results provide a clear demonstration of the variation of primary kinetic isotope effects with reaction free energy (Bell–Westheimer effect) which has been discussed extensively for solution proton transfer reactions.[41] Our observations can be rationalized within the conventional framework; the extent of proton transfer in the transition state (and hence the zero point energy differences of the two isotopically distinct channels) decreases as the reaction becomes more exothermic. These initial results are promising in that they demonstrate the utility of this type of photochemical probe into bimolecular reaction dynamics. Further work involving a systematic investigation of the isotope effects for these and related systems is currently in progress in our laboratory. This work may also provide insight into internal energy effects on ion–molecule reactions through investigations of the laser intensity dependence of the reactivity of photochemically generated intermediates.

Conclusion

Through a systematic investigation of the IRMP photochemically induced decompositions of a number of gas-phase alkoxide anions we have elucidated a general stepwise mechanism involving heterolytic cleavage to an anion–ketone intermediate complex for the formal 1,2-elimination of neutral fragments. Evidence for this mechanism is provided by the observed reactivity patterns as well as measured kinetic isotope effects. One finding of this study is an apparent anomalous order of alkyl group leaving abilities, *t*-Bu > Me > *i*-Pr > Et. Although this reactivity order may be taken to reflect the relative alkane acidities, we believe that it can be rationalized by invoking a change in mechanism to one involving an intermediate in which the electron is not bound specifically by the alkyl group: either a radical–ketone radical anion complex produced by homolytic cleavage of a transient anionic cluster. In these systems, this mechanism is important only when the electron affinity of the cleaved radical approaches zero. Our results strongly suggest that methane elimination from *tert*-butoxide anion (and other alkoxide anions) proceeds via a heterolytic mechanism. Furthermore, the photochemical generation of ion–molecule complexes that are purported intermediates in bimolecular ion–molecule reactions can be used to probe the dynamics and potential energy surfaces of such reactions.

Acknowledgment. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The cw CO_2 laser was obtained from the San Francisco Laser Center, supported by N.S.F. We are grateful to the National Science Foundation for graduate fellowship support for W.T. and for postdoctoral fellowship support for R.F.F. W.T. also acknowledges fellowship support from the Fannie and John Hertz Foundation.

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Ionic Structure and Interactions in 1-Methyl-3-ethylimidazolium Chloride–$AlCl_3$ Molten Salts

Kenneth M. Dieter, Chester J. Dymek, Jr.,* Norman E. Heimer, John W. Rovang, and John S. Wilkes

Contribution from the Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, Colorado 80840-6528. *Received August 24, 1987*

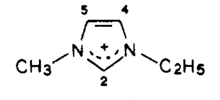
Abstract: Room temperature chloroaluminate molten salts formed by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) with $AlCl_3$ are of interest as electrolytes and nonaqueous reaction media. Results of NMR studies of MEI^+ in melts of various composition (determined by the mole fraction, *N*, of $AlCl_3$ used in forming a melt) were originally explained by a stack model of the ionic structure. In this model, the anions are located between stacked "parallel" MEI^+ ring planes. An alternative model has been suggested in which Cl^- forms ion pairs with MEI^+ by a H-bonding interaction through the H on the C-2 in the ring. Our IR studies, particularly on deuteriated MEI^+, now show that Cl^- interacts with the hydrogens at the C-2, C-4, and C-5 members of the MEI^+ ring.

One of the most widely studied room temperature melt systems is the 1-methyl-3-ethylimidazolium chloride–$AlCl_3$ (MEICl–$AlCl_3$) melt which is liquid at room temperature for compositions between 33 and 67 mol % $AlCl_3$.[1,2] This melt exhibits acid–base chemistry which is dictated by the following reactions:

$$MEI^+Cl^- + AlCl_3 \rightleftharpoons MEI^+AlCl_4^- \qquad K \gg 1 \qquad (1)$$

$$MEI^+AlCl_4^- + AlCl_3 \rightleftharpoons MEI^+Al_2Cl_7^- \qquad K \gg 1 \qquad (2)$$

