

Alkane cracking, alkene polymerization, and Friedel–Crafts alkylation in liquids containing the acidic anions HX_2^- , $\text{XH}(\text{AlX}_4)^-$, $\text{XH}(\text{Al}_2\text{X}_7)^-$, and Al_2X_7^- (X = chlorine, bromine)

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Abstract

Sequential GC–MS studies of gas and liquid in equilibrium were the principal measurements made to investigate the cracking of alkanes, the oligomerization of alkenes and the Friedel–Crafts alkylation of benzene and toluene by alkenes, in various ionic liquids. It was shown that alkenes of the same or near half the size of cracked alkanes readily polymerize in the same medium and it is suggested that this is the driving force of the alkane cracking. The acids responsible for these processes in liquid organic haloaluminates and halohydrogenates are all anionic, ranging from the mild HX_2^- , of limited action, to the more potent superacids $\text{XH}(\text{Al}_2\text{X}_7)^-$ and Al_2X_7^- . The latter is postulated to act upon an alkane via hydride abstraction, forming AlX_3H^- , a species stable in Lewis acidic systems, but sensitive to $\text{XH}(\text{Al}_2\text{X}_7)^-$. At ambient temperatures alkene polymerization is the fastest of the three processes while alkane cracking is slow, but requires less acidic conditions. © 2004 Elsevier B.V. All rights reserved.

Keywords: Cracking; Ionic liquids; Haloaluminates; Halohydrogenates; GC–MS

1. Introduction

Semi-organic salts offer a wide variety of low-melting liquids containing moderate concentrations of ions (usually 3–6 M each for cations and anions) [1]. Several of them have low vapor pressures and provide alternative systems for many reactions previously carried out in molecular organic solvents [2,3]. It has been found that yields of products are good and in some cases, isomeric distributions quite different. In addition to acting as solvents, some ionic liquids can be used as catalysts e.g. those derived from the Lewis acids AlCl_3 , AlBr_3 , ZnCl_2 , SnCl_2 , etc. or as actual reactants e.g. the salts of the Brønsted acids HCl_2^- , HBr_2^- , etc. [4].

Preliminary studies in this laboratory showed that acidic ionic liquids cracked *n*-alkanes slowly at ambient temperatures [5,6]. The primary products identified by glc were C_4 – C_7 iso-alkanes from C_8 – C_{14} alkanes with only small amounts of alkenes. The questions arose as to whether gases

such as H_2 and C_2H_4 were produced and escaped detection or whether the unsaturated products were polymerizing and thus being missed. It has been shown that acidic ionic liquids can polymerise alkenes [7–10], but also that they can catalyse the Friedel–Crafts addition of alkenes to arenes [11–13]. Since we have an interest in both alkane cracking for the upgrading of heavy oil and alkylarene synthesis for detergent manufacture, we undertook a further study of the interaction of a number of ionic liquids with hydrocarbon systems.

2. Experimental

All manipulations involving aluminum chloride (Fluka, twice vacuum sublimed), Et_3SBr [14], 1-butyl-3-methyl-1*H*-imidazolium chloride (BmimCl), pyridinium chloride (Py-HCl) (Fluka) and ionic liquids derived therefrom were performed in a glovebox (Mbraun LabMaster 100) under an atmosphere of dry nitrogen. The preparation of haloaluminate ionic liquids by careful mixing of the components and of halohydrogenates from HCl gas (Mattheson ethene-free) and semi-organic salt is well-established. The last protons (1–10 mM in concentration) could be removed by the addition of sufficient CaH_2 or EtAlCl_2 . For cracking experiments

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n-nonane (99%, Aldrich), 2-methylpentane (>99%, Aldrich) or tetradecane (practical, J.T. Baker) was dried by molecular sieves and added to the ionic liquid in a 25 or 50 ml flask with vacuum distillate or injected into a scintillation vial with a rubber septum seal. The systems were stirred. Volatile products were collected over water and liquid layers collected by decantation or transferred through a syringe. The alkenes 1-octene (97%), 1-pentene and 2-pentene (>99%), were used as supplied (Aldrich).

