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Gas-Phase Nucleophilic Addition Reactions of Negative Ions with Transition-Metal Carbonyls. 2. Solvated Anions

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Abstract: Gas-Phase reactions of $Fe(CO)_5$ with a series of partially solvated negative ions are described. In most cases, complete solvent displacement from cluster ions of the general formula $X(XH)_n^-$ is observed to yield exclusively the corresponding iron tetracarbonyl acyl anion, $(CO)_4FeC(O)X^-$. Homoconjugate clusters of hydroxide, alkoxides, and thiolates all react in this manner, while acetate/acetic acid clusters are unreactive. Ammonia clusters of OH^- and NH_2^- react with $Fe(CO)_5$ to yield metal ion products in which CO loss accompanies solvent displacement. The observed cluster ion reactivity generally differs from that of bare anions, which commonly produce metal ion products from which CO ligands are expelled. Kinetic measurements show that association of the first solvent molecule with a negative ion may increase the efficiency of its reaction with $Fe(CO)_5$ compared to the bare anion, while further solvation slows the reaction down. A mechanism for solvated ion reactions is proposed wherein the reactant ion becomes partially desolvated by strong electrostatic interaction with $Fe(CO)_5$ within an ion–molecule collision complex. Subsequent nucleophilic addition of the negative ion to a carbonyl ligand releases excess energy into the collision complex, resulting in complete dissociation of the weakly bound solvent molecules. Comparison of the anion binding energies of $Fe(CO)_5$ with the corresponding solvation energies of the anions provides a thermochemical rationale for the observed reactivity patterns. If the total solvation energy of the negative ion exceeds $D[(CO)_4FeC(O)\text{–}X^-]$, then no reaction will occur between the cluster ion and $Fe(CO)_5$. If it is less, then acyl ion formation will proceed with complete solvent displacement, while if the difference is greater than 34 kcal/mol, then CO loss from the acyl ion will accompany solvent expulsion. The computed free energy changes for each of the solvated ion reactions appear to reliably account for the observed reactivity. Side products of the reaction between $Fe(CO)_5$ and $OH(NH_3)$ are also described which are attributed to solvent-catalyzed decarboxylation of a $(CO)_4FeCO_2H^-$ intermediate.

Defining the specific effects of solvation on the dynamics and energetics of ionic reactions in solution continues to be a central problem in experimental and theoretical chemistry. Key breakthroughs in our understanding of solvation effects on nucleophilic reactions involving negative ions in particular have been achieved within the last 15 years. For example, the development of experimental techniques for examining anionic S_N2 reactions in the gas phase has permitted an unveiling of intrinsic reactivity patterns for anionic nucleophiles which are unperturbed by medium effects.[1-9] The "double-well potential" model for gas-phase nucleophilic substitution reactions described by Brauman[3,10] represents an important conceptual milestone which has proven useful in the analysis of numerous other classes of ion–molecule reaction.[11] Theoretical confirmation for this model has been achieved with accurate ab initio SCF-MO calculations,[12] and an elegant consolidation of the gas-phase and condensed-phase energy profiles for an anionic S_N2 reaction was recently established by Jorgensen and Chandrasekhar.[13] Recent experimental methods for creating and manipulating partially solvated gas-phase ions bearing up to four or five "passenger" solvent molecules have enabled evaluation of the influence of stepwise solvation on the kinetics and thermodynamics of acid–base reactions,[14-18] electron transfers,[19] nucleophilic substitutions,[2a,20-23] and nucleophilic additions.[24-25]

