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Gas-Phase Chemistry of Li^+ with Monofunctional and α,ω-Bifunctional Organic Molecules. How Does the Presence of a Second Functional Group Enhance Reactivity?

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Abstract: It is surprising that both univalent transition-metal ions and alkali ions can induce the dehydrohalogenation of some alkyl halides (RX) in the gas phase. The mechanisms must certainly be very different. The surface on which $[Li^+ + RX]$ reactions occur has been established. The initial step following complexation involves X^- transfer/charge transfer to form $[LiX]R^+$. If sufficient charge can be generated on the alkyl group, the reaction usually proceeds to products. When R contains a halogen ($R = (CH_2)_nY$), the mechanism is substantially altered. Following charge generation, haloalkyl cations rapidly cyclize, which has dramatic effects on subsequent mechanistic steps, final reaction products, and their distributions. The chemistry of Li^+ with a series of α,ω-bifunctional compounds is presented. The results provide additional insights into the mechanisms by which alkali ions can react.

Introduction

In the past decade, a substantial fraction of the research being pursued concerning gas-phase, bimolecular ion-molecule reactions has been dedicated to characterizing the chemistry of bare (+1) transition-metal ions with organic molecules.[1] Alkali ions have also been found to be reactive in the gas phase, although not as reactive as ions such as Fe^+ and Co^+. A number of studies have appeared concerning alkali ion binding energies to small molecules[2-8] and reactions of alkali ions with alkyl halides and alcohols.[6,9-16]

In 1979, Allison and Ridge[14] reported the gas-phase chemistry of Li^+ with a series of alcohols and chloroalkanes. When reactions were observed, they were similar to those observed for transition-metal ions, e.g.,

$$M^+ + i\text{-}C_3H_7Cl \rightarrow M^+(C_3H_6) + HCl \qquad M = Li^+, Co^+ \quad (1)$$

however, the mechanism obviously must be very different. The reactivity of Li^+ with RX (X = Cl, OH) seemed to parallel the heterolytic bond strengths of RX, ΔH for the process $RX \rightarrow R^+ + X^-$, and it was suggested[14] that the reactions proceed on the surface shown in Figure 1. The first step is the formation of the ion-molecule complex. The barrier to the reaction involves charge generation on the alkyl group. The height of the barrier, as reflected by reactivity, appears to be related to the *difference* between the affinities of Li^+ and R^+ for the anion X^-; this difference will be referred to as the (anion) exchange energy, $\Delta H_{ex} = D(R^+-X^-) - D(Li^+-X^-)$. For most alcohols and chloroalkanes, ΔH_{ex} is positive. The alkyl group has a greater affinity for Cl^- or OH^- than does Li^+, so separation to the products (LiX and R^+) cannot occur exothermically (see Table I). The next step appears to be a H shift, occurring as an internal proton transfer from R^+, resulting in charge migration back onto the alkali atom, with the RX molecule now rearranged to two "ligands"—an olefin (R-H) and HX. This complex then dissociates to the observed products.

Table I. Heterolytic Bond Strengths (kcal/mol)[a]

R^+	$D(R^+-Cl^-)$	$D(R^+-Br^-)$	$D(R^+-OH^-)$
Li^+	155	148	186
CH_3^+	227	220	278
$C_2H_5^+$	191	183	242
$n\text{-}C_3H_7^+$	188	180	239
$n\text{-}C_4H_9^+$	186	178	236
$n\text{-}C_5H_{11}^+$	180	174	232
$i\text{-}C_3H_7^+$	171	163	223
$t\text{-}C_4H_9^+$	155	147	208
$\underline{CH_2CH_2Br}^+$	174	165	226
$\underline{CH_2CH_2CH_2CH_2Br}^+$	142	134	193
$\underline{CH_2CH_2Cl}^+$		174	233
$\underline{CH_2CH_2CH_2CH_2Cl}^+$		149	205
$\underline{CH_2CH_2CH_2CH_2CH_2Cl}^+$		141	200
$\underline{CH_2CH_2OH}^+$	173	166	
$\underline{CH_2CH_2CH_2OH}^+$	162	156	
$\underline{CH_2CH_2CH_2CH_2OH}^+$	146	137	
$\underline{CH_2CH_2CH_2CH_2CH_2OH}^+$	140		

[a] See Appendix for computational details.

The reactions reported are typically dehydration and dehydrohalogenation reactions. A few cases have been studied in which $\Delta H_{ex} < 0$, allowing for alkyl cation formation, reaction 2. For

$$M^+ + RX \rightarrow MX + R^+ \qquad (2)$$

example, this has been observed for M = Li and $RX = t\text{-}C_4H_9Br$,[9] M = Na and $RX = (CH_3)_2BrCC(CH_3)_2Br$,[9] M = Cs and $RX = C_6H_5CH_2Cl$,[12] and M = Li and RX = 1-chloroadamantane.[14]

Figure 1 allows for reactivity trends to be understood. Those systems that are reactive correspond to small positive or negative values of ΔH_{ex}, which is the case when $D(M^+-X^-)$ is relatively large and/or $D(R^+-X^-)$ is relatively small. This also correlates with the fact that reactivity of the alkali ions (M^+) follows the trend $Li^+ > Na^+ > K^+ > Cs^+$, since $D(M^+-X^-)$ increases as the size of M^+ decreases for $X^- = Cl^-, Br^-$, and OH^-. More details will follow concerning the mechanism. Here we contrast the chemistry of Li^+ with a series of mono- and bifunctional com-

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(1) See, for example: (a) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (b) *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Press: New York, 1989.

(2) Guo, B. C.; Conklin, B. J.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6506.

(3) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

(4) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920.

(5) Freiser, B. S.; Staley, R. H.; Beauchamp, J. L. *Chem. Phys. Lett.* **1976**, *39*, 49.

(6) Weddle, G. H.; Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 105.

(7) Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

(8) Woodin, R. L.; Beauchamp, J. L. *Chem. Phys.* **1979**, *41*, 1.

(9) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964.

(10) Hodges, R. V.; Beauchamp, J. L. *Anal. Chem.* **1976**, *48*, 825.

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(12) Safron, S. A.; Miller, G. D.; Rideout, F. A.; Horvat, R. C. *J. Chem. Phys.* **1976**, *64*, 5051.

(13) Miller, G. D.; Safron, S. A. *J. Chem. Phys.* **1976**, *64*, 5065.

(14) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(15) Creasy, W. R.; Farrar, J. M. *J. Chem. Phys.* **1987**, *87*, 5280.