2.1. Gas chromatography (glc)

A HP 5890 capillary gas chromatograph with 30 m DB1 (methyl from J&W scientific) or Ultra-2 fused silica capillary with i.d. = 0.25 mm, thickness = 0.25 μm was used. The column head pressure was 21 psi, a flow rate 30–45 ml/min. FID was the detector, and the oven temperature was programmed: $T_{\text{init}} = 35\text{ }^{\circ}\text{C}$, $t = 5\text{ min}$, ramp = $15\text{ }^{\circ}\text{C}$, $T_{\text{final}} = 260\text{ }^{\circ}\text{C}$, $t = 20\text{ min}$. The carrier gas flow rate was 30–45 ml/min. $T_{\text{inj}} = 270\text{ }^{\circ}\text{C}$, injection volume = 1 μl , injection mode: split.

The GC–MS procedure is described in detail elsewhere [15]: consecutively sampled gas and liquid phases of the same system can be analyzed within a few minutes of each other. The identification of an unknown is based on matching peaks ($M^+ \equiv$ molecular ion) to the databases which contain >300,000 spectra.

FTIR spectra were obtained with a Perkin-Elmer 1600 FTIR Spectrometer with a 400–2500 cm^{-1} range. Dry KBr salt plates were used for the sample holder and materials were loaded in the glovebox.

The molar masses of oligo-octene samples were determined by the freezing-point depression of cyclohexane (cryoscopic constant 20 kg/mol).

3. Results and discussion

3.1. Cracking of alkanes

It was shown by Olah and Molnar [16] and Olah [17] that when aliphatic hydrocarbons are treated with superacids, cracking, alkylation, isomerization, and polymerization occur. In particular, Magic acid or fluoroantimonic acid converted butane or isobutene into *tert*-butyl cation with the release of hydrogen, the reaction beginning with carbenium anion formation and continuing through various intramolecular and intermolecular routes which result in alkene and larger alkane formation together with eventual proton release. Polyethylene could be cracked into light alkanes in an acidic ionic liquid [18]. Elrutb [5] found that the series of *n*-alkanes C_8H_{18} through $\text{C}_{14}\text{H}_{30}$ gave rise to essentially the same set of iso-alkanes when contacted with various Lewis acidic haloaluminate liquids. For a given hydrocarbon, an all-bromide system was distinctly more reactive than an all-chloride system, a Lewis acid mole fraction $\sim 2/3$ was

most favorable and increased temperature and stirring improved the product yield.

In the present work the cracking of nonane, tetradecane, and 2-methylpentane by selected acidic haloaluminate liquids was investigated. The total ion chromatograms (TIC's) of the gas phase above the system nonane/acidic $\text{AlCl}_3\text{-PyHCl}$ after 3 h was reported previously [15]. Product identification for the gas and liquid hydrocarbon phases appears in Fig. 1 and Table 1. The isoparaffins, 2-methylpropane, 2-methylbutane, and 2-methylpentane are the principal gaseous products while the liquids show the light isoparaffins, uncracked nonane, and higher molecular weight hydrocarbons formed through alkylation of nonane by cracked moieties. We note the increase in 2-methylpentane and *n*-hexane (D) at the expense of 2-methylbutane, *n*-pentane, and the dimethylpentanes (B) in the gas over time and the formation of larger molecules than the substrate in the liquid.

The cracking of tetradecane was not observable, using GC and NMR, at ambient temperatures but took place at $70\text{ }^{\circ}\text{C}$. The hydrocarbon liquid phase products ranged from C_7 to C_{14} substrate. In contrast, the cracking of 2-methylpentane was observable at $23\text{ }^{\circ}\text{C}$ with 2-methylpropane and 2-methylbutane being the principal gaseous products.

Taking the volume of gas evolved as a measure of nonane cracking, four ionic liquids were compared (Table 2) each containing 64 mol% AlCl_3 . The moles of Al_2Cl_7^- used were the same in the first three systems and thus the molarities differed. While there is some correlation between cracking and Al_2Cl_7^- molarity, it is NOT linear. However, for a given system, treatment of the ionic liquid with a proton scavenger— EtAlCl_2 or CaH_2 —reduced the rate of crack-

Table 1
GC-MS analysis of liquid sample from elongated cracking of nonane in 64% $\text{AlCl}_3\text{-PyHCl}$