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While the relevance of these experiments to ionic reactions taking place in bulk solution has recently been questioned,[22] it has become clear from these studies that the presence of even a single solvent molecule can radically alter the kinetics, energetics, and mechanism of a gas-phase ion–molecule reaction, often in a direction which directly extrapolates to bulk solution. Moreover, there is no doubt that experimental studies of partially solvated ions can yield useful new information about the dynamics of gas-phase ion–molecule reactions,[22] as well as important physical data related to atmospheric chemistry,[26] combustions,[27] and radiolysis.[28] Several recurrent features in the effects of stepwise solvation on ion–molecule reactions have been recognized and reviewed by Bohme:[14] (i) rates of binary ion–molecule reactions generally decrease with increasing reactant ion solvation, eventually becoming immeasurably slow when reaction is rendered endothermic; (ii) reaction exothermicity often manifests in the "boiling-off" of solvent molecules from the product-ion complex, with the minimum number required to maintain overall exothermicity being retained; (iii) cluster ions tend to react in such a way as to achieve a more stable solvent shell by exchange of solvent molecules in binary "switching" reactions; (iv) reactive participation of solvent molecules may occur which completely changes the outcome of a reaction relative to the unsolvated-ion version.

In a recent paper we presented a comprehensive account of the kinetics, thermodynamics, and mechanisms for gas-phase reactions between unsolvated negative ions and $Fe(CO)_5$.[29] Carbonyl ligand dissociation from the nucleophilic addition complexes was evident in many reactions which is unprecedented for the analogous reactions taking place in solution. In the present work we examine the influence of stepwise solvation on the kinetics and product distributions of these reactions and show how they more closely resemble their condensed-phase counterparts when carried out under solvated-ion conditions.

Experimental Section

All experiments were carried out at 300 ± 2 K in a flowing afterglow apparatus which has been documented previously.[30] Unless otherwise specified, all experiments used 0.4 torr total pressure with a helium flow rate and bulk flow velocity of 190 (STP) $cm^3\ s^{-1}$ and 9400 $cm\ s^{-1}$, respectively. Partially solvated reactant anions were generated using several different procedures. In most cases, NH_2^- and OH^- were first produced in the upstream ion source region by electron impact on NH_3 and a CH_4/N_2O mixture, respectively. Homoconjugate cluster ions, i.e., those of the general composition $X(XH)_n^-$, were then synthesized by adding a relatively high flow rate of the solvating neutral compound (XH) to the reactor through an inlet located approximately 15 cm downstream from the ion source. Under these conditions, rapid proton transfer to NH_2^- or OH^- produces X^-, which subsequently undergoes sequential termolecular association reactions with excess conjugate acid to yield a *kinetic* mixture of cluster ions containing up to four solvent molecules (eq 1). Certain other neutral compounds were occasionally

$$NH_2^- \xrightarrow{XH} X^- \xrightarrow[He]{XH} X(XH)^- \xrightarrow[He]{XH} X(XH)_2^- \ldots X(XH)_n^- \quad (1)$$
$$n = 0\text{–}4$$

added along with the solvent vapors to enhance the rate of cluster formation. For example, as reported in our earlier study involving $HO(H_2O)_n^-$ ions,[30] addition of a small amount of tetrahydrofuran (THF) to the liquid water reservoir attached to the solvent inlet produced a dramatic increase in the rate of disappearance of the OH^- "seed" ion, as well as a significant shift in the $HO(H_2O)_n^-$ cluster size distribution to higher values of *n*. This is believed to be due to an enhancement in the termolecular addition rates by the larger, polyatomic third-body THF. A complementary technique has been used in subsequent studies in which *N,N*-dimethylformamide is first allowed to react with OH^- to produce $HO(HN(CH_3)_2)^-$ by a Riveros-type reaction.[24b,31] Addition of water vapor through the next downstream inlet results in rapid solvent switching to yield $HO(H_2O)^-$, which then undergoes sequential hydration (eq 2).

$$OH^- + HCON(CH_3)_2 \xrightarrow{-CO} HO(HN(CH_3)_2)^- \xrightarrow{H_2O}$$
$$HO(H_2O)^- \xrightarrow[He]{H_2O} HO(H_2O)_2^- \ldots HO(H_2O)_n^- \quad (2)$$