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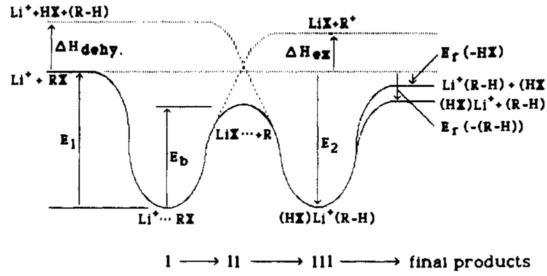

RX	E_1[a]	ΔH_{ex}	E_b	ΔH_{dehy}	E_2	$E_r(-HX)$	$E_r(-(R-H))$
i-C_3H_7Cl	+30	+16	+24.7	+17.3	-15	- 5.1	- 1.2
1-C_4H_9OH	+46	+22	+36.9	+12.9	-40	-11.0	-18.0
i-C_3H_7Br	+31	+15	+28.0	+19.2	-14	- 3.7	- 0.9

a. All energies are in kcal/mol. See text for discussion.

Figure 1.

pounds, which provides additional insights into the reactivity of Li^+. The discussion will propose why, for example, Li^+ is unreactive with C_2H_5OH and C_2H_5Cl but does react with ClC_2H_4OH.

Experimental Section

All experiments were performed on an ion cyclotron resonance mass spectrometer of conventional design that has been previously described.[17] Mass spectra were obtained with use of a frequency swept detector.[18] Li^+ ions were generated by thermionic emission. A thermionic emitter was made by coating a rhenium wire with a lithium aluminosilicate as described by Blewett and Jones.[19] This was placed directly into the ICR source region and resistively heated, and a small positive bias was applied. Depending on the age of the emitters, other ions such as Na^+ and K^+ are also formed in addition to copious amounts of Li^+.

The organic compounds were obtained from the following sources: The compounds 2-bromoethanol, 3-bromopropanol, 1-bromobutane, and 4-bromobutanol were obtained from Alfa. The 2-chloroethanol, 1-bromopropane, 1-chloropropane, 1-bromo-3-chloropropane, 3-chloro-1-propanol, 4-chloro-1-butanol, and 1-bromopentane were obtained from the Aldrich Chemical Co. The bromoethane was obtained from Mallinckrodt. The 1-bromo-2-chloroethane and 1-chloropentane were obtained from Fluka. The 1-bromo-4-chlorobutane was obtained from Fairfield Chemicals. The 1-bromo-5-chloropentane was obtained from the Columbia Organic Chemical Co., and 1-chloro-5-pentanol was obtained from K&K. Most of the compounds were sufficiently pure to be used without further purification, although in some cases, bifunctional compounds are only available at a purity of 95%. Problems may arise when impurities are much more volatile than the compound selected for these experiments. Usually the mass spectrum of the organic vapors will indicate if impurities are present, although for some of the bifunctional compounds, impurities such as lower homologues may be difficult to detect. When impurities appeared to be present, the compounds were vacuum distilled. This usually increased the sample purity to an acceptable level. In some cases, unusual experimental results prompted further investigations of sample purity. For example, in our study of the reactions of Li^+ with 2-bromoethanol, a product ion was observed at m/z 95 that could not be explained. The NMR spectrum of the bromoethanol sample contained an impurity peak, a singlet at 3.7 ppm, which appeared to be due to the presence of dioxane. Distillation led to a substantial decrease in the formation of the product, although the dioxane could not be completely removed. To further investigate the possibility of dioxane as a contaminant, the gas-phase chemistry of Li^+ with dioxane was investigated. Only an addition product was observed, yielding an adduct ion at m/z 95.

In a typical experiment, the purity of the organic reactant was first checked by electron impact ionization (EI). If a satisfactory mass spectrum was obtained, the EI filament was turned off and the thermionic emitter turned on. Pressures of the organic compounds used were typically 7×10^{-6}–3×10^{-5} Torr. Double resonance experiments were always performed to determine reactant–product relationships when Li^+, Na^+, and K^+ were present as ionic reactants. Even when only Li^+ was generated by the thermionic emitter, it is still important to eject Li^+ to be assured that all product ions disappear as well—to confirm that the products are indeed due to gas-phase ion–molecule reactions, not products of surface chemistry on the hot emitter. The results of these experiments are listed in Tables II–IV.

Table II. Reactions of Li^+ with Chloroalkanes and Bromoalkanes

	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$Li^+ + C_nH_{2n+1}Cl$				
$\rightarrow LiC_nH_{2n}^+ + HCl$	NR[a]	100%[a]	100%[a]	100%
$\rightarrow LiHCl^+ + C_nH_{2n}$	NR			
$Li^+ + C_nH_{2n+1}Br$				
$\rightarrow LiC_nH_{2n}^+ + HBr$	NR	100%	100%	100%
$\rightarrow LiHBr^+ + C_nH_{2n}$	NR			

[a] Taken from ref 14.

Table III. Reactions of α,ω-Bromochloroalkanes with Li^+

	$n = 2$	$n = 3$	$n = 4$	$n = 5$
$Li^+ + Cl(CH_2)_nBr$				
$\rightarrow LiC_nH_{2n-1}Br^+ + HCl$		100%	8%	12%
$\rightarrow LiC_nH_{2n-1}Cl^+ + HBr$			2%	5%
$\rightarrow LiC_nH_{2n-2}^+ + HCl + HBr$			3%	7%
$\rightarrow LiCl + C_nH_{2n}Br^+$			84%	73%
$\rightarrow LiBr + C_nH_{2n}Cl^+$			3%	3%

Table IV. Reactions of Li^+ with Bromoalcohols

	$n = 2$	$n = 3$	$n = 4$
$Li^+ + Br(CH_2)_nOH$			
$\rightarrow LiC_nH_{2n}O^+ + HBr$	5%	100%	17%
$\rightarrow LiHBr^+ + C_nH_{2n}O$	95%		
$\rightarrow LiC_nH_{2n-1}Br^+ + H_2O$			4%
$\rightarrow LiC_nH_{2n-2}^+ + HBr + H_2O$			2%
$\rightarrow LiOH + C_nH_{2n}Br^+$			77%

When Na^+ and K^+ ions were formed, adduct formation with neutral organic molecules was frequently observed. There was only one case where Na^+ was observed to react. The Na^+ ion induces HBr elimination from $Br(CH_2)_4OH$ to form the $NaC_4H_8O^+$ product ion.

Results and Discussion

First, a brief discussion on the reactions of Li^+ with the monofunctional compounds will be presented to set the stage for the discussion of the reactions involving the bifunctional compounds. In the discussion, thermochemical data are presented. Sources of ionic and neutral heats of formation that were used are discussed in the Appendix.