When the mole fraction of $AlCl_3$ (*N*) used in preparing the melt is less than 0.5, it contains Cl^-, which acts as a Lewis base, and is basic. For compositions with $N > 0.50$, the melt is considered acidic because it contains $Al_2Cl_7^-$, which acts as a Lewis acid. At $N = 0.50$ the melt is neutral, with $AlCl_4^-$ the only detectable anion. These melts exhibit several attractive features such as large electrochemical windows and high conductivities. The structure of MEI^+ is shown below:



MEI^+

A better understanding of the physical and chemical properties of these melts has been sought through investigation of their ionic interactions. The crystal structure of MEICl's iodide analogue, MEII, has been reported, and based upon the C-2 hydrogen–iodide distance and position, an interaction involving hydrogen bonding through the C-2 hydrogen has been suggested.[3] Previous investigations have also used this model to explain composition dependent features in the IR spectra of basic MEICl–$AlCl_3$ melts.[4] In the work reported here we studied both normal and deuteriated

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MEI$^+$ in melts of various composition. We also examined the bromide analogues of these melts, the effects of solvent addition, and the replacement of the C-2 hydrogen with methyl. Semiempirical molecular orbital calculations were used to supplement our experimental observations and explore possible structures through which the ions interact in these melts.

Experimental Section

General Procedures. The purification of AlCl$_3$ and the preparation of MEICl from 1-methylimidazole and ethyl chloride have been presented earlier.[1] Bromide analogues of these melts were prepared with the same techniques. 1,2-Dimethyl-3-ethylimidazolium chloride (MMEICl) was prepared in the same way with 1,2-dimethylimidazole and ethyl chloride. Benzene-d_6 (Aldrich) and dichloromethane-d_2 (Aldrich) for solvent studies were used as received. Benzene (Aldrich, HPLC grade) and dichloromethane for the dilution of melts (Baker, HPLC grade) were purified by refluxing over P_2O_5 for several days followed by fractional distillation.

The IR spectra were recorded on an IBM Model 32 FTIR spectrometer. The solutions were run between NaCl plates (Wilmad, 41 × 32 × 6 mm) as thin films or with lead spacers of appropriate thickness. All loading of IR cells was done in a He-filled drybox with less than 10 ppm H_2O/air.

Preparation of MEICl-*2-d*$_1$. A solution of 4 g of MEICl in 10 mL of D_2O was allowed to stand for 3 days. The water was evaporated under reduced pressure and then, to remove the remaining water, the resulting material was suspended in benzene and distilled until the distillate was clear. IR analysis of the material dried by this procedure showed that there was still a small amount of water present so the material was suspended in about 30 mL of benzene and treated with about 0.5 mL of thionyl chloride. After the solution was left to stand for 0.5 h, the benzene and thionyl chloride were removed under reduced pressure and the resulting semisolid was stored under vacuum overnight. The material prepared in this manner showed no water when analyzed by IR, and its ^{1}H NMR spectrum showed only a small peak, about 4% hydrogen at C-2.

Preparation of MEICl-*2,4,5-d*$_3$. A solution of 4.0 g of dry MEICl in 45 mL of D_2O and about 200 mg of dry K_2CO_3 was heated to about 100 °C for 15 h and the water removed under reduced pressure on a rotary evaporator. The residue was mixed with benzene and distilled to remove excess water, and then 0.5 mL of $SOCl_2$ was added to complete the removal of water. The benzene and thionyl chloride were then removed under reduced pressure and the resulting material dried under vacuum by heating to about 80 °C. This material, when analyzed by ^{13}C NMR, showed about 5% hydrogen at C-2, and no detectable hydrogen at C-4 or C-5.

Theoretical Considerations. Theoretical calculations were carried out with the standard AM1[5] and MNDO[6] models as incorporated in the MOPAC program.[7] Geometries were fully optimized with the DFP method[8] and refined by minimizing the scalar gradient of the energy.[9] True minima were characterized by the absence of negative force constants,[9] and vibrational frequencies were calculated for the normal modes.[10]

AM1 was preferred over MNDO due to the problem of excessive long-range repulsions associated with MNDO and the capability of AM1 to predict hydrogen bonding.[5,11] Unfortunately, determination of AM1 parameters for aluminum is not yet completed. Consequently, the MNDO parameters for aluminum were used in AM1 calculations involving the interaction of AlCl$_4^-$ ions with MEI$^+$. This less than ideal procedure was justified in this study since the AM1 results for AlCl$_4^-$ (using MNDO parameters for Al only) were similar to straight MNDO results.[12] Also the interaction between AlCl$_4^-$ and MEI$^+$ is primarily electrostatic in nature or involves only the chlorine atoms. There is no direct interaction of aluminum with the MEI$^+$ and essentially no change in bonding to aluminum is involved.