Similarly, spiking the methanol reservoir which was used for forming $CH_3O(CH_3OH)_n^-$ (n = 1–3) ions with methyl formate leads to faster clustering and increased size distributions. In this case, free CH_3O^- is rapidly transformed by a Riveros reaction[20b,31] with HCO_2CH_3 into $CH_3O(CH_3OH)^-$, which then associates with additional methanol. Each of the other alkoxide–alcohol clusters was produced by unaided termolecular association reactions. The two ammoniates, $NH_2(NH_3)^-$ and $OH(NH_3)^-$, were generated by adding a high flow of anhydrous NH_3 (ca. 1 STP $cm^3\ s^{-1}$) to the ion source region, and to a preformed OH^- ion stream, respectively. In forming $NH_2(NH_3)^-$, a variable amount (30–50%) of $HO(NH_3)^-$ is also produced from reaction with adventitious water in the system. With reduced flow rates of NH_3 in the system, the $OH(NH_3)^-$ impurity is attenuated somewhat, but only at the expense of the $NH_2(NH_3)^-$ yield since the NH_2^-/NH_3 association rate is relatively slow. Thus, uncomplexed NH_2^- remains in the flow reactor which complicates the product analysis. Our solution takes advantage of the increase in electron binding energy for $NH_2(NH_3)^-$ over that for NH_2^- (0.74 eV)[32] by an amount approximately equal to the solvation energy in the cluster (0.52 eV; vide infra). Addition of SF_6 (EA = 1.0 eV)[33] to the flow reactor results in rapid decay of the free NH_2^- signal intensity, while the $NH_2(NH_3)^-$ concentration remains essentially unperturbed (eq 3). In this way we could achieve good starting concentrations of $NH_2(NH_3)^-$ which were free of reactive NH_2^-.

$$NH_2^-, NH_2(NH_3)^- \xrightarrow{SF_6} NH_2(NH_3)^-, SF_6^- \quad (3)$$

Kinetics measurements for reactions between solvated ions and $Fe(CO)_5$ utilized both variable reaction distance and variable neutral flow rate methods.[34] Studies involving sequentially formed cluster ions require special precautions because of the potential influence of precursor ion depletion on the observed daughter ion decays.[20b] Simulations of the observed cluster ion distributions in our experiments by numerical integration of estimated rate laws for the consecutive association reactions show that substantial concentrations of the reactant cluster ions are formed by the time they reach the $Fe(CO)_5$ reaction region in the flow tube. Under typical high solvent concentration conditions, the simulations indicate that precursor ion depletion can account for no more than 1–5% of the observed decay of a particular cluster. In general, multiple kinetic measurements were made for each system using a wide range of solvent vapor concentrations. No significant variation in the measured rate coefficients were found, thereby confirming the relative unimportance of precursor depletion effects under the present conditions. Furthermore, as will be described later, certain of the cluster ions were found to be *unreactive* with $Fe(CO)_5$. The absence of any decay in these ion signal intensities while the reactive precursors were depleted in the presence of $Fe(CO)_5$ further indicates the absence of precursor depletion effects. As with the kinetic runs described in our earlier work,[29] SF_6 was also added to the system through an upstream inlet (ca. 0.1 STP $cm^3\ s^{-1}$) in order to minimize the formation of $Fe(CO)_4^-$ from free-electron capture by $Fe(CO)_5$. All reagent gases were obtained from commercial sources and were of the following purities: He, 99.995%; NH_3, 99.99%; N_2O, 99.0%; CH_4, 99.0%; H_2S, 99.5%; SF_6, 99.8%. Liquid samples were also obtained commercially and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable impurities.