1-Chloroalkanes. It has been reported[14] that Li^+ does not react with methyl or ethyl chloride but does react with i-C_3H_7Cl, n-C_4H_9Cl, and t-C_4H_9Cl. We add to the list n-$C_5H_{11}Cl$ as being reactive (see Table II). Exemplary of the chloride reactions, details for the $Li^+ + i$-C_3H_7Cl case are presented here and summarized in Figure 1. When the initial encounter complex, I, is formed, approximately 30 kcal/mol[4] are released, the electrostatic binding energy $D(Li^+–ClC_3H_7) = E_1$. The energy associated with chloride exchange is $\Delta H_{ex} = D(i\text{-}C_3H_7^+–Cl^-) - D(Li^+–Cl^-) = 171 - 155 = +16$ kcal/mol (using the heterolytic bond strengths in Table I). Farrar et al.[15] have suggested that the barrier height, E_b, is 24.7 kcal/mol. In their work,[15] it is suggested that the barrier height does not only depend on charge development on the alkyl group but also involves the H atom migration to some extent. Note that, in this case, $E_b > \Delta H_{ex}$, however $E_b < E_1$, so intermediate II is thermodynamically accessible, and the reaction can proceed. Whatever the nature of intermediate II, conversion from II to III requires a H shift. If substantial charge generation on R^+ occurs, the H shift can be considered as a proton-transfer step. In the case of i-C_3H_7Cl, conversion of II to III would involve an intermediate of the type $(LiCl)H^+(C_3H_6)$. Would proton transfer from the complexed alkyl cation be favored? The proton affinity (PA) of propene is 179.5 kcal/mol.[20] From $\Delta H_f(LiHCl^+) = 121$ kcal/mol,[15] we compute that PA(LiCl) = 197.9 kcal/mol; thus,

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[17] Stepnowski, R.; Allison, J. *J. Am. Chem. Soc.* **1989**, *111*, 449.
[18] Wronka, J.; Ridge, D. P. *Rev. Sci. Instrum.* **1982**, *53*, 491.
[19] Blewett, J. P.; Jones, E. J. *Phys. Rev.* **1936**, *50*, 464.
[20] Lias, S. G.; Liebman, G. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*.

in the gas phase, LiCl is a stronger base than propene, and conversion of II to III should readily occur. We estimate E_2 as follows: Energy must be put *in* to i-C_3H_7Cl to form propene and HCl. ΔH for dehydrohalogenation and dehydration reactions (RX → (R-H) + HX) will be referred to as ΔH_{dehy}. For i-C_3H_7Cl, ΔH_{dehy} = +17.3 kcal/mol. Energy is released when propene and HCl bind to Li^+. Farrar[15] suggests $D(Li^+–C_3H_6)$ = 23.1 kcal/mol and $D(Li^+–HCl)$ = 19.1 kcal/mol. Thus, if the binding energies were additive, we would conclude that $E_2 = \Delta H_{dehy} - D(Li^+–C_3H_6) - D(Li^+–HCl) = -24.9$ kcal/mol. However, we would not expect the binding energies to be additive. The data in ref 7 for first and second binding energies of molecules to Li^+ can be used to estimate the extent to which binding energies of two molecules to Li^+ are *not* additive. For example, Li^+ forms a complex with CH_3OH with a binding energy of 38.1 kcal/mol; a second methanol molecule binds to $LiMeOH^+$ with an energy of 26.2 kcal/mol, approximately 10 kcal/mol less than the first. We will use a "correction factor" of +10 kcal/mol to indicate that the binding energies are not additive when *two* molecules are bound to the Li^+, thus we suggest that $E_2 = \Delta H_{dehy} - D(Li^+–C_3H_6) - D(Li^+–HCl) + 10 \approx -15$ kcal/mol. Finally ΔH for the overall reaction $Li^+ + i\text{-}C_3H_7Cl \rightarrow LiC_3H_6^+ + HCl$ has been estimated[15] to be −5.1 kcal/mol, and −1.2 kcal/mol for the $LiHCl^+ + C_3H_6$ products. (With use of values reported above, these two processes are exothermic by 5.8 and 1.8 kcal/mol.) Thus, the reaction should occur. The reaction does not occur for smaller chloroalkanes such as C_2H_5Cl because ΔH_{ex} is larger than for i-C_3H_7Cl, and thus one expects E_b to be larger as well. In general, since E_1 increases as the size of RX increases for a given X, we expect E_1 to be smaller for C_2H_5Cl than it is for i-C_3H_7Cl, thus intermediate II is energetically inaccessible for C_2H_5Cl and dehydrochlorination products are not formed.

1-Alcohols. As shown in Table I, the situation is very different for alcohols since their heterolytic bond strengths are substantially higher than those for the corresponding chloroalkanes. Alcohols are less reactive than chloroalkanes. Only *tert*-butyl alcohol has been observed[14] to react with Li^+. For the ($Li^+ + t\text{-}C_4H_9OH$) case, E_1 = 46 kcal/mol.[16,21] Farrar[16,21] suggests that E_b = 36.9 kcal/mol. From Table I, ΔH_{ex} = +22 kcal/mol. Approximately 13 kcal/mol are required to dehydrate *tert*-butyl alcohol. We estimate E_2 to be −40 kcal/mol (as described above). The overall ΔH of the processes yielding the two products have also been estimated by Farrar[21] and are listed in Figure 1.

Again, ΔH_{ex} and E_b are less than E_1, allowing the reaction to proceed to intermediate II. If the reaction proceeds from II to III via a proton transfer, we again conclude that proton transfer will occur readily since PA(LiOH) = 241 kcal/mol[22] > PA(i-C_4H_8) = 195.9 kcal/mol.[20] It is not unreasonable, from the data in Table I, that straight chain alcohols are unreactive, since the larger heterolytic bond strengths for these molecules lead to larger values of ΔH_{ex}, contributing to larger E_b's, prohibiting conversion of I to II, i.e., prohibiting sufficient charge generation on the alkyl groups.

To reinforce the importance of the reaction barrier, consider i-C_3H_7Cl and i-C_3H_7OH. The Li^+ ion reacts with i-C_3H_7Cl (reaction 1) to yield $LiC_3H_6^+$ and HCl. For isopropyl chloride, ΔH_{dehy} = 17.3 kcal/mol. Thus, for the final products to be formed in an exothermic process, $D(Li^+–C_3H_6)$ must be ≥17.3 kcal/mol. For isopropyl alcohol, ΔH_{dehy} = 12.1 kcal/mol; *less* energy is required to form propene from the alcohol than from the chloride, thus the overall reaction 3 *must be exothermic*. The reaction does

$$Li^+ + i\text{-}C_3H_7OH \rightarrow Li^+(C_3H_6) + H_2O \qquad (3)$$

not occur because ΔH_{ex} is sufficiently large that intermediate II is inaccessible for the thermal energy interaction of Li^+ with isopropyl alcohol.