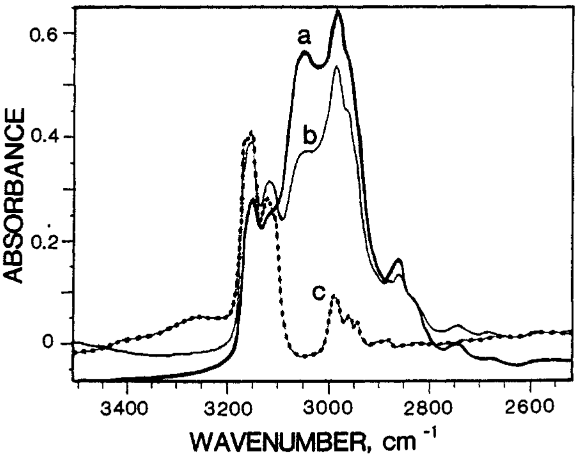

Figure 1. IR spectra of CH bands of MEI$^+$ in MEICl-AlCl$_3$ melt at (a) $N = 0.33$, (b) $N = 0.40$, and (c) $N = 0.50$.

Results and Discussion

The vibrational spectra of the MEICl-AlCl$_3$ ambient temperature melts carried out by Tait and Osteryoung[4] were re-examined. They found that the IR spectra of MEI$^+$ in acidic and neutral melts were the same, but that in basic melts, which contain Cl$^-$, some bands changed in intensity and a new broad band appeared in the C-H stretching region. They suggested that Cl$^-$ might form a hydrogen bond with the C-2 hydrogen of the MEI$^+$ cation to explain this observation.

In ^{1}H NMR studies,[13] the proton chemical shifts of the C-2 hydrogen show the largest changes as the composition of the melt is changed. This provides supportive evidence for the hydrogen-bonded complex, but it was noted that the chemical shifts of the C-4 and C-5 hydrogens are also functions of composition in basic melts.

IR Spectra. The IR spectra of $N = 0.33$, 0.40, and 0.50 melts of MEICl-AlCl$_3$ are shown in Figure 1. The most obvious feature in this set of spectra is the appearance of the broad band at 3049 cm^{-1} as the melts become more basic, i.e., as more Cl$^-$ is present. We call this band the Cl$^-$ interaction band. The bands between 3100 and 3200 cm^{-1} appear to decrease in intensity as the fraction of Cl$^-$ is increased. However, because we used a thin film whose thickness was not precisely controlled, this is only a qualitative observation based on comparison with other spectral features. For example, the bands at 2900–3000 cm^{-1} in basic and neutral melts would not be expected to differ significantly in intensity after the Cl$^-$ interaction band is subtracted out. There is a further drawback to the lack of control over the sample thickness. We do not obtain the clear isosbestic point that Tait and Osteryoung[4] identified at 3103 cm^{-1} and attributed to the presence of at least two species whose concentrations vary with acidity.

Our theoretical predictions of the IR spectra of an isolated gas-phase MEI$^+$ ion (see next section) identify the band at 3118 cm^{-1} as the C-2 hydrogen stretch frequency and the bands at 3150–3200 cm^{-1} as the C-4 and C-5 hydrogen stretches. The bands at 2900–3000 cm^{-1} are due to C-H stretches in the methyl and ethyl groups.

The Cl$^-$ interaction band was compared with the Br$^-$ interaction band in IR spectra of $N = 0.33$ melts of MEIBr-AlBr$_3$ and MEICl-AlCl$_3$. The important result of this comparison is that the spectral features are virtually the same except that the frequency of the Br$^-$ interaction band is at 3063 cm^{-1}. Thus the interaction with Br$^-$ appears to be weaker than that with Cl$^-$, with its larger charge/volume ratio. While these spectra confirm that the band is due to halide interaction with MEI$^+$, it does not tell us which C-H stretch (or stretches) we are observing in the interaction band.

