-trichloro-4-methoxy-3-penten-2-one (**1**) and *(E)*-1,1,1-trichloro-4-methoxy-3-methyl-3-buten-2-one (**2**) are reported. The chemical shifts of carbonyl group of the two molecules show similar dependencies (in ppm) on the solvent polarity-polarizability (-17π*, -15π*) and the solvent hydrogen-bond-donor (HBD) acidities (-7α, -6α). The influence of the solvent hydrogen-bond-acceptor (HBA) basicities is significant for compound **1** (3β) and small for compound **2** (0.7β).

*Author to whom the correspondence should be addressed

The chemical shifts of the methoxy group of the two molecules shows the same dependence (in ppm) on the solvent polarity-polarizability (9π*) and the influence of the solvent hydrogen-bond-donor (HBD) acidities. Note that the solvent hydrogen-bond-acceptor (HBA) basicities were negligible. The data obtained from MO calculations suggest that the solvent effects on compounds **1,2** reflect their conformational structure.

INTRODUCTION

Several papers have been devoted to the empirical and theoretical studies of solvent effect on the ^{17}O chemical shifts in different organic compounds[1-3]. Special attention has been devoted to the study of solvent effects in amides, where the ^{15}N and ^{17}O nuclei are observed[2,3]. However, a multi-linear-regression analysis using the Kamlet-Abboud-Taft (KAT) solvatochromic parameters in order to elucidate and quantify the solvent effects on the ^{17}O chemical shifts of amides[3] seems the most convenient model to extend to other compounds. According to the KAT formalism, the observed chemical shift of compound X at infinite dilution in solvent Y, δ^X_Y, would be given by the relationship[2] shown in Equation 1.

$$\delta^X_Y = \delta^X_{CH} + s^X(\pi^*_Y + d^X\delta_Y) + a^X\alpha_Y + b^X\beta_Y \qquad [1]$$

The solvent effects are described by the solvent parameters δ^X_{CH}, π^*_Y, δ_Y, α_Y and β_Y. The π^*_Y scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole due to its dielectric effect. The α_Y scale of solvent hydrogen-bond-donor (HBD) acidities describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond. The β_Y scale of hydrogen-bond-acceptor (HBA) basicities measures the ability of the solvent to accept a proton (*i.e.*, to donate an electron pair) in a solute-to-solvent hydrogen bond. The δ_Y parameter is a polarizability correction term for polychlorinated ($\delta_Y = 0.5$) and aromatic ($\delta_Y = 1.0$) solvents. The coefficients s^X, a^X and b^X in Eq. [1] define the sensitivity of δ^X_Y to solvent dipolarity/polarizability, acidity and basicity, respectively. The product of coefficients s^Xd^X defines the sensitivity of δ^X_Y for the polarizability correction term. The term δ^X_{CH} is the chemical shift of substrate X measured in cyclohexane since this reference solvent does not form a hydrogen bond ($\alpha_{CH} = \beta_{CH} = 0$) and was selected to define the origin of π^*_Y scale ($\pi^*_{CH} = 0$). The term $s^X(\pi^*_Y + d^X\delta_Y)$ accounts for the difference between the contribution to δ

$^{X}_{Y}$ in solvent Y and in cyclohexane from the solute-solvent interactions other than hydrogen bonding. The terms $a^X \alpha_Y$ and $b^X \beta_Y$ represent the contributions from hydrogen bonds of substrate X with solvents HBD and HBA, respectively.

As a part of our research program we have studied the multi-nuclear NMR chemical shifts[4] of β-alkoxyvinyl halomethyl ketones (used as precursors for the synthesis of 5-, 6- and 7-membered heterocycles[5,6]). Considering the electron *push-pull* structure of these substrates, where there is a donor group (OR) and an acceptor group (CO), they can be used as good models to study the solvent effect in a non protic substrate and with the advantage to allow direct observation of the two oxygen sites involved. Thus, the aim of this work is to elucidate and quantify the solvent effects on the ^{17}O chemical shifts of (*E*)-1,1,1-trichloro-4-methoxy-3-penten-2-one (**1**) and (*E*)-1,1,1-trichloro-4-methoxy-3-methyl-3-buten-2-one (**2**) using the Kamlet-Abboud-Taft (KAT) solvatochromic parameters[2] (Scheme).