1-Bromoalkanes. We report here that straight chain bromoalkanes react with Li^+ except for ethyl bromide (see Table II). It has also been reported[9,15] that Li^+ reacts with i-C_3H_7Br and t-C_4H_9Br. The available and estimated values for E_1, ΔH_{ex}, E_b, ΔH_{dehy}, E_2, and E_r for ($Li^+ + i\text{-}C_3H_7Br$) are listed in Figure 1. As in the other systems discussed above, $E_1 > E_b$, so the reaction can proceed to intermediate II. We note that, again, $E_b > \Delta H_{ex}$.[23] Proton transfer to proceed to intermediate III should again be facile. Using $D(Li^+–HBr)$ = 19.1 kcal/mol,[15] we estimate that $\Delta H_f(LiHBr^+)$ = 134.3 kcal/mol, and from this, PA(LiBr) = 195 kcal/mol. Thus PA(LiBr) > PA(C_3H_6), so proton transfer should occur.

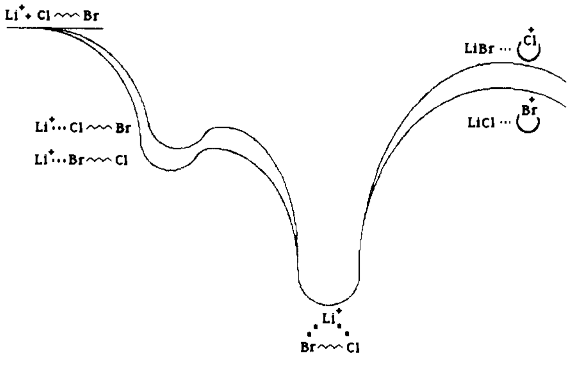


Figure 2. Early stages in the reaction of Li^+ with chlorobromoalkanes.

It has been reported[9] that, in addition to dehydrobromination, reactions 4 and 5, Li^+ reacts with *tert*-butyl bromide by bromide exchange, reaction 6. We note that this system represents a case

$$Li^+ + t\text{-}C_4H_9Br \rightarrow LiC_4H_8^+ + HBr \qquad (4)$$

$$\rightarrow LiHBr^+ + C_4H_8 \qquad (5)$$

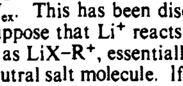
$$\rightarrow C_4H_9^+ + LiBr \qquad (6)$$

where ΔH_{ex} is *negative*, thus, complete Br^- abstraction by Li^+, reaction 6, can occur exothermically. Also, we note that proton transfer can occur; however, PA(LiBr) ≈ PA(i-C_4H_8) = 195 kcal/mol. Apparently proton transfer via $[LiBr]H^+[C_4H_8]$ and dissociation of $[LiBr]C_4H_9^+$ both occur at competitive rates, since both products are observed.

α,ω-Bromochloroalkanes. As shown in Table III, 1,2-bromochloroethane does not react with Li^+. Its monofunctional analogues chloroethane and bromoethane do not react either. Two trends are apparent from Table III. First, it appears that Li^+ reacts with the Cl substituent to a greater extent than with the Br group. Also, for the longer chains, alkyl cations are formed, which are not and cannot be formed for the monofunctional analogues. Consider the formation of intermediate II in the case of $Cl(CH_2)_4Br$, with Li^+ attacking the Cl end. If II has a structure similar to that expected for chlorobutane, IIa, then dissociation would not be expected. However, if sufficient charge is generated on the alkyl group to allow for the formation of a cyclic bromonium ion as shown in IIb, then the reaction can

$LiCl\cdots{}^{+}CH_2CH_2CH_2CH_2Br$

IIa



IIb

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[21] Creasy, W. R.; Farrar, J. M. *J. Phys. Chem.* **1986**, *85*, 162.

[22] See Appendix.

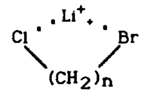
[23] We note that, for the three cases in Figure 1 where values for E_b have been proposed, that for each case, $E_b > \Delta H_{ex}$. This has been discussed by Farrar et al.[15] Would this be expected? Suppose that Li^+ reacts with RX and intermediate II can be simply described as $LiX–R^+$, essentially an ion-molecule complex of an alkyl cation with a neutral salt molecule. If this were the case, then, to convert I → II, energy would have to be put *in* to cleave the $Li^+–XR$ bond (E_1), more energy would be required to transfer X^- (ΔH_{ex}), and energy is released when the $R^+–LiX$ bond is formed, therefore $E_b \approx D(Li^+–XR) + \Delta H_{ex} - D(R^+–LiX)$ which is $>\Delta H_{ex}$. This suggests that $D(Li^+–XR) - D(R^+–LiX) > 0$, or $D(Li^+–XR) > D(R^+–LiX)$. With this model, if the ion-molecule binding energies in I and II were equal, E_b would be equal ΔH_{ex}. While binding energies of organic cations to lithium salts have not been investigated to date, we note that, for a common neutral such as H_2O, Li^+ binds more strongly than does an alkyl cation (e.g. $D(Li^+–H_2O)$ = 34 kcal/mol, $D(t\text{-}C_4H_9^+–H_2O)$ = 11.2 kcal/mol[2]). However, since the dipole moment of, e.g., LiCl is larger than RCl, it is difficult to address this aspect of the E_b values. It does, however, seem reasonable to assume that E_b will be $\geq\Delta H_{ex}$ for the systems studied here.

proceed. Thus, if we consider $C_4H_8Br^+$ to take the cyclic form, Table I suggests that $\Delta H_{ex} = -14$ kcal/mol; elimination of LiCl can occur exothermically. Thus, we must consider intermediate II in the following discussions involving bifunctional molecules, as involving a salt molecule electrostatically bound to a cyclic ion.

How should early stages of the reaction be envisaged? Presumably, the initial complex can take the form of Ia, Ib, or Ic.

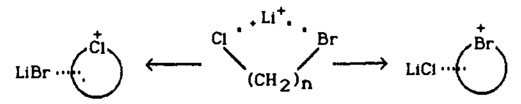
$Li^+ \cdots\cdots Cl-(CH_2)_n-Br$ $\quad$ $Li^+ \cdots\cdots Br-(CH_2)_n-Cl$

Ia Ib



Ic

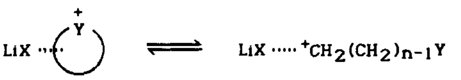
The important question concerns how and where in the reaction the Cl vs Br preference reveals itself. One possibility is in the initial complex formation. We would expect Ib to be slightly more stable than Ia, based on binding energies for bromo- and chloroalkanes.[4] If we consider the formation of type II intermediates via Ic the data in Table I clearly show, based on ΔH_{ex} values, that,



IIc Ic IId

thermodynamically, IId would be favored over IIc, the former having the smaller ΔH_{ex}. Thus we propose that interaction with both functional groups occurs, and at this point, as reflected by ΔH_{ex} values, Cl^- transfer occurs to a greater extent than Br^- transfer, resulting in the observed selectivity for the reaction at the Cl^- end of these molecules. (This proposal is for the bromochloroalkanes, a specific situation where there is no strong preference for Li^+ binding to either of the two ends. As will be discussed, the situation is different for halo alcohols.) Early stages of the reaction for the bromochloroalkanes might then be represented as shown in Figure 2. Apparently the stability of the cyclic halonium ions increases as the ring size increases to the point where the ΔH_{ex} values become negative, yielding halide abstraction products for $Cl(CH_2)_nBr$ when $n = 4$ and 5.