One way of determining if the Cl$^-$ interaction band is the stretching frequency of the C-2 hydrogen with a Cl$^-$ interacting

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(12) The MNDO heat of formation for AlCl$_4^-$ is −273.4 kcal/mol, the Al-Cl bond length is 2.15 Å, and the atomic charges on Al and Cl are 0.90 and −0.47, respectively. The corresponding AM1 results are −263.2 kcal/mol, 2.07 Å, 0.64, and −0.41.

(13) Fannin, A. A., Jr.; King, L. A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem.* **1984**, *88*, 2609.

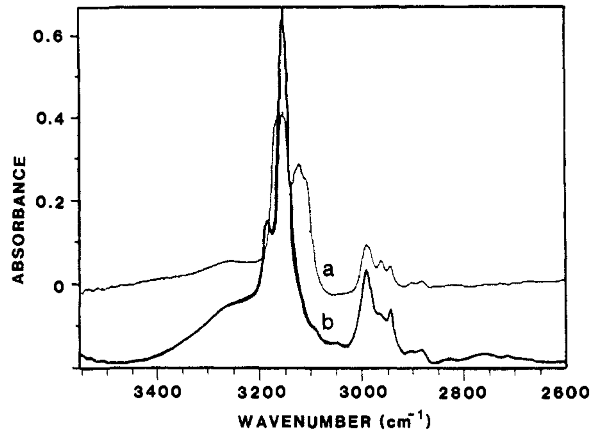

Figure 2. IR spectra of CH bands of (a) MEI^+ and (b) $MMEI^+$ both in $N = 0.50$ melt.

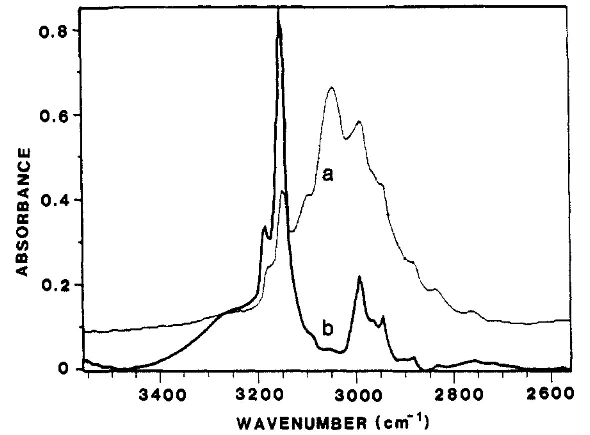

Figure 3. IR spectra of CH bands of $MMEI^+$ in MMEICl–$AlCl_3$ melt at (a) $N = 0.33$, $T = 140$ °C and (b) $N = 0.50$, $T = 100$ °C.

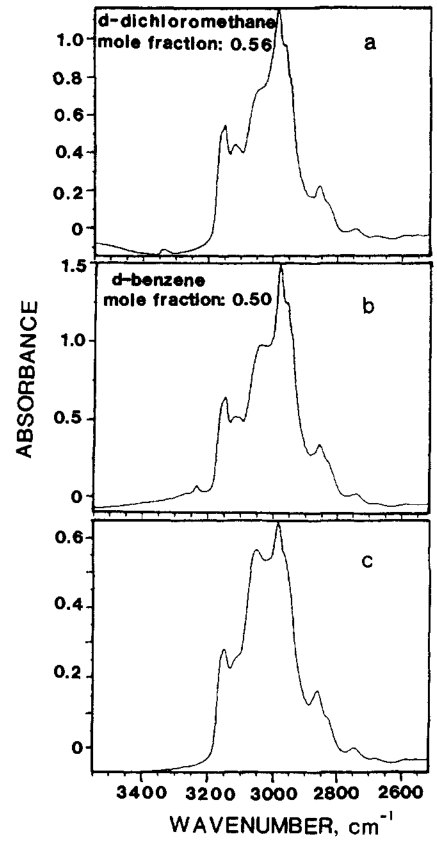

Figure 4. IR spectra of CH bands of MEI^+ in $N = 0.33$ melt and nonaqueous solutions of this melt: (a) dichloromethane-d_2, (b) benzene-d_6, (c) neat melt.