Retention time	Possible compounds
2.51–2.61	Nonane
2.64	2,5-Dimethylnonane
2.68	2,5-Dimethyloctane
2.73	2,7-Dimethyloctane
2.78	2,6-Dimethyloctane
3.03–3.05	2,5,6-Trimethyldecane
3.32–3.36	2,6,6-Trimethyldecane
3.50–3.54	2,5,6-Trimethyloctane
4.24–4.25	2,5,6-Trimethyldecane
4.32–4.34	2,6,7-Trimethyldecane
4.43–4.47	2,6,10,14-Tetramethylheptadecane
4.58–4.61	Nonadecane
5.29–5.32	2,6-Dimethylundecane
5.81–5.86	2,7,10-Trimethyldodecane
7.77–7.83	3-Methyldodecane
8.09–8.13	3,9-Dimethylundecane
8.23–8.25	2,6,6-Trimethyldecane

Reaction conditions: 3.0 g 64% $\text{AlCl}_3\text{-PyHCl}$ reacted with 1.0 g of nonane in the glovebox at a temperature of $28\text{ }^{\circ}\text{C}$ for 15 days. Liquid portion was diluted with ethyl acetate. The TIC was recorded after 2 min.

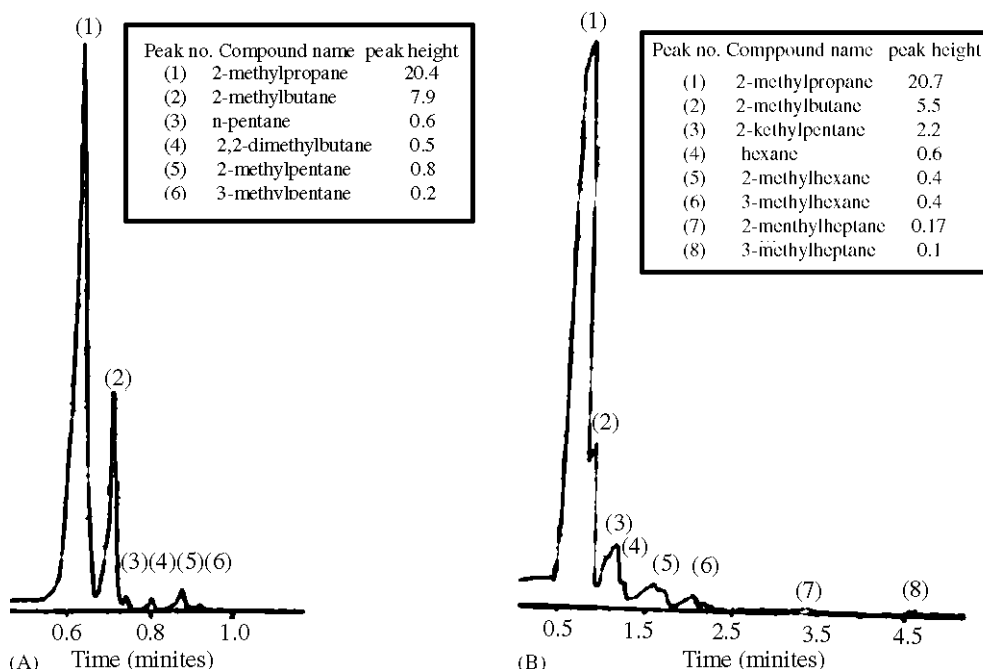


Fig. 1. GC-MS analysis of the products of cracking *n*-nonane in 64% AlCl_3 -PyHCl. (A) TIC of gas obtained after 3h and (B) TIC of gas obtained after 15 days.

ing while addition of protons through HCl gas increased the rate of cracking. Thus, a protic species as well as the Lewis acidic anion is a catalyst. It is apparent also from Table 2 that the evolved gas volumes in themselves are small. If the loss of substrate from the hydrocarbon phase is considered, the evolved gas, excluding substrate, only represents a small fraction of the cracking products.

3.2. Alkene reactions

The polymerization of small alkenes (C_2H_4 – C_4H_8) in Lewis acidic ionic liquids was studied by Golezinowski [7], Ambler [8], and Abdul-Sada [9] and that of decene by Ranwell and Tshamano [10] who found the product distribution of approximately equal amounts of C_{30} , C_{40} , and C_{50} oligomers with small amounts of C_{20} , C_{60} and higher species. It was not determined whether or not pro-

tons were necessary to initiate a cationic polymerization process.