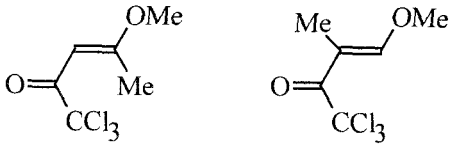
RESULTS AND DISCUSSION

The synthesis of compounds **1,2** was described elsewhere[5]. The ^{17}O chemical shifts of (*E*)-1,1,1-trichloro-4-methoxy-3-penten-2-one (**1**) and (*E*)-1,1,1-trichloro-4-methoxy-3-methyl-3-buten-2-one (**2**) in various solvents are listed in Table 1. These values were determined by extrapolation to infinite dilution from spectral data obtained in several concentrations (0.5M to 6M) relative to external water, at 303 K, (see experimental). The Kamlet-Abboud-Taft (KAT) solvatochromic parameters (π^*_Y, α_Y, β_Y and δ_Y) used in the present work are also given in Table 1. Considering the ^{17}O NMR chemical shifts of oxygen atoms of the carbonyl group and methoxy group on compounds **1,2** and according to the KAT formalism, we can re-write the Equation 1 as Equations 2 and 3 (where X = CO and OMe).

$$\delta^{CO}_{Y} = \delta^{CO}_{CH} + s^{CO}(\pi^*_Y + d^{CO}\delta_Y) + a^{CO}\alpha_Y + b^{CO}\beta_Y \quad [2]$$

$$\delta^{OMe}_{Y} = \delta^{OMe}_{CH} + s^{OMe}(\pi^*_Y + d^{OMe}\delta_Y) + a^{OMe}\alpha_Y + b^{OMe}\beta_Y \quad [3]$$

Table 2 presents the least-squares-fitted solute (**1,2**) estimates using Equations 2,3. Preliminary comparison shows that the response values of the oxygen chemical shifts to the solvent-solute dipolarity-polarizability (parameter s^X) are the most important and nearly the same for both CO groups (-17π*, -15π*) and OMe groups (9π*) in the two molecules. The response to the solvent HBD acidities



1 2

SCHEME

TABLE 1

^{17}O NMR chemical shifts of compounds 1, 2 at infinite dilution[a] and solvent parameters[b] used in Equations 2,3.

Solvent (Y)	1 (X)		2 (X)		Solvent Parameters			
	C=O	OMe	C=O	OMe	π*	α	β	δ
n-Hexane	477.73	107.72	508.13	75.05	-0.11	0.00	0.00	0.0
Chloroform	462.35	113.78	493.17	80.53	0.69	0.44	0.00	0.5
Acetone	466.87	115.90	499.09	83.20	0.62	0.08	0.48	0.0
Acetonitrile	463.01	117.03	495.46	84.49	0.66	0.19	0.31	0.0
Toluene	470.82	112.14	498.61	77.66	0.49	0.00	0.11	1.0
Dichloromethane	462.92	114.29	494.00	80.34	0.73	0.30	0.00	0.5
Dimethylsulfoxide	459.33	118.66	491.81	83.90	1.00	0.00	0.76	0.0
Methanol	460.69	115.19	492.43	81.25	0.60	0.93	0.62	0.0
Tetrachloromethane	473.16	109.60	503.57	75.41	0.21	0.00	0.00	0.5
Dimethylformamide	464.15	116.99	494.26	85.43	0.88	0.00	0.69	0.0

[a]See experimental

[b]From references 2,3.

TABLE 2

Least-square-fitted solute (**1**,**2**) parameters for Equations 2,3.

Compd. (X)	δ^X_{CH}	s^X	sd^X	d^X	a^X	b^X	r / sd
1 (CO)	475.73	-17.44	3.265	-0.19	-7.05	3.33	0.990 / 1.14
2 (CO)	506.93	-14.99	-0.865	0.06	-6.38	0.75	0.992 / 0.88
1 (OMe)	109.12	9.04	-2.138	-0.24	-0.02	1.11	0.977 / 0.99
2 (OMe)	76.55	9.61	-4.458	-0.46	-0.72	-0.38	0.953 / 1.49

(parameter a^X) is important for CO groups (-7α, -6α) and negligible for OMe groups (0α, -0.7α). The response to the solvent HBA basicities (parameter b^X) is small and variable for both groups. The influence of the solvent hydrogen-bond-acceptor (HBA) basicities is significant only for compound **1** (CO group 3β and OMe group 1β).

