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Solvent Effects in the Methyl Resonances Exhibited by Methyltelluronium Salts

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Introduction

Dance and co-workers [1] reported that the chemical shift they observed for the methyl resonance of $(C_6H_5)_2CH_3TeI$ in dimethyl sulfoxide (Me_2SO), 2.69 ppm, differed markedly from that in $CDCl_3$, 3.04 ppm. These investigators suggested that an explanation for the observed effect might lie in the existence of two forms of the salt, 'ionic' and 'covalent'. The former would predominate in polar solvents such as Me_2SO, while the latter would represent the more likely form in a solvent having a low dielectric constant such as $CDCl_3$.

We have made a similar observation and offer an alternate interpretation. Solutions of 10-methylphenoxatelluronium iodide (CH_3PTe^+, I^-) in Me_2SO-d_6 exhibit two separate methyl resonances, but only a single methyl proton resonance is observed in solutions of this compound in dimethylformamide, DMF-d_7. The relative intensities of the methyl resonances in Me_2SO are temperature dependent and reversible. It is suggested that this effect results from the transfer of the methyl group to the solvent molecules.

Experimental

Phenoxatellurine was prepared by the reaction between $TeCl_4$ and anhydrous diphenyl ether at 200 °C for 8 h according to Drew [2]. The resulting phenoxatellurine dichloride was reduced with $Na_2S\cdot 9H_2O$. The phenoxatellurine (PTe) was purified by recrystallization from ethanol and sublimation to a constant m.p. of 76–77 °C. 10-Methylphenoxatelluronium iodide (CH_3PTe^+ I^-) was prepared by heating 1.0 g (3.4 mmol) of PTe with 4.56 g (32.0 mmol) of iodomethane in a sealed glass tube at 70 °C. The PTe dissolved and crystals began to form after 5 min. The heating was continued for 10 h. The tube was opened, the excess iodomethane was allowed to evaporate and 1.4 g (3.2 mmol, 95%) of yellow, crystalline 10-methylphenoxatellurine iodide, m.p. 133–139 °C was obtained. *Anal.* Calcd. (found) for $C_{13}H_{11}OTeI$: C, 35.67 (35.59); H, 2.53 (2.63); I, 28.90 (28.91). ^1H NMR (DMF-d_7) δ (ppm) 7.77 (d, 2H), 7.29 (m, 6H), 2.27 (s, 3H).

^{1}NMR spectra were recorded on a Jeol Model JNM-PS-100 high resolution NMR spectrometer equipped with a Nicolet 1080 E data processing system in the T-1 mode. $CDCl_3$ was the source of an internal deuterium lock and temperature dependent spectra were obtained with the use of a Jeol Model JNM-VT temperature controller.

Results and Discussion

The proton NMR spectrum of CH_3PTe^+, I^- in DFM-d_7 is consistent with the structure in every respect. However, in Me_2SO-d_6 at 30 °C, two separate singlets were observed at 2.32 and 2.07 ppm. The sum of the intensities of the singlets corresponded to three protons when compared with the intensities of the eight protons in the aromatic region. As the temperature was increased, the intensity of the peak at 2.07 ppm decreased. The process was found to be reversible, *i.e.*, both peaks returned to their original intensities upon cooling. Because the separate resonances were not observed in DMF, the separate singlets are ascribed to an interaction involving the solvent which can be represented as

$$CH_3PTe^+, I^- + (CD_3)_2SO \rightleftarrows PTe + [(CD_3)_2SOCH_3]^+, I^-$$

This observation is not unique and it is quite reasonable, especially in view of the results reported by Smith and Winstein [3], to formulate the solvent cation as an O-methyl species. Smith and Winstein were able to isolate O-alkyl salts of the type $Me_2SO{-}R^+X^-$ by the reaction between RX and Me_2SO at low temperatures. When MeI and Me_2SO were taken to reflux temperatures, S-alkyl salts of the type $RMe_2SO^+X^-$ were formed [4]. Inasmuch as solutions of CH_3PTe^+, I^- in $(CD_3)_2SO$, as exhibited by the ^1H NMR spectral studies, show a reversible transfer of the methyl group, the proposed methyl–solvent species cannot be of the S-methyl type because the equivalence of the methyl groups in such a structure should have resulted in the transfer of a CD_3 group resulting in formation of CD_3PTe^+, I^-. This was never observed.

The equilibrium constant was determined by means of the ratio of the intensities of the two singlets at 2.32 and 2.07 ppm, $K = [PTe]/[CH_3PTe^+, I^-]$. The resonance at 2.32 was assigned to $[(CD_3)_2$-

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$SOCH_3]^+$, I^- since solutions of CH_3I in Me_2SO exhibit a single resonance at 2.32 ppm. Equilibrium constants were calculated at intervals of 10 °C from 303 K to 373 K (Table I). The ΔG° values are also shown in Table I. From a plot of logK *vs.* $1/T$, a slope of -1.81 was obtained from a linear least squares fit. The enthalpy change, ΔH°, calculated from the slope was 8.29 kcal/mol. The ΔS° values were calculated in the conventional manner and are also tabulated. The small enthalpy change indicates that $[(CD_3)_2SOCH_3]^+$, I^- is relatively weak. It would be of interest to learn if such an equilibrium occurs with other alkyltelluronium halides in this same solvent.

TABLE I. Equilibrium Constants and Thermodynamic Values for 10-Methylphenoxatelluronium Iodide–DMSO-d_6 System.

Temp. (°C)	K	ΔG° (kcal mol^{-1})	ΔS° (e.u.)	ΔH° (kcal mol^{-1})
30	2.33	−1.68	32.9	
40	3.74	−2.62	34.8	
50	4.22	−2.86	34.5	
60	6.48	−3.71	36.0	
70	10.2	−4.61	37.6	8.29
80	16.3	−5.55	39.2	
90	18.1	−5.76	38.7	
100	33.6	−6.98	40.9	

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