We observed that the addition of 1-octene to 64% AlCl_3 -PyHCl caused an exothermic reaction at room temperature and the brown product, extracted into hexane, showed (a) by GC-MS, the isomerization to 2-octene and the formation of complex species: 2,4,6-trimethyloctane, decahydro-2-3-dimethylnaphthalene, 1,3,5,7-tetramethyladamantane, *n*-eicosane, and hexadecene (the products were transferred into hexane and residual ionic liquid removed with water before the analysis); (b) by FTIR (Table 3) the formation of an oligo-octene resembling polypropylene and polyethylene [19]; and (c) by freezing point depression an average molecular weight of 700–900 D, i.e. the formation of $(\text{C}_8\text{H}_{16})_{7\pm 1}$. The oligomerization of 1-octene occurred in basic 46% AlCl_3 - Et_3SBr , but the yield was low (9%); no reaction took place if the basic ionic liquid was pre-treated

Table 2

Comparison of the cracking ability of different ILs with the same amount of catalyst (64 mol% AlCl_3 in each liquid)

RX	BmimCl	PyHCl	Et_3SBr	BuPyHCl ^a
MW of RX	173.5	114.5	199	170.5
MW of IL	410.5	351.5	436.0	407.5
Weight of IL (g)	14.440	12.333	15.254	8.3436
Moles of anions	3.52×10^{-2}	3.51×10^{-2}	3.50×10^{-2}	2.0×10^{-2}
Density (g/ml)	1.3194	1.4759	1.4607	1.33
Molarity (mol/l)	3.21	4.20	3.35	3.26
V_{gas} (ml)	30	96	45	77 ^b
Moles of gas ($\times 10^3$)	1.34	4.29	2.00	3.44

^a BuPyH⁺: *N*-butylpyridinium.

^b Cracking of 6.0 g nonane at 70 °C for 24 h, except this was with 3.5 g of nonane.

Table 3

Comparison of 1-octene and oligooctene with polypropylene and polyethylene by FTIR [19]

1-Octene	Oligooctene	Polypropylene	Polyethylene	Vibrational modes
3077				=C–H stretching
2966, 2933	2923	2959, 2924	2899	CH ₂ antisym stretching
2861	2852	2833	2857	CH ₂ sym stretching
1644				C=C stretching
1462	1464	1460	1466	CH ₂ bending
1379	1377	1379, 1361	1381, 1372	CH ₂ wagging
	1304		1355, 1302	CH ₂ wagging
997	1154	1167		CH ₂ twisting–CH ₂ rocking
909, 720		997	1082	Skeletal
	935, 722	973, 842	731, 720	CH ₂ rocking–CH ₂ twisting

with CaH₂ to remove protons. Acidic 64% AlCl₃–Et₃SBr oligomerized 1-octene readily even after CaH₂ treatment but the yield dropped from 94 to 75% and the reaction was slower.

When a common cracking product (2-methylpentane) and a similar-sized alkene were added (10:1 volume ratio) to 64% AlCl₃–BmimCl, alkylation of the isoalkane occurred as evidenced by GC–MS (Table 4), but the degree of cracking decreased.

Thus, we deduce that alkenes produced by cracking alkanes will both oligomerize and alkylate, to some extent, the isoalkanes generated.

3.3. Friedel–Crafts alkylation

Examples of Friedel–Crafts alkylation in ionic liquids include the formation of dodecylbenzene (27.6% yield) in Me₃NHCl–AlCl₃ at 80 °C in 1 h [11], the improvement of yield and selectivity of this reaction by supporting the liq-

uid on a polymer [12] and enhancing the reaction by adding HCl [13], which clearly formed a superacidic species.

Since alkenes are polymerized by acidic ionic liquids, either the arene should be pre-mixed with the ionic liquid or with the alkene.

The alkenes 1-pentene, 2-pentene, and 1-octene and benzene and toluene were investigated in Lewis acidic AlCl₃–Et₃SBr and PyHCl–AlCl₃, without and with removal of impurity protons by EtAlCl₂ before use. It was found that the removal of protons slowed but did not stop the reaction.

