triplet state than the a_2^* for the acceptor-substituted case, and the a_2^* more than the b_1^* in the donor-substituted case led to a ready rationalization of the experimental results. In the cases reported here, it is the LUMO (b_1^*) polarization in the acceptor-substituted case and the HOMO (b_1) polarization in the donor-substituted case which promote ortho regioselectivity.

Computations on triplet states of simplified models of **2** by the CNDO/S method,[6] using a complex of substituted benzene and ethylene situated in parallel planes separated by 2.5 Å,[2] verify the importance of the HOMO polarization in the triplet state of donor-substituted **2** and the LUMO polarization in the acceptor-substituted **2**. Figure 3 shows the singly occupied molecular orbitals of these complexes. The CNDO/S calculations, which include configuration interaction between singly excited configurations, suggest that the configuration involving single occupation of the HOMO and LUMO orbitals such as those shown is by far the main contributor to the lowest triplet (~86% for NH_2, MeO, Me, F, CO_2Me, and CN substituents), whereas isolated benzenes have lowest triplets consisting of nearly equal contributions of $a_2 \rightarrow a_2^*$ and $b_1 \rightarrow b_1^*$ configurations.

Considering first the acceptor-substituted case, as exemplified by the benzonitrile–ethylene complex (Figure 3), the LUMO, which is half-occupied in the triplet state, is the bonding combination of ethylene LUMO and the a_2^* orbital of benzonitrile. Most significantly, a small admixture (6%) of the b_1^* orbital occurs, since the ortho and meta coefficients are unequal in this orbital. This small admixture, in a net bonding fashion to the ethylene LUMO, leads to significantly different ortho and meta coefficients in the LUMO of the complex, and distortion of the triplet state of the molecule toward an *ortho*-bridged diradical is significantly favored. Since the occupied b_1 orbital of benzonitrile is much less polarized, b_1 mixes to a smaller extent into the complex HOMO.[7]

In the donor-substituted case, exemplified by an anisole–ethylene complex in Figure 3, the HOMO of the complex is significantly more polarized than the LUMO. The ethylene HOMO mixes in mainly the a_2 anisole orbital in an antibonding fashion, but some admixture of the anisole b_1 orbital in a net antibonding fashion results in a larger anisole ortho coefficient. Again, ortho bonding is favored. The donor-substituted molecules are expected to show less regioselectivity than the acceptor-substituted cases, since the HOMO and LUMO of the complex work in opposite directions for the donor case, and polarization appears smaller in the donor case.

Weak donors (e.g., methyl or fluoro) are expected to show very low regioselectivity, since these groups cause only small polarizations of the occupied b_1 orbitals. In general, the ratio of relative rates of ortho and meta bridging should increase as the strength of the donor substituent or of the acceptor substituent increases. The experimental results (Table I) are in good agreement with this prediction of the model.

We note as a general caution that the exact magnitude of the polarization is rather sensitive to the type of calculation, and the numbers in Figure 3 are of qualitative significance at best. Nevertheless, these considerations provide a theoretical framework which reveals the origin of ortho- and para-bridging regioselectivity found in donor-substituted benzonorbornadienes.

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(8) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1972–1977; Alfred P. Sloan Foundation Fellow, 1975–1977.

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Reactions of Transition Metal Ions with Alkyl Halides and Alcohols in the Gas Phase: Evidence for Metal Insertion and β-Hydrogen Atom Shift

Sir:

Recently, vaporized transition metal atoms[1-3] and gaseous ionized transition metal complexes[4-10] have been found to have a rich and interesting chemistry. We have examined the gas-phase chemistry of transition metal ions with a number of alkyl halides and alcohols and find it to be instructive and interesting. In particular, we wish to report evidence for two important elementary processes in the reactions of gas-phase metal ions. The first is the insertion of transition metal ions into a C–X bond. Numerous reactions of vaporized transition metal atoms[1] and metal complexes in solution[11] appear to involve such a metal insertion. The second process is the shift of a hydrogen atom in a metal alkyl complex from the β carbon onto the metal. This process is also assumed to be important in a variety of reactions involving transition metals.[11-15] We believe the present results to be the first direct evidence that transition metal ions insert into R–X bonds ad participate in β-hydrogen atom shifts in bimolecular gas-phase reactions. Since theories and models of chemical reactions are frequently constructed in terms of gas-phase bimolecular processes, it is of interest that these processes, which are important in a wide variety of useful reactions, occur in the gas phase.