Calculations

Estimates of the solvation energies for $HO(NH_3)^-$ and $NH_2(NH_3)^-$ were obtained from ab initio SCF-MO calculations of the optimum structures and total energies of each of the clusters, free ions, and neutral

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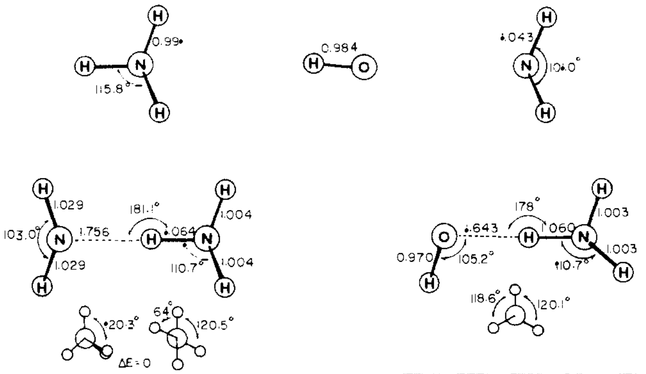
Table I. Computational Results for $NH_2(NH_3)^-$ and $OH(NH_3)^-$



species	$-E$(4-31G//4-31G)	$-\Delta E_{solv}$	$-E$(4-31+G//4-31G)	$-\Delta E_{solv}$
OH^-	75.22979		75.28989	
NH_2^-	55.39184		55.44245	
NH_3	56.10669		56.11499	
$NH_2(NH_3)^-$	111.53257	21.4	111.57640	11.9
$OH(NH_3)^-$	131.37476	24.0	131.42508	12.7

[a] Total energies in hartrees; solvation eneries calculated for eq 4 in kcal mol^{-1}.

Table II. Reactions of Homoconjugate Cluster Ions with $Fe(CO)_5$ at 0.4 Torr

cluster ion	n	k_{obsd}[a]	efficiency[b]	primary product ions
$HO(H_2O)_n^-$[c]	0	2.1	0.69	$(CO)_3FeOH^-$
	1	2.3	1.0	$(CO)_4FeCO_2H^-$
	2	2.1	1.1	$(CO)_4FeCO_2H^-$
	3	1.8	1.1	$(CO)_4FeCO_2H^-$
	4	0.97	0.64	$(CO)_4FeCO_2H^-$
$RO(ROH)_n^-$				
R = Me	0	1.8	0.76	$(CO)_3FeOR^-$, $(CO)_4FeCHO^-$
	1	1.7	0.96	$(CO)_4FeCO_2R^-$
	2	1.3	0.84	$(CO)_4FeCO_2R^-$
	3	1.1	0.79	$(CO)_4FeCO_2R^-$
R = Et	0	1.4	0.69	$(CO)_3FeOR^-$, $(CO)_4FeCHO^-$
	1	1.1	0.71	$(CO)_4FeCO_2R^-$
	2	0.95	0.69	$(CO)_4FeCO_2R^-$
R = *t*-Bu	0	1.6	0.95	$(CO)_3FeOR^-$
	1	0.59	0.44	$(CO)_4FeCO_2R^-$
	2	0.74	0.61	$(CO)_4FeCO_2R^-$
R = $MeOCH_2CH_2$	0	1.9	1.1	$(CO)_3FeOR^-$, $(CO)_4FeCHO^-$
	1	0.96	0.72	$(CO)_4FeCO_2R^-$
	2	0.79	0.66	$(CO)_4FeCO_2R^-$
R = *tert*-amyl	0	1.0	0.63	$(CO)_3FeOR^-$
	1	0.51	0.40	$(CO)_4FeCO_2R^-$
	2	0.44	0.38	$(CO)_4FeCO_2R^-$
R = *sec*-hexyl	0	1.4	0.93	$(CO)_4FeCO_2R^-$, $(CO)_4FeCHO^-$
	1	0.85	0.69	$(CO)_4FeCO_2R^-$
	2	0.61	0.54	$(CO)_4FeCO_2R^-$
R = CF_3CH_2	0	1.3	0.86	$(CO)_3FeOR^-$
	1	0.83	0.67	$(CO)_4FeCO_2R^-$
	2	0.17	0.15	$(CO)_4FeCO_2R^-$
$HS(H_2S)^-$	0	0.78	0.34	$(CO)_4FeC(O)SH^-$
	1	1.0	0.57	$(CO)_4FeC(O)SH^-$
$EtS(EtSH)^-$	0	1.2	0.67	$(CO)_4FeC(O)SEt$
	1	1.4	0.98	$(CO)_4FeC(O)SEt^-$
$CH_3CO_2(CH_3CO_2H)^-$	0	0.14	0.08	$(CO)_4FeC(O)O_2CCH_3^-$
	1	<0.002		
	2	<0.002		
$NH_2(NH_3)^-$	0	2.3	0.72	$(CO)_3FeNH_2^-$
	1	2.1	0.90	$(CO)_3FeNH_2^-$ $(CO)_4FeNH_2^-$ $(CO)_4FeC(O)NH_2^-$