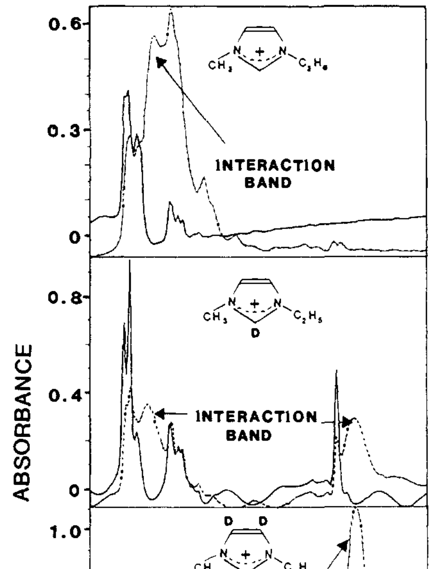

Figure 5. IR spectra of undeuteriated MEI^+ in $N = 0.50$ melts (no interaction bands) and $N = 0.33$ melts (with interaction bands indicated).

with it through a hydrogen bond is to replace the C-2 hydrogen with a methyl group to form 1,2-dimethyl-3-ethylimidazolium chloride (MMEICl). In Figure 2 we show the spectra of MEI^+ and $MMEI^+$ in $AlCl_3$ melts with $N = 0.50$. The absence of the band at 3118 cm^{-1} in the $MMEI^+$ spectrum confirms our assignment of this band as the C-2 hydrogen stretch in MEI^+. In Figure 3 the $N = 0.33$ and 0.50 melts of $MMEI^+$ are compared. The appearance in the $MMEI^+$ spectrum of the Cl^- interaction band at 3049 cm^{-1} is the first strong evidence that this band in the MEI^+ spectrum cannot be attributed solely to a C-2 hydrogen stretching frequency shifted by hydrogen bonding with Cl^-.

Further evidence that the Cl^- interaction band is not a hydrogen-bonded C-2 hydrogen-stretching frequency is shown in Figure 4. Here the IR spectrum of a neat MEICl–$AlCl_3$ melt with $N = 0.33$ is compared with those of solutions of this same melt with dichloromethane-d_2 and benzene-d in the concentrations shown. The effect of these solvents is to reduce the intensity of the interaction band. This effect, especially with benzene, would not be expected if the Cl^- were forming a hydrogen bond with the MEI^+, unless the bond was quite weak.

To determine which C–H stretching frequencies shift to form the Cl^- interaction band, we deuteriated first the C-2 and then the C-2, C-4, and C-5 positions of MEICl. On the basis of NMR analysis and the quantities of D_2O and MEI^+ used in the H–D exchange reactions, we conclude that the MEICl-*2-d* and the MEICl-*2,4,5-d_3* used were deuteriated to the extent of 95–97% and 90–95%, respectively. The IR spectra of the $N = 0.33$ and 0.50 deuteriated melts are compared with those of the undeuteriated melts in Figure 5. In each spectrum we observe only the normal C–H or C–D stretches in the $N = 0.50$ melts and the appearance of the Cl^- interaction band in the $N = 0.33$ melts. With only the C-2 position deuteriated, interaction bands appear in both the C–H and C–D stretching regions. Clearly the C-2 deuterium stretch at 2350 cm^{-1} is shifted to about 2280 cm^{-1} by the presence of Cl^-. However, the C-4 and C-5 hydrogen stretches apparently are also shifted to form the interaction band at about 3060 cm^{-1}. When C-4 and C-5 are also deuteriated, the interaction

