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Notes

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Limitations of the Salt/Molecule Technique in Matrix Isolation Studies

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The salt/molecule technique has been used often in conjunction with matrix isolation for the formation and isolation of unusual anionic species.[1-3] This technique involves the gas-phase reaction of an alkali halide molecule (after vaporization from a high-temperature oven) with a Lewis acid diluted in an excess of argon. The transfer of a halide anion from the alkali halide molecule to the Lewis acid has been shown to occur, forming a halide-containing anion of interest. This technique has been shown to be particularly successful in forming anions that are not accessible through normal, room-temperature synthetic techniques. Anions that have been formed, isolated, and characterized in this manner include CO_2F^-, COF_3^-, $SO_2F_3^-$, and GeF_5^-.[4-7] However, the fate and the role of the resulting alkali-metal cation in the product complex is usually not considered in any detail, and this note is intended to address this question.

While the salt/molecule technique has been quite effective for a variety of systems, it is clear that the technique has several drawbacks. First, distortion of the product anion has been observed in several cases,[5,8,9] leading to splitting of otherwise degenerate vibrational modes. In addition, some shifting of band position is noted as the cation is varied through the range Na^+ to Cs^+. Second, a number of reactions do not occur that would be anticipated on the basis of chemical experience. In most reactions involving the salt/molecule technique, fluoride transfer occurs readily, while more often than not the analogous chloride salt reaction does not occur. For example, the reaction of CsF with COF_2 readily forms the COF_3^- anion in the $Cs^+COF_3^-$ ion pair, but the reaction of CsCl with either COF_2 or $COCl_2$ to form the product ion does not occur.[5] If the reaction were strictly an ion-molecule reaction, then one would anticipate a reaction in virtually all cases. The ion-dipole interaction alone should hold the reaction complex together, if not an actual chemical bond, and most ion-molecule reactions have little if any barrier to reaction. Rather, the cause of product ion distortion and of lack of reaction is an electrostatic interaction with the positive charge of the alkali-metal cation. Moreover, these phenomena have been shown to be dependent on the particular cation in question, and any systematic attempt to characterize the phenomena must account for this as well.

Table I. Halide Ion Affinities of Alkali-Metal Cations and Selected Neutral Lewis Acids

cation	FA, kcal/mol[d]	CA, kcal/mol[e]	Lewis acid	FA, kcal/mol[c]
Li^+	180.5[a]	150[a]	HF	50
Na^+	151[a]	130[a]	SiF_4	68
K^+	136[a]	115[a]	BF_3	71
Rb^+	131[a]	110[a]	COF_2	34
Cs^+	128[a]	110[a]	CO_2	32
Tl^+	162[b]	148[b]	SO_2F_2	43
Cu^+	186[b]	179.7[b]	PF_5	71

[a] Data from ref 15. [b] Calculated from thermodynamic cycle; data taken from: "Handbook of Chemistry and Physics", 50th ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1970. [c] From ref 12-14. [d] Fluoride ion affinity; i.e., ΔH°_{298} for $MF(g) \rightarrow M^+(g) + F^-(g)$. [e] Chloride ion affinity; i.e., ΔH°_{298} for $MCl(g) \rightarrow M^+(g) + Cl^-(g)$.

A relatively straightforward way (although not the only way) in which to view the effect of the alkali-metal cation in terms of Lewis acidity and basicity.[10] The halide anion in the salt/molecule technique is serving as a Lewis base, and the overall reaction is a competition between two Lewis acids for the Lewis base halide anion. The halide acceptor molecule, whether it be COF_2, HF, or any of the other species that have been employed, has always been treated as a Lewis acid. It must be recognized, however, that the metal cation is itself a strong Lewis acid and will compete with the acceptor molecule for the halide anion. Qualitatively, it is this competition that gives rise to the phenomena of anion distortion and lack of reactivity.

Chemists have devised a number of scales and ordering systems for Lewis acidity and basicity, the most recent of which come from gas-phase ion cyclotron resonance studies[11-14] and are solvent independent. Basicities are most often quoted in terms of proton affinities,[11] while Lewis acidities are given in terms of fluoride ion affinity.[12-14] These are known for a number of the neutral Lewis acids employed in conjunction with the salt/molecule technique and range from 30 to 70 kcal/mol. Fluoride ion affinities of the alkali-metal cations, defined as ΔH°_{298} of the reaction $MF(g) \rightarrow M^+(g) + F^-(g)$, have not been measured directly from ICR studies. However, these may be calculated from thermodynamic data, inasmuch as the fluoride ion affinity of a metal cation is just the *heterolytic* bond dissocn. energy of the gas-phase alkali fluoride salt molecule. These values (taken from the extensive data of Brewer[15] et al.) are tabulated in Table I, along with values for selected neutral Lewis acids.