For the bromochloroalkanes, dehydrohalogenation is also observed, which is apparently *not* competitive with cyclic halonium ion formation, when it does occur. This prompts the question of whether proton transfer from cyclic halonium ions can occur. We propose that it does not to any great extent. A number of factors should be considered. Noting that cyclic halonium ions are usually written with the charge on the halogen,[9] one might suggest that proton transfer would not occur because the charge does not reside on a carbon center that could yield a proton. However, theoretical descriptions[24,25] do not show a substantial positive charge on the halogen but a distributed charge throughout the cyclic structure. However, we expect proton transfer from c-$(CH_2)_nX^+$ to require more energy than from $^+CH_2(CH_2)_{n-1}X$, and the latter may be the only species that could protonate a neutral lithium halide. (We note that ion–molecule reactions of cyclic halonium ions have been reported but do not involve proton transfer.[26]) Thus, we propose that sufficient energy is available such that the structure is dynamic, sampling both cyclic and acyclic possibilities, IIe and IIf (X, Y = halogens), and it is the IIf form that can undergo an



IIe IIf

internal proton transfer to yield intermediate IIIa. The experimental data suggest that the IIe/IIf distribution favors the IIe structure.

$(HX)Li^+(CH_2{=}CH-(CH_2)_{n-2}Y)$

IIIa

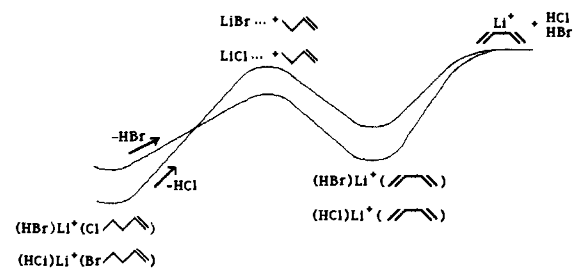
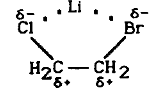


Figure 3. Features of the potential energy surface on which bromochlorobutane reacts to form $Li(C_4H_6)^+$.

If the data in Table I are considered with regard to $ClCH_2CH_2Br$, the question arises as to why no reaction was observed, when ΔH_{ex} values would predict that a reaction should occur. This observation may again point to the importance of the initial complex in the form Ic. As the two halogens compete to form intermediate II involving Cl^- *or* Br^- transfer, the charge distribution shown in Id may be of sufficiently high energy, since it



Id

involves partial cationic character on two adjacent C atoms, that the complex dissociates to reactants. Other thermodynamic considerations of the mechanism would suggest that a reaction would occur.

Another feature of the reactions of the bromochloroalkanes is the double dehydrohalogenation processes that occur when $n \geq 4$ to form a Li^+–diene complex as the final product. This is a minor pathway, and qualitative features of the additional aspects of the potential energy surface for the second dehydrohalogenation step, for 1-bromo-4-chlorobutane, are suggested in Figure 3. We note that PA(butadiene) = 193 kcal/mol, which is <PA(LiX), thus proton transfer from $C_4H_7^+$ to either LiCl or LiBr can readily occur.

There are some thermochemical implications of the reactions in Table III that merit comment. The formation of butadiene by reaction 7 requires 31 kcal/mol, therefore $D(Li^+-C_4H_6) > 31$

$$Cl(CH_2)_4Br \rightarrow C_4H_6 + HCl + HBr \qquad (7)$$

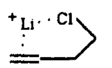
kcal/mol. This is slightly higher than the binding energy of 28 kcal/mol that was suggested by Farrar et al.[16]

Reactions 8 and 9 were observed and are assumed to be exothermic, $\Delta H < 0$. The implication is that $\Delta H_f(LiC_4H_7Br^+) <$

$$Li^+ + Cl(CH_2)_4Br \rightarrow LiC_4H_7Br^+ + HCl \qquad (8)$$

$$\rightarrow LiC_4H_7Cl^+ + HBr \qquad (9)$$

148.6 kcal/mol and $\Delta H_f(LiC_4H_7Cl^+) <$ 135.5 kcal/mol. We have approximated ΔH_f(4-chloro-1-butene) to be 10.4 kcal/mol and ΔH_f(4-bromo-1-butene) to be –0.9 kcal/mol,[22] which then suggests $D(Li^+-C_4H_7Cl) > 37.3$ kcal/mol and $D(Li^+-C_4H_7Br) > 14.7$ kcal/mol. The former bond strength is higher than expected[4] for a Li^+–olefin or Li^+–chloroalkane complex and may suggest a multiple interaction in the final product, structure IV.



IV

Thermochemical data on gas-phase cyclic halonium ions are somewhat scattered.[9,25-27] Limits on their heats of formation can

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[24] Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 2665.

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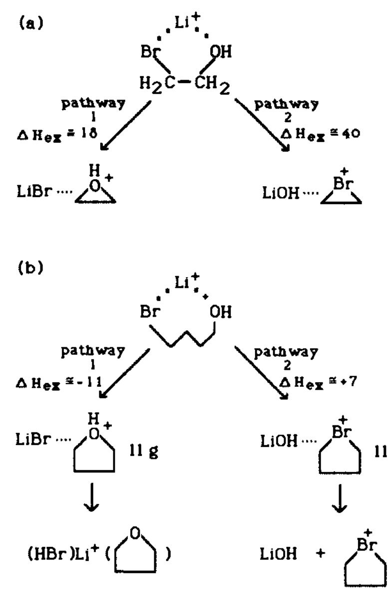


Figure 4. Possible pathways for the interaction of Li$^+$ with bromo alcohols.

be derived from the reactions observed in this work. The chemistry suggests $\Delta H_f(\text{c-C}_4\text{H}_8\text{Br}^+) < 173.28$ kcal/mol, consistent with a value of 160.5 ± 10 kcal/mol, derived from Beauchamp's estimate of the bromide affinity of c-$C_4H_8Br^+$ as 133.6 ± 10 kcal/mol.[9] The limit $\Delta H_f(\text{c-C}_4\text{H}_8\text{Cl}^+) < 163.3$ kcal/mol is reasonable in light of the theoretical estimate[27] of 160.3 kcal/mol. MINDO/3 calculations[25] also suggest $\Delta H_f(\text{c-C}_5\text{H}_{10}\text{Cl}^+) = 151.7$ kcal/mol, and the chemistry reported here suggests the value is <159.3 kcal/mol. We further suggest that $\Delta H_f(\text{c-C}_5\text{H}_{10}\text{Br}^+) < 169.3$ kcal/mol; there are no other reported values to use as a basis for comparison.