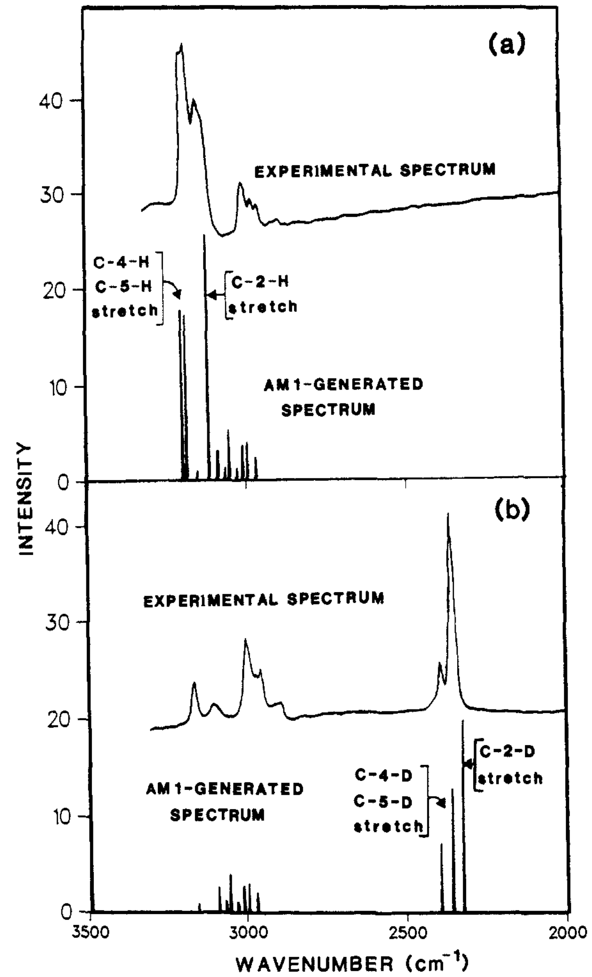

Figure 6. IR spectrum of $N = 0.50$ MEICl-AlCl$_3$ melt and AM1-generated spectrum of isolated MEI$^+$: (a) undeuteriated, (b) MEI$^+$-*2,4,5-d*$_3$.

band appears only in the C–D stretching region along with the normal C-2, C-4, and C-5 deuterium stretching frequencies. Note that this sequence of spectra also confirms our assignments of the C-4 and C-5 hydrogen-stretching frequencies. Figure 5 thus strongly supports a model in which Cl$^-$ can interact nearly equally with all three ring hydrogens.

Theoretical Calculations. While AM1 and MNDO were parametrized with gas-phase data, MNDO results were previously shown to be consistent with the experimental IR spectra of Al$_2$Cl$_7^-$ in molten KAl$_2$Cl$_7$.[14] For the isolated MEI$^+$ ion, AM1 results shown in Figure 6a again provide a reasonable model of the 2900–3300-cm^{-1} region of the experimental IR spectrum results for the $N = 0.50$ melt, in which there is no Cl$^-$ to interact with the MEI$^+$. While the intensity of the C-2 hydrogen stretch is overestimated, its position and the positions and relative intensities of the alkenyl and alkyl C–H stretches are well represented. Thus the AM1 results confirm our assignment of frequencies based on experimental results. In Figure 6b the experimental and calculated spectra of MEI$^+$-*2,4,5-d*$_3$ are compared. Again, the overall features agree very well. Even more remarkable is that the changes in the relative frequencies and intensities of the C-4, C-5, and C-2 hydrogen stretches observed upon substitution with deuterium are nicely predicted by the AM1 results.

We did attempt to find a stable configuration in which Cl$^-$ was hydrogen bonded to the C-2 hydrogen of MEI$^+$. A Cl$^-$ was positioned to hydrogen bond to the C-2 hydrogen and the geometry was optimized. In the predicted stable configuration, the C-2–hydrogen bond was almost totally broken, with the C-2–hydrogen and H–Cl distances optimizing at 1.56 and 1.40 Å, respectively. The C-2–hydrogen stretch was strongly coupled with the H–Cl stretch, two vibrations appearing at 1565 and 711 cm^{-1}. These results are no doubt exaggerated due to AM1 underestimating the stability of the chloride anion ($\Delta H_f = -37.7$ kcal/mol (calcd), -55.9 kcal/mol (exptl)[15]). Further, no other counterions were present in the system, leaving the Cl$^-$ attack on the C-2 hydrogen as its only avenue for stabilization. Interestingly, even when an AlCl$_4^-$ was substituted for the Cl$^-$, the interaction between one chlorine atom and the C-2 hydrogen was strong enough to shift the C-2–hydrogen stretch from 3118 cm^{-1} in the isolated MEI$^+$ to 2492 cm^{-1} in the complex. This shift is too large to be explained fully by the change in reduced mass. While this result is again exaggerated due to the treatment of the complex as a totally isolated ion pair, the gas-phase calculation suggests that a hydrogen bond between a Cl$^-$ and the C-2 hydrogen would cause a larger red shift in the C-2–hydrogen stretch than to the 3049-cm^{-1} frequency observed.