Gas chromatography was used to follow the reaction of 1-octene and benzene in 66% AlCl₃–Et₃SBr; the reaction was complete in 7 h. GC–MS indicated the formation of 1-methylheptylbenzene, 1-ethylhexylbenzene, 1-propylpentylbenzene, and some di- and tri-substituted products. GC analysis (Fig. 2b) showed that 2-pentene and benzene produced three isomeric groups which were shown by GC–MS to consist of (a) methylbutylbenzene, ethylpropylbenzene, and *n*-pentylbenzene; (b)

Table 4

GC-MS analysis of end products from 2-methylpentane cracking with and without 1-pentene

Gas phase:		Liquid phase:		Gas phase:	
2.0 ml 2-methylpentane and 0.2 ml 1-pentene were added to 2.0 g 64% AlCl ₃ –BmimCl ionic liquid and stirred at 23 °C for 28 h				1.0 g 2-methylpentane was added to 3.0 g 64% AlCl ₃ –PyHCl and stirred at 23 °C for 28 h	
Compounds	Peak height	Compounds	Peak height	Compounds	Peak height
2-Methylpropane	18.3	2-Methylbutane	17.2	2-Methylpropane	8.9
2-Methylbutane	21.0	2-Methylpentane	17.5	2-Methylbutane	6.0
2-Methylbutane	16.5	2-Ethylpentane	3.5	2-Methylbutane	1.9
2-Methylbutane	12.7	2,6-Dimethylheptane	0.9	2,2-Dimethylbutane	0.83
2-Methylpentane	10.6	3-Ethylheptane	0.7	2-Methylpentane	0.41
3-Methylpentane	3.9	2,2,3,4-Tetramethylpentane	1.2	3-Methylpentane	0.16
Hexane	0.4	2,2,3-Trimethylhexane	1.1	2-Methylhexane	0.05
2,4-Dimethylpentane	0.5	3,3,5-Trimethylheptane	0.55		
2-Methylhexane	0.7	4-Propylheptane	0.3		
2,4-Dimethylhexane	0.1	4-Methylnonane	0.6		
		2,7-Dimethyloctane	0.4		
		3-Methylnonane	0.8		
		2,6-Dimethyloctane	0.3		
		2-Methylnonane	0.4		
		3,5-Dimethyloctane	0.7		
		2,3-Dimethylnonane	0.6		
		4-Methyldecane	0.4		
		2,3-Dimethyldecane	0.2		