Metal ions are produced for these studies by electron impact on volatile metal complexes such as metal carbonyls. The reactions of the metal ions with the vapors of alkyl halides and alcohols are examined using standard ion cyclotron resonance techniques.[16] Since the studies are carried out at very low pressure (10^{-6}–10^{-4} Torr), only bimolecular ion–molecule processes are observed. Both the reactant neutral and the reactant ion which give rise to a given product ion may be unambiguously identified using the ion cyclotron double resonance technique.[16] The product ion is observed directly and identified from its mass. Isotopic labeling readily provides considerable mechanistic information.

Methyl iodide reacts with transition metal ions by oxidative addition (eq 1). As noted elsewhere, limits on the metal to carbon bond strength in MCH_3^+ may be inferred from eq 1.[4]

Scheme I

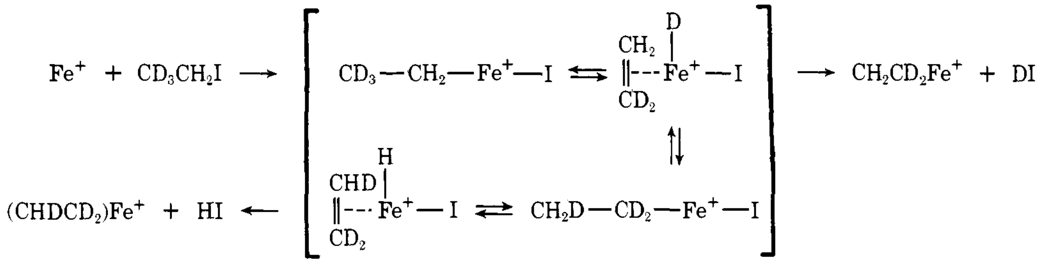


Table I. Product Distributions of reactions of Metal Ions[a] with CH_3I

	Li[b]	Cr	Fe	Co	Ni	Hg[c]
$M^+ + CH_3I \rightarrow MCH_3^+ + I$		0%	52%	27%	0%	0%
$\rightarrow MI^+ + CH_3$		100%	48%	73%	100%	100%

[a] Except as noted, generated by electron impact on volatile metal compounds such as metal carbonyls. [b] Generated thermionically (J. P. Blewett and E. J. Jones, *Phys. Rev.*, 50, 464 (1936)). [c] Generated by electron impact on the metal vapor.

Table II. Product Distributions of Reactions of Metal Ions with C_2D_5I

	Ni	Co	Fe
$M^+ + C_2D_5I \rightarrow MI^+ + C_2D_5$	24%	11%	14%
$\rightarrow MC_2D_4^+ + DI$	32%	78%	86%
$\rightarrow MDI^+ + C_2D_4$	44%	11%	

Branching ratios for the reactions of a number of metal ions are noted in Table I. If the transition state involved in eq 1 is

$$M^+ + CH_3I \rightarrow \begin{cases} MCH_3^+ + I \\ MI^+ + CH_3 \end{cases} \quad (1)$$

of the type $[R\text{-}X\text{-}M^+]$, formation of only MX^+ would be expected. A metal insertion mechanism for eq 1 is suggested by the two sets of products obtained, as well as by other reactions occurring in the methyl iodide-metal carbonyl mixture. For example, $Fe(CO)^+$, produced in addition to Fe^+ by electron impact on $Fe(CO)_5$, reacts according to the equation

$$Fe(CO)^+ + CH_3I \rightarrow FeCH_3I^+ + CO \quad (2)$$

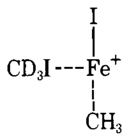
The ionic product of (2) which presumably differs from the activated complex for (1) only in energy content, reacts with another molecule of methyl iodide according to the equation

$$FeCH_3I^+ + CD_3I \rightarrow FeICD_3I^+ + CH_3 \quad (3)$$

If both CH_3I and CD_3I are present, double resonance[16] establishes that the methyl group lost in eq 3 comes exclusively from the reactant ion as indicated. This eliminates any structure such as **1**, which is symmetric with respect to the methyl groups for the activated complex for reaction 3. Structure **2**

