

Ternary Hydrogen Halide/Base/Benzene Mixtures: A New Generation of Liquid Clathrates

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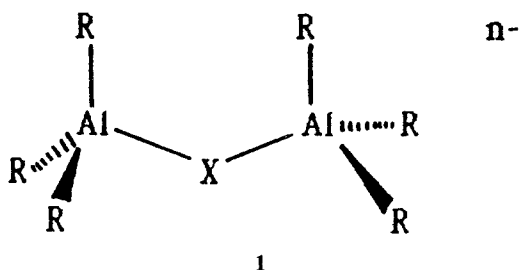
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Abstract. Liquid clathrates have been prepared via contact of excess hydrogen halide (chloride or bromide) with benzene solutions of various simple organic nitrogen containing bases. The liquid clathrates or solutions so formed have been characterized via ^1H NMR and shown to be, as expected, ternary mixtures of hydrogen halide, benzene and salt.

Key words. liquid clathrate, room temperature melts, NMR.

1. Introduction

Liquid clathrates, which were first described in detail by Atwood in 1977 [1], have been a subject of increasing interest in recent years as evidenced by the fact that several groups are currently active in the field [2]. Activity to date has focused primarily upon salts of complex trialkylaluminum-containing anions of type 1, which are typically low melting point solids or even liquids in their pure form [3]. The attention that has been directed towards these salts is quite natural since virtually all such salts (with counter cations as varied as NR_4^+ , alkali metal cations, crown ether complexed cations and organotransition metal cations) spontaneously form liquid clathrates under ambient conditions when contacted with an excess of liquid aromatic hydrocarbon.



R = Me, Et, Pr, Bu; X = halide, oxyanion, azide; $n = 1, 2$

Recently, we have discovered that appropriately large organic cations may facilitate liquid clathrate formation when countered with moderately-sized, air stable anions Al_2Cl_7^- and AlCl_4^- [4]. Coupled with other studies on chemically different but structurally similar anions such as hexamethyldisilazide and 2,6-di-*t*-butyl-4-methylphenoxide which may also sustain liquid clathrate behaviour [5], the inference is that liquid clathrate behaviour is a

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phenomenon that is dependent more upon the physical than the chemical nature of the ions involved. A reasonable approach to seek new liquid clathrate sustaining salts would therefore be to investigate other salts that are known to be low melting point solids or room temperature liquids, as are several organic cation salts of $Al_2Cl_7^-$ [6]. This communication deals with such an approach in that we have focused upon organic cation salts of anions of the type $[(HX)_nX]^-$ ($n = 1-3$, $X = Cl, Br$), **2**, which are generally well characterized [7] and have long been known to be liquids or low melting solids [8].

2. Experimental

Our preliminary studies have focused upon the hydrogen halide salts of the following simple organic nitrogen-containing bases: pyridine, 2-ethylpyridine, 2,4,6-collidine, quinoline, *N,N*-dimethyltoluidine, 1-methylimidazole, 1-methylpyrrolidine and piperidine. The appropriate hydrogen halide salts were prepared *in situ* at room temperature via contact of a benzene solution of each base (1 mL base/20 mL benzene) with a slow stream (i.e. 1 atm) of dried HCl or HBr. In all instances the hydrogen halide salt precipitated within 10–20 seconds, but the stream of gas was continued for up to 17 minutes, facilitating formation of anions of type **2**. The gas flow was ceased prematurely only if the salt was seen to dissolve and form a solution, but in most cases dissolution was accompanied by formation

Table I. 1H NMR data for lower phase of HX/base/benzene ternary systems.

Parent Base	HX, X =	Type of Interaction ^a	Benzene Content ^b	δ , anion ^c	δ , N—H ^c	n^d
pyridine	Cl	1	1.8	^e	11.2	^e
	Br	1	1.7	7.28	14.0	^e
2-ethylpyridine	Cl	1	7.9	^e	15.5	^e
	Br	1	6.2	4.73	14.6	2.2
2,4,6-collidine	Cl	1	8.3	7.40	14.6	2.9
	Br	1	5.4	5.31	13.9	2.4
quinoline	Cl	1	6.4	^e	15.0	^e
	Br	1	2.4	^e	15.6	^e
<i>N,N</i> -dimethyltoluidine	Cl	2	—	—	—	—
	Br	1	6.7	^e	11.2	^e
1-methyl imidazole	Cl	1	1.7	8.53	13.6	1.8
	Br	1	1.6	5.83	12.7	1.8
1-methyl pyrrolidine	Cl	1 ^f	3.8	9.82	10.0	^e
	Cl	1 ^g	7.4	8.38	9.8	1.8
	Cl	2 ^h	—	—	—	—
	Br	1	5.8	3.97	9.0	2.0
piperidine	Cl	2	—	—	—	—
	Br	3	—	—	—	—

^a 1 = 2 liquid phases; 2 = solution; 3 = benzene insoluble salt.