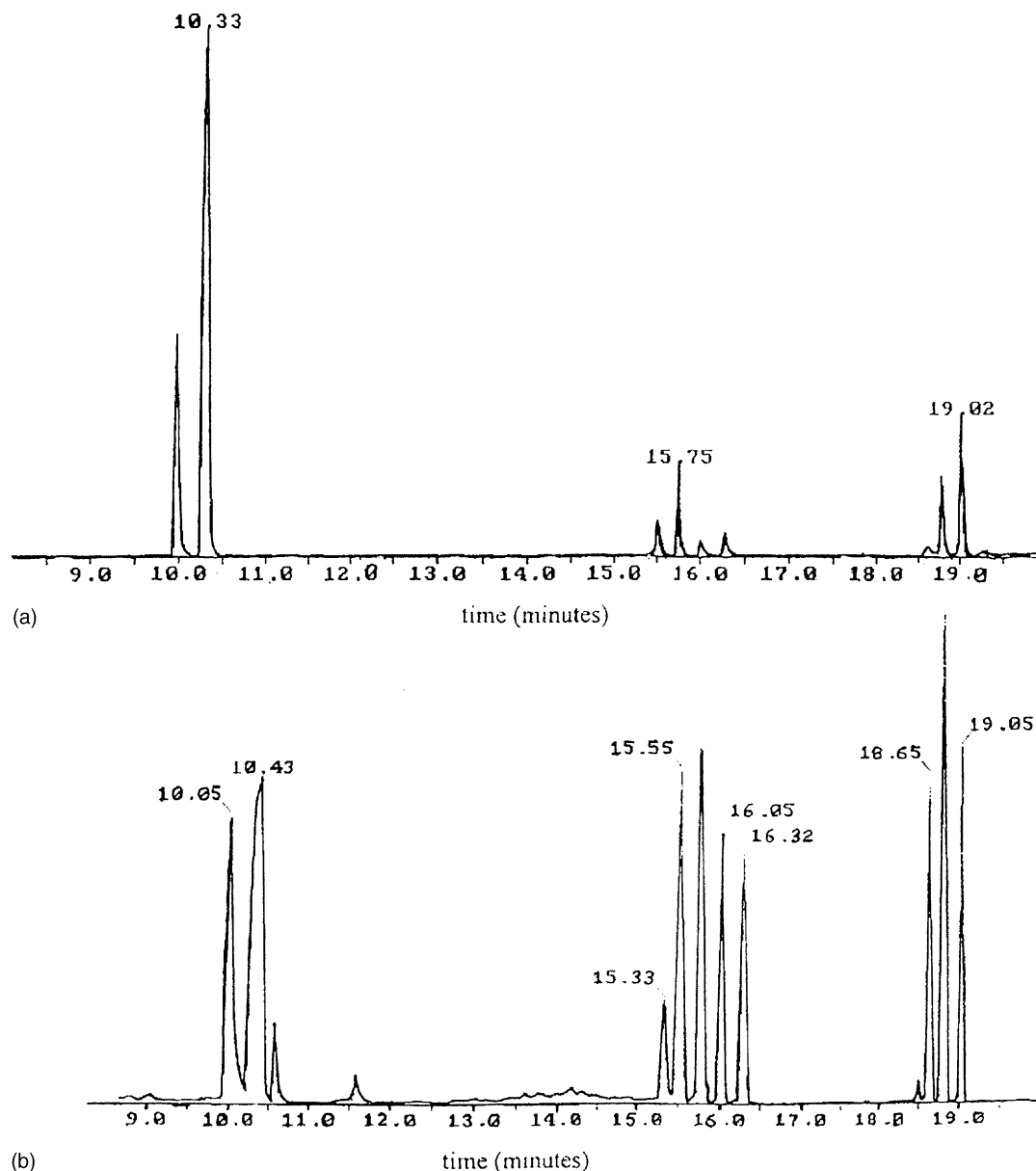


Fig. 2. Gas chromatograms of the products obtained from (a) 1-pentene and (b) 2-pentene reacting with benzene in 64% $\text{AlCl}_3\text{-Et}_3\text{SBr}$.

1,4-di-(ethylpropyl)benzene, 1-ethylpropyl-4-methylbutylbenzene, 1,4-di-(methylbutyl)benzene, 1,2-di-(ethylpropyl)benzene, and 1-ethylpropyl-2-methyl-butylbenzene; (c) 1,2,4-triethylpropylbenzene, 1,2,4-trimethylbutylbenzene, and 1,4-diethyl-propyl-2-methylbutylbenzene. Similar structured products were obtained from 1-pentene and benzene (Fig. 2a) and in the corresponding reactions of toluene with the three alkenes.

Fig. 3 also demonstrates that mono-substitution is favored by a high arene:alkene ratio. Minimizing the acidity (52% AlCl_3) and the amount of ionic liquid also limit the degree of substitution. Comparable overall conversions of toluene (37.3% versus 37.5%) from reactions in 63% $\text{AlCl}_3\text{-PyHCl}$ ($M_{\text{Al}_2\text{Cl}_7^-} = 2.99$) and 66% $\text{AlCl}_3\text{-Et}_3\text{SBr}$ ($M_{\text{Al}_2\text{Cl}_7^-} =$

3.20) were obtained. In a basic 46% $\text{AlCl}_3\text{-Et}_3\text{SBr}$ liquid containing toluene and 1-octene, the reaction was minimal but 2-octene with smaller ($\sim 5\%$) amounts of a xylene, 2,7-dimethyl-2-octene, 2-bromooctane, and bromoethane were observed by GC-MS of the hydrocarbon phase.

When nonane (2.0 g) was cracked in the presence of toluene (0.3 g) in 64% $\text{AlCl}_3\text{-Et}_3\text{SBr}$ for 48 h at 45° , the ratio 2-methylbutane:propyltoluene:butyltoluene found in the gas phase was 215:1:3.1. This indicates that $\sim 2\%$ of the alkenes produced upon cracking underwent Friedel-Crafts alkylation. Incidentally, a small amount of bromotoluene was found ($\sim 4\%$ of the 2-methylbutane quantity).