α,ω-Bromohydroxyalkanes. While the bromide and chloride groups are fairly equivalent chemically and the thermochemical aspects of reactions at either the chloro or bromo end of the bromochloroalkanes are relatively similar, the OH group introduces a very different set of conditions. Table I shows that the heterolytic R^+X^- bond strengths are substantially larger for X = OH than for X = Cl or Br. While the cyclic halonium ions undergo dramatic increases in stability as ring size increases, the effect is not as pronounced for the cyclic analogues from hydroxyalkyl cations, protonated cyclic ethers. The data in Figure 1 suggest that the binding energies for Li$^+$ to alcohols are substantially higher than to alkyl halides. If this were the controlling factor in early stages of the reaction, Ie would be more stable than If, suggesting that bromo alcohols might react as their monofunctional alcohol analogues, rather than as bromoalkanes. If

$Li^+ \cdots HO{-}(CH_2)_n{-}X$ Ie $\qquad$ $Li^+ \cdots X{-}(CH_2)_n{-}OH$ If

we consider, as we did for the mixed halogen compounds in the previous section, the relative exchange energies, we might expect preferential reaction at the Br$^-$ end of the molecule. For example, Figure 4 shows the ΔH_{ex} values, assuming that Br$^-$ or OH$^-$ exchange would result in the formation of intermediate II which contains the corresponding cyclic cation. What we see from the data in Table IV is that reaction occurs at the Br end for the smaller compounds and at the OH end, predominantly, for the $Br(CH_2)_4OH$. It appears that the stability of the cationic component of intermediate II again controls the product distribution.

First consider bromoethanol. As shown in Figure 4a, the exchange energy associated with formation of intermediate II at the OH end, 40 kcal/mol, is larger than that for isopropyl alcohol, which does *not* react with Li$^+$, therefore, we assume that E_b is sufficiently large to prohibit reaction via pathway 2 in Figure 4a. The exchange energy prohibits significant charge transfer to the bromoethyl group. At the Br end, the exchange energy is 18 kcal/mol (Figure 4a), which is less than ΔH_{ex} for the *n*-bromoalkanes, which do react, so E_b must be sufficiently small that the reaction can proceed via pathway 1 of Figure 4a. Proton transfer via $[LiBr]H^+[\text{c-CH}_2\text{CH}_2\text{O}]$ should occur since PA(c-CH_2CH_2O) = 187.9 kcal/mol < PA(LiBr) = 195 kcal/mol. Also, protonated oxirane *can* transfer a proton, unlike a cyclic halonium ion. Thus, it is clear why bromoethanol reacts as a bromide.

Table V. Reactions of Li$^+$ with Chloroalcohols

	n = 2	n = 3	n = 4	n = 5
$Li^+ + Cl(CH_2)_nOH$				
$\rightarrow LiC_nH_{2n}O^+ + HCl$	100%	100%	64%	91%
$\rightarrow LiC_nH_{2n-1}Cl^+ + H_2O$			15%	5%
$\rightarrow LiH_2O^+ + C_nH_{2n-1}Cl$			1%	1%
$\rightarrow LiC_nH_{2n-2}^+ + HCl + H_2O$			4%	3%
$\rightarrow LiOH + C_nH_{2n}Cl^+$			16%	

In the case of $Br(CH_2)_4OH$, both ΔH_{ex} values must be negative. If Li$^+$ reacts with the Br end (pathway 1, Figure 4b), $\Delta H_{ex} \approx -11$ kcal/mol; however, ΔH_{ex} must also be negative when Li$^+$ reacts with the OH end, since complete OH$^-$ transfer occurs, reaction 10. From the data in Table I, ΔH_{ex} for the above reaction is +7

$$Li^+ + HOC_4H_8Br \rightarrow LiOH + \text{c-C}_4H_8Br^+ \qquad (10)$$

kcal/mol. However, the $(R^+{-}OH^-)$ bond strength for R^+ = c-$C_4H_8Br^+$ was calculated by using a thermodynamic value[9] reported to within ±10 kcal/mol. Thus, the heterolytic bond strengths as listed in Table I for c-$C_4H_8Br^+$ may all be too high by as much as 7–8 kcal/mol. Why, then, does the reaction favor pathway 2 of Figure 4b? The simplest explanation is that the initial electrostatic interactions are sufficiently different that Li$^+$ complexation with the HO end is favored over that with the Br end, and *this* determines the eventual distribution of products. Thus, as suggested in Figure 4b, both ends of the molecule react to form IIg and IIh.

In IIg, a mobile proton is present, proton transfer is rapid, and dehydrobromination is apparently more rapid than dissociation to LiBr and protonated oxirane. In contrast, IIh cannot readily transfer a proton, but it *can* dissociate to LiOH and c-$C_4H_8Br^+$, which is observed. Thus, the Li$^+$ interacts with both functional groups to form two type II intermediates, IIg and IIh. Structure IIh is favored. The intermediates react further in very different ways, reflecting the ability of the various cyclic cations to participate in proton transfer within the ion–molecule complex.

We note that, while experimentally determined estimates are available for the heats of formation of c-$C_nH_{2n}Br^+$ for n = 2 and 4,[9] none is available for c-$C_3H_6Br^+$. If we assume that reaction 11 is not observed because it is endothermic, this would set a lower

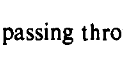
$$Li^+ + Br(CH_2)_3OH \rightarrow LiOH + \text{c-C}_3H_6Br^+ \qquad (11)$$

bound, $\Delta H_f(\text{c-C}_3\text{H}_6\text{Br}^+) > 160.1$ kcal/mol. If reaction 12 is not

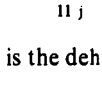
$$Li^+ + Cl(CH_2)_3Br \rightarrow LiCl + \text{c-C}_3H_6Br^+ \qquad (12)$$

observed because it is endothermic, this places a more significant lower bound, $\Delta H_f(\text{c-C}_3\text{H}_6\text{Br}^+) > 180.3$ kcal/mol. If we assume that $\Delta H_f(\text{c-C}_3\text{H}_6\text{Br}^+) = 181$ kcal/mol, then $D(Cl^-{-}C_3H_6Br^+)$ = 156 kcal/mol; this value falls between $D(R^+{-}Cl^-)$ for R^+ = c-$C_2H_4Br^+$ and c-$C_4H_8Br^+$ which is the expected trend.

α,ω-Chlorohydroxyalkanes. In the case of the bromo alcohols, we suggested that Li$^+$ would interact to a greater extent with the OH group than with the Br group. In the case of the chloro alcohols, dehydrochlorination dominates, as shown in Table V. These results need not be conflicting. Apparently, both the chloro and bromo alcohols can "sample" the type II intermediates IIi and IIj. We propose that IIi is formed to a greater extent than



IIi



IIj

IIj. Evidence for passing through IIj is the dehydrohalogenation

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product ion. Since proton transfer does not appear to readily occur via IIi, its formation is only realized if ΔH_{ex} is negative, and the free cyclic halonium ion is produced. Apparently, when X = Br, c-$C_nH_{2n}X^+$ can be formed (when $n = 4$); however, the chloro analogues are not sufficiently stable to do so. Thus, while IIi may be formed when X = Cl, proton transfer does not occur, loss of LiOH is endothermic, and thus no (or very little) products are formed via IIi.