[a] In units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}. [b] Efficiency = $k_{obsd}/k_{Langevin}$, ref 41. [c] Reference 30.

molecules. Computations were performed using a modified version of the GAUSSIAN 76 family of programs[35] on a CDC 6600. Geometry optimizations were carried out using analytically evaluated energy gradients and a 4-31G basis set. Single-point energy calculations were performed with the 4-31G geometries using a diffuse-function augmented 4-31G basis set which has been shown to perform especially well in calculations involving negative ions (4-31+G//4-31G).[36] The solvation energy for either cluster, ΔE_{solv}, represents the difference in the total energies computed for the cluster and the separated ion-molecule pair (eq 4). It can be shown that electron correlation and zero-point vibrational

$$AH + B^- \xrightarrow{\Delta E_{solv}} AHB^- \qquad (4)$$

energy corrections very nearly cancel in ΔE_{solv},[37] so the computed solvation energies are likely to be close to experimentally measurable ΔH_{solv} values. For purposes of calibration, the computed 4-31+G//4-31G solvation energy for $HO(H_2O)^-$ is 27.5 kcal mol^{-1}, while the experimental solvation enthalpy is 25 kcal mol^{-1}.[38] Table I summarizes the total energies for each ion and neutral along with the optimized structures and evaluated solvation energies for the two clusters.

Results and Discussion

In an earlier study of $HO(H_2O)_n^-$ (n = 0–4) ions, we showed that the presence of even a single solvent water molecule completely changes the outcome of reaction between OH^- and $Fe(CO)_5$ (eq 5).[30] In the case of the "nude" reaction (n = 0),

$$HO(H_2O)_n^- + Fe(CO)_5 \xrightarrow{n = 0} (CO)_3FeOH^- + 2CO$$

$$HO(H_2O)_n^- + Fe(CO)_5 \xrightarrow{n = 1\text{-}4} (CO)_4FeCO_2H^- + nH_2O \qquad (5)$$

nucleophilic addition of OH^- to $Fe(CO)_5$ is accompanied by loss of two CO ligands from iron. In contrast, each hydrate up to n = 4 reacts to produce an iron hydroxycarbonyl complex from which all the water molecules are expelled. The present results for a larger series of homoconjugate cluster ion reactants show this behavior to be quite general. With few exceptions, most all solvated anion reactants examined react rapidly and efficiently with $Fe(CO)_5$ to yield exclusively the corresponding iron tetracarbonyl acyl anion product (eq 6). Table II provides a listing

$$X(XH)_n^- + Fe(CO)_5 \rightarrow (CO)_4FeC(O)X^- + nXH \qquad (6)$$

of the measured kinetic data and observed primary ionic products for 12 different homoconjugate cluster ions. Also shown are the corresponding data for each bare anion reactant taken from our earlier study.[29] Inspection of the products listed in Table II exposes several common features among the reactions. Retention of solvent molecules by the product metal ion complexes is never observed.[39]