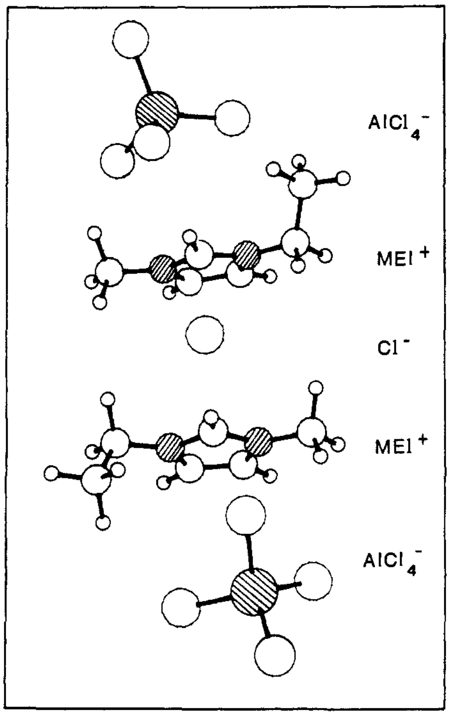

Figure 7. Fully optimized configuration of the AlCl$_4^-$–MEI$^+$–Cl$^-$–MEI$^+$–AlCl$_4^-$ system calculated with AM1.

According to AM1 calculations, the pπ orbital of C-2 contributes 50% to the lowest unoccupied molecular orbital (LUMO) of the isolated MEI$^+$. When a Cl$^-$ was centered above the ring and the geometry optimized, the Cl$^-$ shifted to form a covalent bond with the C-2. The heat of formation for this covalent species was 4.6 kcal/mol less than that for the "hydrogen-bonded" complex, and the frequency of the C-2–hydrogen stretch was predicted to be 2951 cm^{-1}. When a second MEI$^+$ was positioned parallel to the first MEI$^+$, with the Cl$^-$ centered between the two rings, and the geometry fully optimized, a minimum was located with the Cl$^-$ located slightly in front of the two C-2's and nearly equidistant from both (C-2–H = 2.48 Å, C-2′–H = 2.42 Å). This complex was predicted to be 8.4 kcal/mol more stable than the covalent MEICl species plus an isolated MEI$^+$. The C-2–hydrogen stretch for the complex was red shifted relative to that of the isolated MEI$^+$, its frequency being 3107 cm^{-1} vs 3118 cm^{-1} for the isolated MEI$^+$.

A slightly more extensive stack model was constructed by placing a Cl$^-$ between two parallel MEI$^+$ ions and placing two AlCl$_4^-$'s on the outer sides of the MEI$^+$ ions. The fully optimized geometry calculated for this configuration is shown in Figure 7. Again, in the most stable geometry, the Cl$^-$ is nearly equidistant

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between the two nearly parallel MEI^+ ions. A similar structure with the central Cl^- replaced by an $AlCl_4^-$ was also optimized so that frequencies of the C–H stretches could be compared. The frequency of the C-2–hydrogen stretch for this model was 3111 cm^{-1} compared to the 3107 cm^{-1} for the Figure 7 system with Cl^- thus reproducing the direction (but not the magnitude) of the shift observed to form the Cl^- interaction band. However, the C-4– and C-5–hydrogen stretches shifted from 3225 and 3238 cm^{-1} with no Cl^- present to 3239 and 3251 cm^{-1} in the Figure 7 structure. Thus the calculated shift is in the opposite direction from that observed and leads us to conclude that the AM1 method is not capable of reproducing the experimentally observed Cl^- interaction band frequencies using this model. Nonetheless, two important results were obtained from the AM1 calculations. First is the confirmation of the assignments of the C-2–, C-4–, and C-5–hydrogen stretching frequencies. Second is the identification of Cl^- centered between two adjacent MEI^+'s (Figure 7) as a stable configuration for this system.

