

NMR SPECTRA OF H-SPECIES IN SOCl₂ ELECTROLYTES (EXTENDED ABSTRACT)

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Introduction

It is well known that water is deleterious to Li/SOCl₂ cells [1, 2]. H-NMR is an ideal method for the detection of H-species in SOCl₂ systems where water contamination has occurred during the manufacture of practical cells. There have, however, been few references in the literature to its use for this purpose. In this communication we present some preliminary data on the H-NMR spectra when water is introduced into the SOCl₂, AlCl₃-SOCl₂ and LiAlCl₄-SOCl₂ systems.

Experiments and discussion

SOCl₂

No obvious NMR peak can be detected when SOCl₂ is purified by refluxing with Li metal for 4 h. When SOCl₂ is suspended above water in a closed vessel for some time (sample A) a resonance peak at +0.93 ppm with respect to TMS appears, as shown in Fig. 1(A); no other resonance peaks are detected in the range +50 to -50 ppm. The same spectrum is obtained when dry HCl is passed through SOCl₂ (sample B), Fig. 1(B). It can therefore be concluded that water is present in SOCl₂ as HCl, but not as H₂SO₃ or other H-species, in agreement with Staniewicz and Gary's IR experiments [2] according to the following reaction:



The amount of water contamination in SOCl₂ can also be determined by NMR, since a proportionality relationship is obtained between the integrated intensities under the HCl peaks and the amounts of water deliberately added to SOCl₂, as is shown in Fig. 2.

The AlCl₃(1.5 M)-SOCl₂ system

When sufficient water is added to this system precipitation occurs (sample C). Three additional peaks appear in the NMR spectrum at 7.1, 6.0

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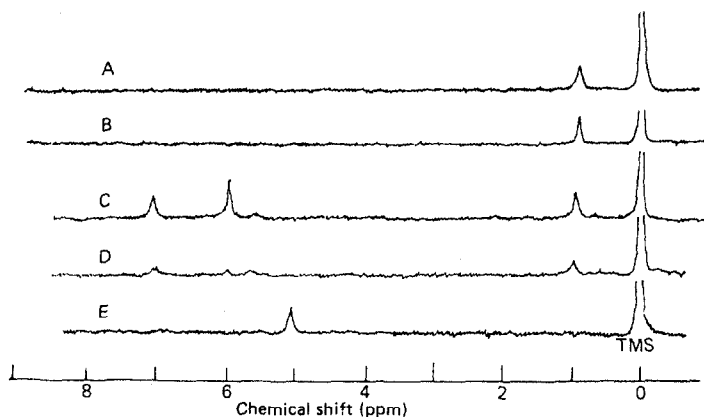


Fig. 1. H-NMR spectra of samples of different SOCl_2 systems. (A) SOCl_2 suspended over water for a prolonged period of time; (B) SOCl_2 with HCl; (C) $\text{AlCl}_3(1.5 \text{ M})\text{-SOCl}_2 + \text{water}$; (D) $\text{AlCl}_3(1.5 \text{ M})\text{-SOCl}_2 + \text{sample A}$; (E) $\text{LiAlCl}_4(\text{water contaminated, } 1.0 \text{ M})\text{-SOCl}_2$.

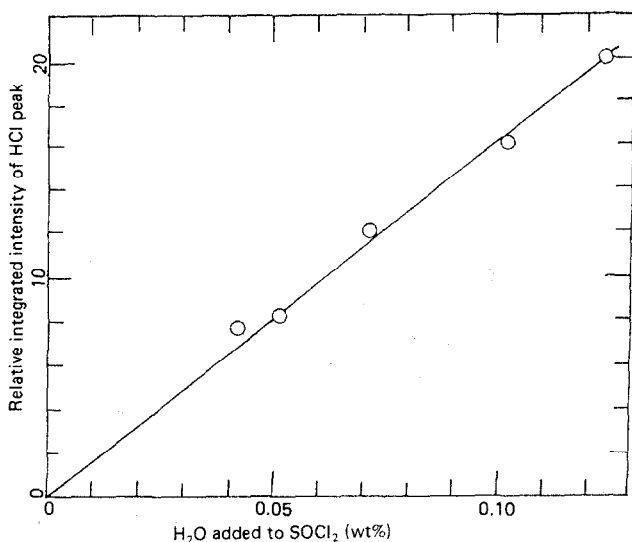


Fig. 2. Plot of relative integrated intensity of HCl NMR peak vs. amount of water added to SOCl_2 .

and 5.8 ppm in addition to the HCl peak at 0.93 ppm (Fig. 1(C)). When sample A is mixed with $\text{AlCl}_3\text{-SOCl}_2$ solution the same NMR spectrum is obtained, but with peaks of lower intensity (Fig. 1(D)). We therefore suggest that an equilibrium is set up for eqn. (1); the H_2O liberated is soon captured by AlCl_3 to give $\text{Al}(\text{OH})\text{Cl}_2$, $\text{Al}(\text{OH})_2\text{Cl}$ and, in far less quantity, $\text{Al}(\text{OH})_3$ corresponding to the 7.1, 6.0 and 5.8 ppm NMR peaks, respectively.

The LiAlCl₄(1.0 M)-SOCl₂ system (sample E)

Since we cannot yet obtain LiAlCl₄ reagent completely free from water, an NMR spectrum with a single peak at 5.1 ppm, without an obvious HCl peak, is obtained (Fig. 1(E)). The same NMR spectrum is obtained when water is added to sample E (white precipitate formed), and there is no obvious change in the spectrum even after 4 h. Since no NMR spectra can be observed for solid suspensions in liquid samples under the present experimental conditions, we assumed some H-species, such as solvated AlCl₃·H₂O, may be present in the LiAlCl₄-SOCl₂ solution in the case of water contamination. AlCl₄⁻ would capture H₂O, preferably in the solution phase of SOCl₂, with the precipitation of LiCl.

Literature

- 1 K. French, P. Cukor, C. Persiani and J. Aurborn, *J. Electrochem. Soc.*, 121 (1974) 1045.
- 2 R. J. Staniewicz and R. A. Gary, *J. Electrochem. Soc.*, 126 (1979) 981.