The contributions (in ppm) to the ^{17}O chemical shifts of CO and OMe for compounds **1,2** from terms of Equations 2,3 (Table 2) are listed in Table 3. The solvent-solute dipolarity-polarizability (parameter $s^X\pi^*$) show a shielding effect for chemical shift of CO groups (**1,2**) in all solvents, except for *n*-hexane, arranged as follows: dimethylsulfoxide > dimethylformamide > dichloromethane > chloroform > acetonitrile > acetone > methanol > toluene > tetrachloromethane. The solvent HBD acidities (parameter $a^X\alpha$) show a shielding effect for chemical shift of CO groups (**1,2**) in some solvents arranged as follows: methanol > chloroform > dichloromethane > acetonitrile > acetone. The response to the solvent HBA basicities (parameter $b^X\beta$) show a deshielding effect for chemical shift of CO groups (**1,2**) in some solvents arranged as follows: dimethylsulfoxide > dimethylformamide > methanol > acetone > acetonitrile > toluene.

The solvent-solute dipolarity-polarizability (parameter $s^X\pi^*$) shows a deshielding effect for a chemical shift of OMe groups (**1,2**) in all solvents, except for *n*-hexane, arranged in the same order observed for CO groups. The solvent HBD acidities (parameter $a^X\alpha$) and HBA basicities (parameter $b^X\beta$) show a negligible effect for chemical shift of OMe groups (**1,2**) in all solvents ($< |0.8|$ ppm).

The predominant conformational structures of compounds **1,2** were determined by energy minimization calculations using the AM1 semiempirical method[7,8]. These data, listed in Table 4, show that the primary conformation of **1** is IV (99%) while the compound **2** has two main structures I and III. Conformation IV has the dihedral angles O=C-C=C and C=C-O-Me equal zero. The resonance in the conjugated system is 100%. For both conformations I and III, the carbonyl group is about 40° out of the C-C=C plane. The resonance in the conjugated system is about 50%. This difference in resonance of the conjugated system could explain the greater sensitivity of s^X, a^X, b^X for the carbonyl oxygen atom of compound **1** compared to compound **2**. Also the b^X of the methoxy oxygen atom in compound **1** is much larger than that in compound **2**. Finally, the net charges for oxygen atoms of **1,2** are in agreement with the solvent effect observed (Table 4).

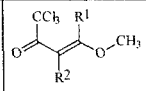
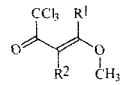
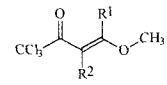
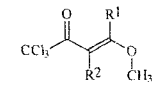
TABLE 3

Contributions (in ppm) to the ^{17}O chemical shift of CO and OMe on compounds **1**,**2** from terms of Equations 2,3.

Compd./ X	**1** / CO				**2** / CO			
Solvent (Y)	$s^X\pi^*$	$sd^X\delta$	$a^X\alpha$	$b^X\beta$	$s^X\pi^*$	$sd^X\delta$	$a^X\alpha$	$b^X\beta$
n-Hexane	1.9	0.0	0.0	0.0	1.7	0.0	0.0	0.0
Chloroform	-12.0	1.6	-3.1	0.0	-10.3	-0.4	-2.8	0.0
Acetone	-10.8	0.0	-0.6	1.6	-9.3	0.0	-0.5	0.4
Acetonitrile	-11.5	0.0	-1.3	1.0	-9.9	0.0	-1.2	0.2
Toluene	-8.5	3.3	0.0	0.4	-7.3	-0.9	0.0	0.1
Dichloromethane	-12.7	1.6	-2.1	0.0	-10.9	-0.4	-1.9	0.0
Dimethylsulfoxide	-17.4	0.0	0.0	2.5	-15.0	0.0	0.0	0.6
Methanol	-10.5	0.0	-6.6	2.1	-9.0	0.0	-5.9	0.5
Tetrachloromethane	-3.7	1.6	0.0	0.0	-3.1	-0.4	0.0	0.0
Dimethylformamide	-15.3	0.0	0.0	2.3	-13.2	0.0	0.0	0.5
Compd./ X	**1** / OMe				**2** / OMe			
Solvent (Y)	$s^X\pi^*$	$sd^X\delta$	$a^X\alpha$	$b^X\beta$	$s^X\pi^*$	$sd^X\delta$	$a^X\alpha$	$b^X\beta$
n-Hexane	-1.0	0.0	0.0	0.0	-1.1	0.0	0.0	0.0
Chloroform	6.2	-1.1	0.0	0.0	6.6	-2.2	-0.3	0.0
Acetone	5.6	0.0	0.0	0.5	6.0	0.0	-0.1	-0.2
Acetonitrile	6.0	0.0	0.0	0.3	6.3	0.0	-0.1	-0.1
Toluene	4.4	-2.1	0.0	0.1	4.7	-4.5	0.0	0.0
Dichloromethane	6.6	-1.1	0.0	0.0	7.0	-2.2	-0.2	0.0
Dimethylsulfoxide	9.0	0.0	0.0	0.8	9.6	0.0	0.0	-0.3
Methanol	5.4	0.0	0.0	0.7	5.8	0.0	-0.7	-0.2
Tetrachloromethane	1.9	-1.1	0.0	0.0	2.0	-2.2	0.0	0.0
Dimethylformamide	8.0	0.0	0.0	0.8	8.5	0.0	0.0	-0.3

TABLE 4

Structural data[a] obtained by AM1 calculations for compounds **1**,**2**.