$CD_3I\text{---}Fe^+\text{---}ICH_3$

1



$$CD_3I\text{---}\overset{\overset{\displaystyle I}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Fe^+}}$$

2

is, however, consistent with the isotopic labeling results. This suggests that the reactant ion in eq 3 has structure **3** and that Fe^+ initially inserts into the C–I bond in reaction 1, forming an activated complex which also has structure **3.**

$CH_3\text{—}Fe^+\text{—}I$

3

When the metal ions react with an alkyl halide with β-hydrogens somewhat different products appear as indicated in Table II. As with methyl iodide a metal-ethyl iodide complex is formed by ligand substitution (eq 4). Subsequent reaction 5 is a displacement process, indicating that deuterated

$$NiCO^+ + C_2D_5I \rightarrow NiC_2D_5I^+ + CO \quad (4)$$

$$NiC_2D_5I^+ + C_2H_5I \rightarrow NiC_2D_4C_2H_5I^+ + DI \quad (5)$$

ethyl iodide is bound to the metal as ethylene and DI. Only DI loss is observed in reaction 5. Reactions of CD_3CH_2I provide evidence that the metal attacks ethyl iodide by insertion into the C–I bond followed by a β-hydrogen shift. Both HI and DI are displaced from CD_3CH_2I as indicated in Scheme I, which seems to provide the best rationalization of loss of both HI and DI. The ratio of DI to HI loss is nearly statistical (1.57 ± 0.05), indicating that the H-atom migrations are fast relative to the lifetime of the complex.

We observe analogous processes for metal ions with larger alkyl halides and with alcohols. Transition metal ions, for example, eliminate HCl from $i\text{-}C_3H_7Cl$ and H_2O from $i\text{-}C_3H_7OH$. In the case of alcohols, the chemistry of methanol with iron ions provides evidence for a metal insertion mechanism. The methanol chemistry differs somewhat from that of methyl iodide. The only ionic product of the reaction of Fe^+ with methanol, for example, is $FeOH^+$. No $FeCH_3^+$ product is observed. It is evident from the chemistry of $FeCO^+$ with methanol, however, that metal insertion occurs. The processes of interest are the reactions 6 and 7.

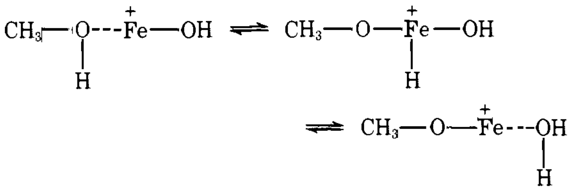
$$FeCO^+ + CH_3OH \rightarrow FeCH_3OH^+ + CO \quad (6)$$

$$FeCD_3OH^+ + CH_3OH \rightarrow FeOHCH_3OH^+ + CD_3 \quad (7)$$

Isotopic labeling establishes that the methyl group eliminated in reaction 7 comes exclusively from the $FeCH_3OH^+$ reactant. As in the analogous reaction involving methyl iodide this suggests that the $FeCH_3OH^+$ species is actually $CH_3\text{-}Fe\text{-}OH^+$. It is interesting to note that methanol displaces water from the ionic product of eq 7.

$$FeOHCH_3OH^+ + CH_3OH \rightarrow Fe(OCH_3)(CH_3OH)^+ + H_2O \quad (8)$$

It seems probable that $FeOHCH_3OH^+$ forms initially in reaction 7 as a complex between methanol and $FeOH^+$. Elimination of water from this species would then be facilitated by



$$CH_3\text{—}\overset{+}{\underset{H}{O}}\text{---}Fe\text{—}OH \rightleftharpoons CH_3\text{—}O\text{—}\overset{+}{\underset{H}{Fe}}\text{—}OH \rightleftharpoons CH_3\text{—}O\text{—}\overset{+}{Fe}\text{---}\underset{H}{OH} \quad (9)$$

the H-atom shift indicated in eq 9. These results thus suggest that transfer of an active H atom between ligand and metal may be quite general in gas-phase processes involving transition metal ions.