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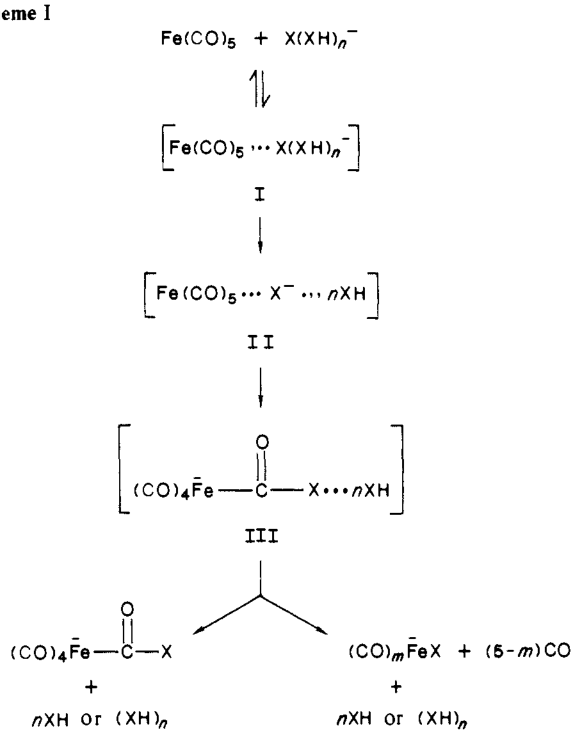
(39) An alternate explanation for the complete absence of solvated metal ion products is that they are only weakly bonded species which are fragmented in the lens system between the sampling orifice and the quadrupole. While we cannot rule this out unequivocally, we deem such an effect unlikely, since solvated product ions still do not appear when the lens voltages are minimized, nor do the observed distributions for other cluster ions change with variation of the lens settings.

Scheme I



Transfer of an ion from the cluster to $Fe(CO)_5$ is either accompanied by complete solvent expulsion, or reaction does not occur at all (e.g., $CH_3CO_2(CH_3CO_2H)^-$). The actual fate of the solvent molecules in the reactive encounters is indeterminable in our experiments; they may emerge from the product complexes in associated forms (e.g., $(XH)_n$) or as separate entities (vide infra). Furthermore, reactant ion solvation appears to totally quench CO loss from the product metal ion in all cases except $NH_2(NH_3)^-$. In this latter reaction, metal ion products exhibiting losses of zero, one, and two CO ligands are observed. The presence of solvent molecules also appears to shutoff hydride transfer to $Fe(CO)_5$ from primary and secondary alkoxides.[40] The kinetic data in Table II also exhibit several recurrent features. With the exception of the last four entries in the alkoxide ion series and the acetate ion, addition of the first solvent molecule to an ion results in an increase in the efficiency ($k_{obsd}/k_{Langevin}$)[41] of its reaction with $Fe(CO)_5$. For example, an approximately 30% increase in efficiency occurs for $HO(H_2O)^-$ and $EtS(EtSH)^-$ relative to the nude reactions, and ca, 20% increases are evident for $CH_3O(CH_3OH)^-$, $HS(H_2S)^-$, and $NH_2(NH_3)^-$. Additional solvation of the reactant ion (n = 2–4) results in a regular decrease in reaction rates for all but the ^{t}BuO(^{t}BuOH)$_2^-$ cluster. When the decreasing ion–molecule collision rates for clusters of increasing size are taken into account, it can be seen that a slightly decreasing efficiency for reaction with $Fe(CO)_5$ generally accompanies further solvation of the first cluster.