^b Determined via 1H NMR integration of benzene hydrogen atoms vs. cation alkyl hydrogens (N—H cation proton was used if no alkyl groups present).

^c In p.p.m, benzene itself was used as a reference.

^d n in $[(HX)_nX]^-$.

^e Not resolvable due to interference from other resonances.

^f 4 minutes contact with 1 atm HCl.

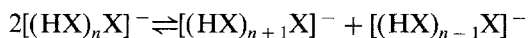
^g 6 minutes contact with 1 atm HCl.

^h 10 minutes contact with 1 atm HCl.

of the two liquid phase effect that is characteristic of liquid clathrate formation. ^1H NMR was used to show that phase compositions became constant after 5 to 15 minutes, but below those times the amount of HX incorporated into the denser liquid clathrate phase was seen to be variable and low. This is illustrated best by the 1-methylpyrrolidine/HCl system, which initially (within 1 minute) absorbed HCl to give a binary phase system, but slowly absorbed (over 10 minutes) enough HCl to become a solution (see Table I). The liquid clathrate phases were found to be indefinitely stable if stored in an enclosed vessel under an atmosphere of HX, but in an open vessel they quickly dissipated due to loss of HX and subsequent salt precipitation. A summary of our observations and the results of ^1H NMR analyses [9] of the liquid clathrate phases are tabulated in Table I.

3. Results and Discussion

As can be seen from Table I three types of interaction were observed between the complex salts and benzene. Most salts dissolved to give liquid clathrate binary liquid phases, but three of the HCl derived salts dissolved to form normal solutions with one, 1-methylpyrrolidine/HCl, exhibiting both types of effect depending upon how much HCl was allowed to incorporate. In one instance, piperidine/HBr, the only result was formation of a benzene-insoluble salt. The liquid clathrate phases themselves were shown to be the expected ternary mixtures of hydrogen halide salt, hydrogen halide and benzene, the latter two substances being present in non-stoichiometric quantities. The amounts of the latter two components, although quite variable from one base to another, were shown to be fully reproducible (to within *ca.* 5%) as long as moisture was kept away from the reaction. The amount of HX incorporated into the liquid clathrate phases, n , was determined simply by NMR integration as the anion resonance appeared as a singlet in the range 4–10 δ . In some instances interference from either the dominant benzene peak or cation aromatic peaks precluded accurate assignment of the anion resonance but the overall trend was still evident, indicating that fast equilibrium between complex anions was occurring:



or



The observed chemical shift and composition ranges for the anionic moieties are fully consistent with a spectroscopic report on the pure liquid pyridine/HCl system [10]. This report demonstrated that a temperature dependent nonstoichiometric amount of HCl could be absorbed by pyridine to yield a series of melts and that at ambient temperature and pressure, *ca.* 1.9 moles of HCl was present in the melt. Also of relevance to this communication is that broad N—H resonances were observed at low field (> 10 ppm) and that the chemical shift of the $[(\text{HCl})_n\text{Cl}]^-$ anion varied from *ca.* 9 δ to -1 δ as the HCl content was increased from 60 to 95 mole percent. In our study broad aromatic N—H resonances, sometimes in a triplet pattern, were detected between 11 and 16 δ , and broad aliphatic N—H resonances were observed at slightly higher field. The suggested equilibria are consistent with observations we have made upon trialkylaluminum-containing liquid clathrates, in which it was demonstrated that free trialkylaluminums could be leached via the less dense free aromatic phase [11]. The existence of a mixture of equilibrating complex hydrogen-halide containing anions is also consistent with earlier studies on such systems [7, 8] and interestingly the chemical shift of the singlet assigned to this mixture, although

variable, was observed to be quite dependent upon the value of n (Table I). This is well-illustrated by the 1-methylpyrrolidine/HCl systems as they progressively changed with increasing HCl absorption.

We are currently investigating several aspects of the new generation liquid clathrates, including more thorough investigation of the variability of n , initiation of studies upon mixed halide anions, and the conducting of X-ray structural investigations upon the parent salts [12]. The latter studies are expected to demonstrate that structural similarities exist between anions of type **2** and other liquid clathrate sustaining anions (e.g. HCl_2^- is thought to be angular [13]).

In summary, a new class of air stable liquid clathrate has been prepared and characterized. The fact that the new systems are chemically quite different from earlier two phase systems but are physically related (i.e. low lattice energy due to steric bulk of the ions involved) suggests not only that even more classes of liquid clathrate phase are attainable but that they may be logically designed, a concept that we are already pursuing with other low melting point salts [4].

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