Chloroethanol reacts with Li^+ and HCl is eliminated. If we consider this as a chloroalkane and as an alcohol, $\Delta H_{ex}(Cl) = 18$ kcal/mol, $\Delta H_{ex}(OH) = 47$ kcal/mol. If one compares these values with ΔH_{ex} for alcohols and chloroalkanes that do and do not react, we would expect E_b for OH^- exchange to be prohibitively large and would predict that this molecule should react as a chloroalkane, which it does. Chloroalkanes do not show alcohol-like products until the alkyl chain contains at least four carbon atoms. Again, this is consistent with the correlation of reactivity with ΔH_{ex}. Recall that isopropyl alcohol ($\Delta H_{ex} = 37$ kcal/mol) does not react with Li^+, while *tert*-butyl alcohol ($\Delta H_{ex} = 22$ kcal/mol) does. $\Delta H_{ex}(OH)$ for $Cl(CH_2)_4OH$ is 19 kcal/mol, less than that for *tert*-butyl alcohol, predicting a sufficiently small barrier height that chlorobutanol should exhibit reactions characteristic of an alcohol, as well as a chloroalkane.

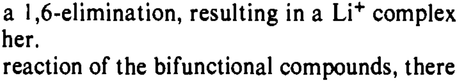
In a previous section, an observed reaction for $Cl(CH_2)_5Br$ suggested that $\Delta H_f(c\text{-}C_5H_{10}Cl^+) < 159.3$ kcal/mol. Since Li^+ does not form this ion from chloropentanol, this places a lower bound on $\Delta H_f(c\text{-}C_5H_{10}Cl^+)$ of >137.2 kcal/mol, thus these results suggest $\Delta H_f(c\text{-}C_5H_{10}Cl^+) = 148 \pm 11$ kcal/mol, again supporting the theoretical estimate[25] of 151.7 kcal/mol.

Unfortunately, Table V suggests that Li^+ reacts with chlorobutanol to form a small amount of c-$C_4H_8Cl^+$, which would imply $\Delta H_f(c\text{-}C_4H_8Cl^+) < 141.2$ kcal/mol, which is exceedingly low. This would further suggest that $D(c\text{-}C_4H_8Cl^+\text{–}OH^-) < 185.6$ kcal/mol, which does not correlate with the heterolytic bond strengths in Table I. In all other cases, when cyclic halonium ions could be formed, they dominated the products. Here this is not the case, thus we must conclude that the $C_4H_8Cl^+$ ion observed was the product of some impurity reacting with Li^+ and is probably not a product from chlorobutanol.

Conclusions

For the functional groups studied here, X = Cl, Br, and HO, α,ω-bifunctional alkanes exhibit a richer chemistry than their monofunctional analogues. The reaction mechanism involved X^- "exchange", transfer of X^- from R^+ to Li^+. When $R^+ = C_nH_{2n+1}{}^+$, proton affinity data are consistent with a H-shift occurring as a proton transfer, resulting in dehydrogenation and dehydrohalogenation products when ΔH_{ex} is low enough for the first barrier to be overcome. In the case of the bifunctional compounds, the intermediate is sufficiently long-lived that the ${}^+CH_2(CH_2)_{n-1}X$ component takes on a cyclic structure. When X = halogen, proton transfer does not occur readily; however, the cyclic halonium ions can be sufficiently stable that dissociation can occur, resulting in the loss of LiX. When X = OH, a protonated cyclic ether is formed, complexed to LiX, which can participate in a facile proton transfer. This suggests that, for example, while Li^+ reacts with *n*-chloropentane to eliminate HCl by a 1,2-elimination, forming Li^+(1-pentene), HCl elimination from *n*-chloropentanol is essentially a 1,6-elimination, resulting in a Li^+ complex of cyclopentyl ether.

In the reaction of the bifunctional compounds, there is always a preference exhibited for reaction at one functional group over the other. Apparently, at early stages of the reaction, Li^+ can sample a number of initial complex geometries, involving single or multiple interactions as shown in reaction 13.



(13)

Apparently, when X and Y have similar affinities for Li^+, this equilibrium lies to the left, and it is the cyclic complex that leads to type II intermediates. However, when X = OH, Y = halogen, this equilibrium appears to lie to the right; the choice is made before the reaction proceeds. This latter case is similar to that observed in collisionally induced dissociation studies of protonated α,ω-bifunctional compounds. A considerable amount of work has been done to characterize protonated α,ω-diamines[28-30] and α,ω-amino alcohols.[31,32] Evidence for cyclic structures is fairly conclusive, even when the two groups are separated by 10 or more methylene units. In 1981, Cooks et al.[33] discussed the differences in fragment ions formed following protonation of amino alcohols in a high-pressure chemical ionization source and those formed by CID of protonated amino alcohols. They proposed that, in the CI source, near-equilibrium conditions led to thermodynamically controlled fragmentation, while for the isolated ion undergoing CID, kinetic control exists, in which cyclic structures were converted to linear structures before fragmentation. The reactions of Li^+ with the halo alcohols under the low-pressure conditions in the ICR experiment appear to be under kinetic control as well.

One final aspect of the enhanced reaction of bifunctional compounds with Li^+ should be addressed. There is some evidence that the initial interaction or binding energy that is produced when an ion and a molecule form a complex is important for overcoming barriers in the earliest stages of the reaction.[34] When a compound has two functional groups, we can expect larger binding energies to Li^+. Does this interaction contribute to enhanced reactivity? While such a scenario may be relevant when transition metal ions react, in which the charge is usually retained on the metal, it should not be a contributing factor in the reactions discussed here, in which charge migration is a key component of the chemistry. Thus, we believe that the major effect of the second functional group lies in the stability of the ion cyclic structures that can be formed as the reactions proceed.