Conclusion

In basic melts of MEICl and $AlCl_3$, our IR spectral analysis showed that Cl^- interacts with MEI^+ to cause similar shifts in the frequencies of the C-2–, C-4–, and C-5–hydrogen stretches. Thus the description of the interaction of MEI^+ with Cl^- cannot be restricted to ion pair formation solely by hydrogen bonding of Cl^- through the C-2 hydrogen. Our experimental results are consistent with a stack model for the interaction of MEI^+ with the anions in the melt, although the inability to theoretically predict the experimental shifts in ring C–H frequencies leaves the exact nature of the interactions an open question.

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Photodissociation of Conjugated Diene Radical Cations: Methyl Substituent Band Shifts

Robert C. Dunbar* and Hun Young So

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44118. *Received September 18, 1987*

Abstract: Photodissociation spectroscopy (PDS) in an ion cyclotron resonance (ICR) spectrometer was used to investigate the methyl substituent effects on the observed PDS bands of nine gas-phase methyl-substituted butadiene radical cations. The lower energy PDS bands, the I bands, are located between 1.61 and 2.56 eV, depending on the position and number of methyl groups. Methyl substitution on an inner-carbon atom gives a red shift of the I band compared with butadiene cation, while outer-carbon substitution results in a blue shift. The higher energy PDS bands, the A bands, were located between 3.5 and 4.2 eV. Inner-carbon substitution gave no significant shift of the A bands relative to butadiene cation, while outer-carbon substitution gave a red shift increasing with the number of methyl groups. The observed trends in the PDS I band shifts are compared with energy shifts measured by photoelectron spectroscopy (PES). The prior assignment of the PES band near 11 eV as a π orbital is strongly confirmed. Shifts in the PDS A band are compared with results from electron transmission spectra and optical spectra of the corresponding neutrals, and the results are found to be correlated but with considerable scatter. Theoretical calculations using the CNDO/S-CI program clarify the nature of the electronic transitions involved in these open-shell cations. The CNDO/S method is somewhat successful in predicting the substituent effects in both of the spectroscopic bands of butadiene ion, confirming the utility of the method for open-shell ion transitions.

Systematic study of substituent perturbations of a spectroscopic transition has been a central theme in developing theoretical understanding and practical applications of electronic spectroscopy of polyatomics. While such ideas have been extensively worked out for neutral closed-shell molecules, much less understanding exists of the spectroscopy of radical cation chromophores. This is mainly due to the intrinsic difficulty in building up a sufficient density of gas-phase ions to permit direct absorption-spectroscopic measurements, while the extreme reactivity of these species often precludes condensed phase spectroscopy. Much useful spectroscopic information about gas-phase ions has come from the indirect approach of photodissociation spectroscopy (PDS). We describe here the use of the PDS technique in a systematic study of the methyl group substituent effects on the spectroscopy of the butadiene radical cation chromophore.

Besides PDS, other sources of information on the energy levels and optical transitions of radical cations include absorption spectroscopy in low-temperature glassy matrices, gas-phase emission spectroscopy, photoelectron spectroscopy (PES), and theoretical calculations. The butadiene radical-ion chromophore is not among the few systems (mostly halobenzenes and acetylenes) from which fluorescence emission has been observed, so this is not a useful avenue. Some glassy matrix spectra of butadiene-ion derivatives have been reported, as noted below, but their interpretation is not straightforward, and they are of limited interest for comparison with our results. Electron transmission spectroscopy (ETS) and optical absorption spectroscopy of the neutrals both give some information about the empty excited orbitals of the system, and the correlation with the cation results will be explored, although the correlation is not found to be very close. We will try to build up understanding of the spectroscopy of this system principally by correlating PDS results, PES results, and theoretical calculations by using the method, CNDO/S, which currently seems most useful for this purpose.

PDS results for several conjugated diene radical cations have been reported previously. Butadiene cation, the first conjugated diene radical cation system studied by the PDS technique, was considered in a correlation of PDS spectra with optical absorption spectra, PES, and theoretical calculations, elucidating the nature of the two observed dissociation bands in the UV-vis region.[1] 2,4-Hexadiene and its isomers were also studied by PDS to determine the structure of the ions and to investigate the rearrangement involving migration of a double bond into conjugation.[2] PDS results for pentadiene, octadiene, cyclohexadiene, and cyclooctadiene radical cations were reported more recently from the

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[1] Dunbar, R. C. *Chem. Phys. Lett.* **1975**, *32*, 508.
[2] Benz, R. C.; Dunbar, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1799.

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