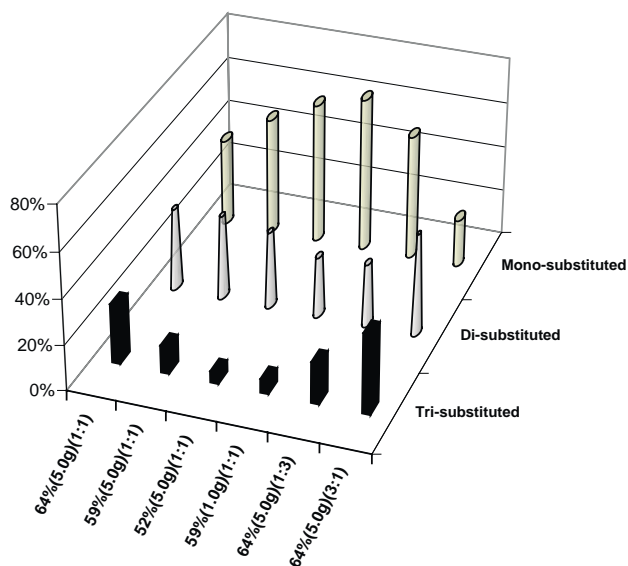


Fig. 3. Distribution of the substitution products obtained when 2-pentene reacted with benzene in $\text{AlCl}_3\text{-Et}_3\text{SBr}$ ionic liquid (64, 59, and 52% are the AlCl_3 mole percentages, 5.0 and 1.0 g are the ionic liquid masses, 1:1 (1.79 ml:2.16 ml), 1:3 and 3:1 are the mole ratios of 2-pentene to benzene).

3.4. The mechanisms and the acids

Mechanisms for Friedel–Crafts alkylation by alkenes, alkene oligomerization, and alkane cracking are well established in the literature with the PROTON as the initiating agent and a series of steps involving carbenium ions [20]. Lewis acids serve to catalyze these processes by forming stable species such as AlCl_4^- and/or by increasing the Brønsted acidity of the medium. Implicit in these schemes is the notion of the proton being free or solvated by neutral molecules and of existing in solution with an anion and little of the latter's conjugate acid.

In haloaluminate(III) and halohydrogenate(I) ionic liquids the speciation is somewhat novel. The cations are spectator ions, to a first approximation, and the anions are acids, neutral species or bases. We have shown that the liquids formed

from 1-ethyl-3-methyl-1*H*-imidazolium chloride (EmimCl) and HCl contain the anions HCl_2^- , H_2Cl_3^- , or H_3Cl_4^- , according to the HCl mole fraction and that these anionic acids have a Hammett acidity of -2 to -4 [21]. Further, the dissolution of HCl in Lewis basic $\text{AlCl}_3\text{-EmimCl}$ produces HCl_2^- and $\text{ClH}(\text{AlCl}_4)^-$ [22]. G.P. Smith et al. [23] demonstrated that HCl in a Lewis acidic $\text{AlCl}_3\text{-EmimCl}$ liquid behaved as a superacid and partially protonated toluene; we measured the solubility of HCl in this system and studied its electrochemistry as a function of pressure, leading us to propose the existence of two distinct adducts, $\text{ClH}(\text{AlCl}_4)^-$ and $\text{ClH}(\text{Al}_2\text{Cl}_7)^-$ with the latter being the superacid [22]. The formation of these adducts was supported by theoretical calculations [24], an extension of which showed that $\text{ClHAl}_2\text{Cl}_7^-$ is 36.57 kJ/mol more stable than a structure with the proton located between two AlCl_4^- units [25].

We note that there is no evidence for the existence of the simple HAlCl_4 or HAl_2Cl_7 . We have estimated the Hammett acidity of acidic $\text{HCl-AlCl}_3\text{-EmimCl}$ as ~ -14 and from the protonation of benzene by $\text{HBr-AlBr}_3\text{-Me}_3\text{SBr}$ [26] and the ambient temperature cleavage of anisole by HBr-HmimBr [4] ($\text{Hmim} \equiv 3\text{-methylimidazolium}$) we suggest that these two all-bromide ionic liquids have H_0 's of ~ -17 and ~ -6 , respectively. Thus, we have a good perspective of the anionic protic acids in these systems.

As discussed above and shown in Table 5, both alkane cracking and alkene oligomerization take place in liquids from which the protons were removed. In addition, while these reactions are accelerated by increasing the temperature, the solubility of HCl is reduced. There has been speculation as to how the Scholl reaction (of 1-phenylpyrene for example) can occur in liquid KAl_2Cl_7 with the production of H_2 and no external proton source or oxidant [27]. We are led to the conclusion that Al_2Cl_7^- is an active acid catalyst in these situations. Since we have shown that the ion AlCl_3H^- is stable in Lewis acid haloaluminates [7,28], it is presumed that Al_2Cl_7^- acts by hydride abstraction.