Appendix: Thermochemical Values, Calculations, and Estimations

The heterolytic bond strengths listed in Table I are the results of calculations of ΔH for the reaction $RX \rightarrow R^+ + X^-$ (X = Cl, Br, OH), using available ΔH_f's from ref 35. All other thermochemical values such as ΔH_{dehy} were calculated by using data in ref 35, unless specified below. ΔH_f(butadiene) was taken from ref 36. The following thermochemical data[37] were used for the LiX(g) species: $\Delta H_f(LiBr(g)) = -36.8 \pm 3.1$ kcal/mol; $\Delta H_f(LiCl(g)) = -46.78 \pm 3.0$ kcal/mol; $\Delta H_f(LiOH(g)) = -5.9 \pm 1.5$ kcal/mol. When calculations could not be performed because data were not available on all of the species involved, values were estimated. For example, from $\Delta H_f(Br(CH_2)_2Br(g))$ from ref 35 and the Br^- affinity of c-$C_2H_4Br^+$ from ref 9, $\Delta H_f(c\text{-}C_2H_4Br^+) = 207.1$ kcal/mol was determined and utilized. Heats of formation of the bisubstituted compounds were estimated when not available. For example, $\Delta H_f(Cl(CH_2)_3Br(g))$ was not known, but $\Delta H_f(Br(CH_2)_3Br(g))$ was known. The former was estimated by assuming that $\Delta H = -14.2$ kcal/mol for the reaction

$$Cl^\bullet + Br(CH_2)_3Br \rightarrow Cl(CH_2)_3Br + Br^\bullet$$

The exothermicity of this halogen-switching reaction was estimated by assuming that typical C–Cl and C–Br bond strengths are 83.8

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and 69.6 kcal/mol. These typical values are those for ethyl chloride and bromide. In this way, the following estimates were made: $\Delta H_f(Cl(CH_2)_nBr(g)) = -28.9$ ($n = 3$), -35.9 ($n = 4$), and -39.9 kcal/mol ($n = 5$).

In a similar fashion, $\Delta H_f(HO(CH_2)_{3,4}Br(g))$ were estimated. The "typical" C-Br bond strength (above) and the "typical" C-OH bond strength (93.4 kcal/mol for ethanol) were used to conclude that $\Delta H = -23.8$ kcal/mol for the process

$$OH^\bullet + Br(CH_2)_{3,4}Br \rightarrow Br(CH_2)_{3,4}OH + Br^\bullet$$

Thus, we estimate that $\Delta H_f(Br(CH_2)_3OH(g)) = -58.2$ kcal/mol and $\Delta H_f(Br(CH_2)_4OH(g)) = -65.2$ kcal/mol.

In a similar way, $\Delta H_f(Cl(CH_2)_3OH) = -67.3$ kcal/mol was estimated from the heat of formation of the dichloride. For $Cl(CH_3)_{4,5}OH$, ΔH_f's had to be approximated from ΔH_f of the dibromides. Again, using the typical homolytic bond strengths cited above, it was assumed that $\Delta H_{rxn} = -38$ kcal/mol for the process

$$Br(CH_2)_{4,5}Br + OH^\bullet + Cl^\bullet \rightarrow Cl(CH_2)_{4,5}OH + 2Br^\bullet$$

which results in the values $\Delta H_f(Cl(CH_2)_4OH(g)) = -77.1$ kcal/mol and $\Delta H_f(Cl(CH_2)_5OH(g)) = -81.1$ kcal/mol.

Heterolytic bond strengths involving c-$C_4H_8Cl^+$ and c-$C_5H_{10}Cl^+$ were computed by using the following estimates from MINDO/3 calculations:[25,27] ΔH_f(c-$C_4H_8Cl^+$) = 160.3 kcal/mol; ΔH_f(c-$C_5H_{10}Cl^+$) = 151.7 kcal/mol.

In the discussion of the reactions of Li^+ with the chloro and bromoalkanes, ΔH_f's were required for $CH_2{=}CHCH_2CH_2X$ (X = Cl, Br). They were estimated by assuming that, for

$$Cl(CH_2)_4Br \rightarrow CH_2{=}CHCH_2CH_2Cl + HBr$$

$\Delta H_{rxn} = +16.5$ kcal/mol, and for

$$Cl(CH_2)_4Br \rightarrow CH_2{=}CHCH_2CH_2Br + HCl$$

$\Delta H_{rxn} = +14.7$ kcal/mol. The reaction enthalpies reflect the energies required to dehydrohalogenate *n*-butyl chloride and *n*-butyl bromide, respectively. This yielded $\Delta H_f(C_4H_7Cl) = 10.4$ kcal/mol and $\Delta H_f(C_4H_7Br) = +14.7$ kcal/mol.

Proton affinities cited for organic molecules were taken from ref 20. The proton affinity of LiOH, 241 kcal/mol, is given in ref 35. Farrar et al.[15] cite $\Delta H_f(LiHCl^+) = 121$ kcal/mol; from this we determined that PA(LiCl) = 198 kcal/mol. Also, from the reported[15] binding energy of Li^+ to HBr of 19.1 kcal/mol, $\Delta H_f(LiHBr^+) = 134$ kcal/mol, thus PA(LiBr) = 195 kcal/mol.

Investigation of Methanol Adsorbed on Zeolite H-ZSM-5 by ^{13}C NMR Spectrometry

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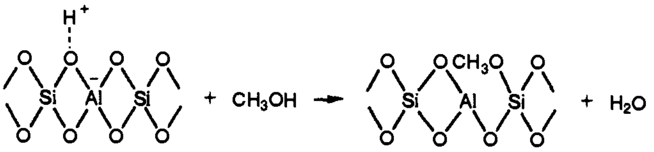
Abstract: ^{13}C CPMAS NMR spectra of methanol adsorbed on H-ZSM-5 samples with different Si/Al ratios indicate that aluminum content affects the conversion of methanol to dimethyl ether. Spin-lattice relaxation experiments suggest the existence of at least three adsorbed methanol species. The reorientation activation energies (E_a) of these species are measured to be 10.0 (±1.2), 1.5 (±0.1), and 2.1 (±0.2) kcal/mol, respectively.

Introduction

A novel process for the straightforward conversion of methanol to hydrocarbons over the synthetic pentasil zeolite H-ZSM-5 was developed over a decade ago.[1,2] The study of methanol adsorbed on zeolites is, thus, of practical and theoretical interest. Derouane et al.[3] investigated the conversion over a H-ZSM-5 catalyst with a single silicon to aluminum (Si/Al) ratio using ^{13}C NMR spectroscopy and vapor-phase chromatography. The NMR spectra showed that a variety of species are formed on the surface of this catalyst. Recently, Anderson and Klinowski[4] have investigated the progress of this reaction to produce a mixture of organic products over a catalyst with Si/Al = 30. Aronson et al.[5] have used carbon NMR spectroscopy and TPD to determine coverages and exchange of chemisorbed $^{13}CH_3OH$ with $^{12}CH_3OH$ in H-ZSM-5 catalysts. They interpret the results in terms of complexes formed by proton transfer from the acid site to adsorbed alcohols and/or clusters of adsorbed molecules at or near the acid site. Salvador and Fripiat,[6] in work on a similar system, showed that the adsorption of methanol on H-Y zeolite produces methoxysilane groups in the zeolite, which they identified by infrared spectrometry. This occurs by a reaction of the type



In another example of the use of ^{13}C NMR to study organic materials at catalytic sites, Haw et al.[7] have detected long-lived

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