As can be seen, the values for the fluoride ion affinities of the alkali-metal cations range from around 130 to 180 kcal/mol, which is substantially above the values for neutral Lewis acids. Consequently, one might anticipate that the alkali-metal cation will be able to compete effectively for the fluoride anion in a salt/molecule reaction. Indeed, one might predict that no reaction would occur, just on the basis of fluoride ion affinities. However, halide ion transfer creates an ion pair, and considerable energy is gained back from the

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cation/anion pairing, sufficient to cause a reaction to occur. Nonetheless, it is this close interaction of cation and anion that leads to the distortion of highly symmetric anions and loss of symmetry.

For comparison, Table I also lists the calculated chloride ion affinities of the alkali-metal cations, and it is clear that, while they are generally less than the analogous fluoride ion affinities, they are still quite substantial. Unfortunately, chloride ion affinities of neutral Lewis acids have not been measured in a solvent-free enivronment, but they are anticipated to be relatively small. Moreover, the chloride ion is larger than the fluoride ion, and consequently the alkali cation cannot approach as closely in the product ion pair. This lessens the ion pairing energy and makes formation of chloride-containing ions through the salt/molecule technique less favorable. Overall, three factors seem to jointly cause the lack of reactivity of alkali chloride salt molecules in the salt/molecule technique. They are the relatively large chloride ion affinity of the metal cation, the relatively low chloride ion affinity of the neutral Lewis acid acceptor molecule, and the larger size of the anions formed through chloride ion attachment, compared to that for fluoride ion attachment.

It is well-known that CsF acts as an effective catalyst for a large number of chemical systems,[16-18] while the effectiveness of the catalytic action drops off as the size of the alkali-metal counterion decreases. As indicated in Table I, the fluoride ion affinity of the metal cations increases with decreasing size of the metal cation, and this would appear to affect the degree of catalytic efficiency. On the other hand, CsCl and other chlorides salts are not at all effective as catalysts, and the arguments given above would seem to be relevant here as well. Even the chloride ion in solution is not nearly as catalytically effective as the fluoride ion, which may be a measure of the fluoride or chloride ion affinity of species in the catalytic reaction.

The distortion of an anion in an anion in an isolated ion pair has been the subject of a number of investigations, including a number of systems studied by Devlin and co-workers in which nitrate, chlorate, and perchlorate salts were vaporized directly and condensed into an inert matrix.[19-21] The magnitude of the distortion, as measured by the splitting of degenerate modes of the anion, was correlated with the polarizing power of the cation, taken from an empirical formulation by Janz and James.[22] However, anomalously large splittings were observed for Tl^+ and Cu^{2+}, and a substantial covalent interaction was invoked to explain the magnitude of interaction. The use of fluoride ion affinities of the cations provides an alternative approach; the degree of distortion varies monotonically and nearly linearly with the fluoride ion affinity of the metal cation, *including* Tl^+. The calculation of the fluoride ion affinity of Cu^{2+} is less straightforward, but even the fluoride ion affinity of Cu^+ is sufficiently large to rationalize the very large splitting observed for ion pairs involving Cu^{2+}. The values for the fluoride ion affinities listed in Table I also confirm the conclusions reached in previous salt/molecule studies, that the cesium cation provides the greatest yield of product anion, with the least distortion to the anion.

In conclusion, the salt/molecule reaction technique has proven useful in the low-temperature matrix synthesis of a number of unusual product anions through halide transfer to a suitable Lewis acid acceptor. This technique is limited by the presence of the alkali-metal cation in the ion pair and the inherent Lewis acidity of the metal cation itself. This competition of Lewis acids for the halide anion manifests itself both in the lack of reactivity of chloride salts relative to that of fluoride salts and in the distortion of the product anion. Nonetheless, comparison of infrared spectra of anions formed through the salt/molecule technique to room-temperature crystalline phase spectra (where available) suggests that these limitations are not overwhelming and that signficant new information can be gained from judicial application of the salt/molecule technique.

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Additions and Corrections

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John J. D'Errico, Louis Messerle, and M. David Curtis*: Metal–Metal Multiple Bonds. 13. Structural Diversity in the Reactions of $Cp_2Mo_2(CO)_4$(*Mo≡Mo*) with Diazoalkanes and Aryl Halides.

Page 849. In the first line above eq 2, read **7a** for **7b**; in the first line below eq 2, read **7b** for **7a**.—M. David Curtis

Richard Komm, R. A. Geanangel,* and Rai Leipins: Synthesis and Studies of Poly(aminoborane), $(H_2NBH_2)_x$.

Pages 1684–1686. The ^{11}B chemical shift of $(H_2NBH_2)_x$ was incorrectly reported as $\delta \sim -50$. The correct shift for the maximum of the very broad (∼100 ppm wide) resonance is $\delta \sim -13$.—R. A. Geanangel