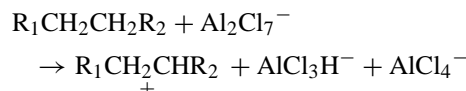


Table 5

Cracking, oligomerization and Friedel–Crafts alkylation in various ambient temperature ionic liquids (MX)

IL type	I Brønsted acidic	II Untreated Lewis basic	III Treated ^a Lewis basic	IV Untreated Lewis acidic	V Treated ^a Lewis acidic
Acids present	HCl_2^- H_2Cl_3^-	HCl_2^- (m) ClHAlCl_4^- (m)	–	$\text{ClHAl}_2\text{Cl}_7^-$ (m) ClHAlCl_4^- (m) $\text{Al}_2\text{Cl}_7^{4-}$	Al_2Cl_7^-
Other anions	Cl^- (m)	Cl^- , AlCl_4^-	Cl^- , AlCl_4^-	AlCl_4^-	AlCl_4^-
Hammett ^b acidity	-2 to -4	< -4	–	-14	–
Alkane cracking	Slight	None	None	2–20% conversion	Less than IV
Alkene oligomer	None	Slow 9% yield	None	Instant 90% yield	Fast 75% yield
F–C alkylation	–	None	–	Fast	Slow

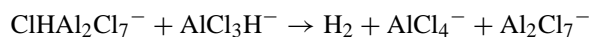
^a Treated with CaH_2 or EtAlCl_2 to eliminate last traces of protons; m: minor component.

^b Substitution of Br^- for Cl^- decreases H_0 by 2–3 units (HBr_2^- vs. HCl_2^- , Al_2Br_7^- vs. Al_2Cl_7^-).

It is concluded that at ambient temperatures:

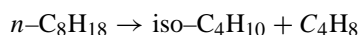
- (i) the weaker Brønsted acids HCl_2^- and $\text{H}_2\text{Cl}_3^{2-}$ crack alkanes with difficulty;
- (ii) the stronger Brønsted acids HBr_2^- and H_2Br_3^- cleave aryl–alkyl ethers readily;
- (iii) the mixed Brønsted acid, $\text{HCl}(\text{AlCl}_4)^-$ slowly polymerizes alkenes;
- (iv) the Lewis acid Al_2Cl_7^- slowly cracks alkanes but quickly polymerizes alkenes;
- (v) the Brønsted superacid $\text{HCl}(\text{Al}_2\text{Cl}_7)^-$ cracks alkanes and instantly polymerizes alkenes;
- (vi) any substitution of bromide for chloride in the latter three species increases their acidity.

In Lewis acidic systems from which the protons are not removed and particularly in systems to which the hydrogen halide is added (note that the HCl solubility [22] in 65% AlCl_3 –EmimCl is 0.036 M at 1 atm HCl), two parallel cracking mechanisms will occur—Lewis acidic and Brønsted superacidic initiated. However, these will interfere with each other, thus reducing the concentration of the scarcer but more virulent Brønsted superacid:

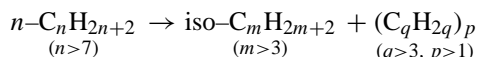


A careful manipulation of the relative catalyst amounts through temperature and HCl pressure may, however, provide a means of cracking alkanes to a controlled degree.

Why does alkane cracking occur in these systems at these temperatures? Standard thermodynamic data [29] indicate that reactions such as:



are decidedly endergonic but that alkene oligomerization is exergonic. The latter we have seen to be exothermic in the acidic ionic liquids. Thus, the “cracking” reaction we observe is better written as:



We have used various cations in these systems and seen no remarkable differences. The cation influences the liquidus temperatures, but not the form of the liquidus curves (maximum mp at MAICl_4 , eutectics either side). Through the liquid packing, the density and the species molarities depend on the cation choice [1]. Chemically, hydride does not attack R_3S^+ [7], while it reacts with Emim^+ and Bmim^+ under Lewis basic conditions [28]. Pyridinium ions favor somewhat increased reactivity, but that is not due to the N–H proton of the cation since pyridine is a strong base in these systems; the more likely reason is the higher impurity water level. Higher temperatures do, however, pose the possibility

of more available protons from the decomposition of PyH^+ and Hmim^+ salts.

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