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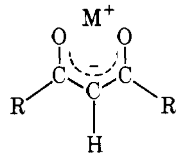
Alkali β-Ketoenolates as Ion Pairs

Sir:

We are presently engaged in a physico-chemical study which aims to cast light on the structure and dissociation of alkali enolate salts in solution. We present here far-infrared spectral evidence for cation–anion interactions and relate it to corresponding conductance and ^{1}H NMR data. Results from these independent techniques are mutually consistent and provide concrete evidence for the previously inferred ion-pair structure of the alkali β-ketoenolates.

The subject compounds were alkali dibenzoylmethides (I) and dipivaloylmethides (II).



I, R = C_6H_5
II, R = *t*-butyl

In Table I are presented spectral and conductivity data in tetrahydrofuran (THF) and dimethyl sulfoxide (Me_2SO) as solvents showing the variation of these properties in response to change of cation (M^+) and anion (I and II). Clearly, all three properties are quite sensitive to changes of the ionic components in a manner which is reasonably relatable to positive charge density on the cation and to the ability of the anion to delocalize negative charge internally. All reported results for alkali salts vary linearly as reciprocal functions of their Pauling cation radii. Such a dependence has been noted previously[1-3] for ion-paired systems and is to be expected for variation of the Coulombic potential between charges.

Of particular interest are the sharp, cation-sensitive, far-infrared bands when THF is solvent. We assign these to cation–anion interactions. Edgell and coworkers[4] also observed bands in this solvent for several inorganic alkali metal salts. They attributed these to vibrations of solvated intimate ion pairs in which the cation–anion interaction was modulated by cation–solvent attraction. However, their frequencies are not related directly to $1/r_{\text{cation}}$ and have a much larger range than do ours. Recently, cation-sensitive bands in the carbonyl region of alkali metal manganese carbonylates have been reported.[5]

Popov[6] and co-workers reported broad bands between 100 and 430 cm^{-1} for alkali cation salts in Me_2SO and other solvents. These are anion independent and were assigned, by Popov, to cation–solvent interactions. We were unable to observe these bands for M^+I^- and M^+II^-, which suggests that the cations in our compounds are predominately anion bound at the concentrations of the infrared studies. Relatively low solubility limits in Me_2SO and strong absorption by this solvent in the working range prevented a search for the 300–450 cm^{-1} bands in this solvent, which we resolved in THF.

The position of the band for the Bu_4N^+ ion is somewhat surprising in view of its large size compared to unsolvated Na^+ and K^+. Other workers[7,8] have described cation–anion bands for tetraalkylammonium salts in the same region reported here.[9] Furthermore, Popov[6] found that the *cation–solvent* bands for Na^+ and NH_4^+ in Me_2SO were similar. Our ob-

Table I. Properties of Metal β-Ketoenolate at 25 °C

	Cation-sensitive IR band in THF, cm^{-1}		τ methide in Me_2SO, ppm rel to Me_4Si		Λ_0 in Me_2SO		$K_{\text{diss}} \times 10^4$ in Me_2SO	
M^+	I	II	I	II	I	II	I	II
H			7.32	5.86				
Li	433.71	426.73	6.48	5.36	N.C.[a]	N.C.[a]	N.C.[a]	N.C.[a]
Na	399.98	391.90	6.37	5.28	19.6	9.96	1.61	3.41
K	339.33	374.30	6.24	5.22	29.7	27.1	19.2	7.47
Cs	337.62	370.74	6.14	5.19	29.8	29.7	68.1	36.9
Bu_4N	351.00		6.29		30.8		61.6	
Instrument	Beckman IR-11, polyethylene cell		Varian A60-D		Leeds & Northrup #4866-60			
Exptl error	±0.50 cm^{-1}		±0.01 ppm		±5%			
Concn range	0.05–0.15 M		0.02–0.05 M		2×10^{-5}–4×10^{-3} M			

[a] Negligible conductance.