Structure		I (*EEE*)	II (*EEZ*)	III (*EZE*)	IV (*EZZ*)
R^1 R^2 1 Me H 2 H Me					
Isomer (%)	**1**	0	0	1	99
	2	46	6	42	6
Dihedral angle O=C-C=C (Degrees)	**1**	-	-	-5	0
	2	134	-128	-41	52
Dihedral angle C=C-O-Me (Degrees)	**1**	-	-	179	0
	2	176	3	179	6
Oxygen Net Charges	**1**	-	-	-	-0.27/-0.20
CO/MeO	**2**	-0.23/-0.20	-	-0.25/-0.21	-
Energy	**1**	-	-	-1676.0	-1679.1
(kcal.mol^{-1})	**2**	-1673.7	-1672.5	-1673.6	-1672.5

[a]See experimental.

EXPERIMENTAL

Compounds

The synthesis of compounds **1**,**2** was developed in our laboratories[5].
^{1}H NMR data: (**1**) 5.91 (H3, s), 2.40 (Me4, s); (**2**) 1.90 (Me3, d, ^4J = 1.1), 7.85 (H4, q, ^4J = 1.1). ^{13}C NMR data: (**1**) 98.4 (C1), 180.4 (C2), 90.8 (C3), 180.7 (C4), 20.3 (Me4), 56.7 (OMe); (**2**) 96.2 (C1), 181.3 (C2), 107.7 (C3), 164.9 (C4), 10.2 (Me3), 62.2 (OMe)

NMR Spectroscopy

The ^{17}O NMR spectra were recorded on a Bruker DPX 400 at 54.25 MHz. The sample temperature was set at 300 ±1 K. The instrumental settings were as follows: spectral width 38 KHz (705 ppm), 8K data points, pulse width 12 μs, acquisition time 54 ms, preacquisition delay 10 ms, 16000-90000 scans, LB of 100 Hz, sample spinning 20 Hz. The spectra were recorded with a RIDE (RIng Down Eliminate)

sequence[16] for suppression of acoustic ringing. The general reproducibility of chemical shift data is estimated to be better than ±1.0 ppm (±0.2 within the same series). The half-height widths were in the range 150-300 Hz.

All spectra were acquired in a 10mm tube, at natural abundance, in *n*-hexane, chloroform, acetone, acetonitrile, toluene, dichloromethane, dimethylsulfoxide, methanol, tetrachloromethane and dimethylformamide as solvents. The concentration of the compounds used in these experiments was 0.5, 1.0, 2.0, 3.0, 4.0 and 6.0 M, and the signals were referenced to external H_2O (in a capillary coaxial tube).

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 (^1H at 200.13 MHz and ^{13}C at 50.32 MHz), 300 K, 0.5 M in chloroform-d_1/TMS. The general reproducibility of chemical shift data was estimated to be better than ±0.01 ppm.

Semiempirical MO Calculations

The MO calculations were carried out by the Austin Model 1 (AM1) semiempirical method[7], implemented in the HyperChem 4.5 package (1995)[8]. Geometries were completely optimized without fixing any parameter, thus bringing all geometric variables to their equilibrium values. The energy minimization protocol employs the Polak-Ribiere algorithm, a conjugated gradient method[8]. Convergence to a local minimum is achieved when the energy gradient is < 0.01 kcal.mol^{-1}. The relative abundance of each species in equilibrium is calculated from the minimum energy associated with each compound employing the relationships: (*i*) $\Delta E = -RT \ln K$ (where ΔE stands for the standard energy difference between two given species, R is the molar gas constant expressed in units of kcal.mol^{-1}.K^{-1}, T is the absolute temperature in K, K is the corresponding equilibrium constant) and (*ii*) [I] + [II] + [III] + [IV] = 100, where [I], [II], [III] and [IV] represent the percentage molar ratio of each conformer in equilibrium. The calculations were performed on a PC Pentium II 400MHz computer equipped with a printer.

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