The changes in kinetics and product distributions accompanying reactant ion solvation can be understood in terms of the generalized mechanism for cluster ion reactions with $Fe(CO)_5$ outlined in Scheme I. Capture collision between a cluster ion and $Fe(CO)_5$ initially produces an energy-rich ion–molecule complex (I). The actual magnitude of the electrostatic interaction energy in the complex ($V(r) \approx -\alpha q^2/2r^4$) may be quite large since $Fe(CO)_5$ possesses a substantial bulk polarizability (α = 28 Å^3).[42] Charge dispersal in the cluster will attenuate the interaction potential compared to that for an unsolvated anion somewhat; however, energies ranging from 10 to 30 kcal mol^{-1} for distances of a few ångströms are not unlikely. As the excess energy distributes among the available rotational and vibrational modes of the complex, scission of the ion–solvent electrostatic bonds (H bonds) may occur. That is, local "heating" of the cluster may partially desolvate the anion. As the anion emerges from its solvent cage (II), bonding interactions with a carbonyl ligand of $Fe(CO)_5$ develop which ultimately give rise to the acyl ion complex III. If the binding energy of the negative ion to $Fe(CO)_5$ exceeds the sum of the solvation energies for the cluster, then formation of the acyl ion is favorable and an additional amount of excess internal energy (relative to reactants) is released into the complex. If the covalent bond energy is less than the total ion solvation energy, then the acyl ion either does not form or it does not persist; i.e., the negative ion is retained in the solvent shell. In the former case, the exothermicity for ion transfer from the cluster to $Fe(CO)_5$ results in exclusive "boil-off" of solvent molecules. The complete absence of CO loss in almost every case implies that the free energy barrier for CO dissociation from the metal is greater than the barrier for solvent expulsion from the complex (vide infra). This is understandable, since once the iron acyl anion is formed, electrostatic interactions involving the solvent molecules must be significantly attenuated owing to the diffuse nature of the charge in the metal ion complex. Computed charge distributions for anionic metal acyls indicate substantial delocalization of negative charge from the metal to the acyl oxygen atom and, to a lesser extent, to the carbonyl oxygens.[43] For example, a recent semiempirical MO study involving $(CO)_4FeCHO^-$ provided the atomic charges shown below.[44] The corresponding partial charges for $Fe(CO)_5$ are +0.57 (Fe), +0.26 av (C), and −0.39 av (O).[45] Furthermore, analysis of the infrared spectra of iron and group 6B metal acyl complexes in mixed solvents has provided evidence for specific hydrogen-bonding and ion-pairing interactions at the acyl and carbonyl oxygens.[46] In the isolated gas-phase collision complexes relevant to this study, charge dispersal should lead to an overall weakening of metal–ion solvent interactions compared to the hydrogen-bonding interactions within the reactant cluster X-$(XH)_n^-$. In support of this, we find that preformed acyl anion complexes such as $(CO)_4FeC(O)X^-$ (X = OH, OCH_3, F) do *not* undergo observable termolecular association reactions with added neutral solvents such as water or alcohols, even at the highest pressures (0.9 torr) and clustering neutral concentrations (ca. 5 × 10^{13} cm^{-3}) available to our instrument.[39] Therefore, the metal ion–solvent binding energies are probably quite small. In contrast, the first Fe–CO bond energy in the iron acyl anions is estimated to nearly 34 kcal mol^{-1}, as determined from the results described in our previous study.[29] Thus, any excess energy in complex III is preferentially removed by cleavage of the weaker metal ion–solvent bonds. The observed increase in reaction efficiency for many of the monosolvated ions relative to the corresponding bare ion provides additional support for this view. Loss of two CO ligands is observed in the nude reactions involving OH$^-$, MeO$^-$, and EtO$^-$. In contrast, the first cluster of each ion undergoes a more efficient reaction with $Fe(CO)_5$ in which only the solvent molecule is displaced. Thus, the barrier for solvent dissociation must be significantly less than the barrier for CO loss, since the latter is the rate-determining barrier in the nude reactions.[29] Indeed, we shall show later that in many cases monosolvation of the reactant ion places the barrier for CO loss from the $Fe(CO)_5$ adduct above the total energy of the reactants, thereby rendering this fragmentation pathway inaccessible. The greater rates and

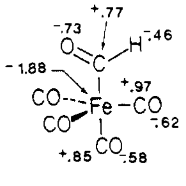


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Table III. Thermochemical Data for Homoconjugate Cluster Ion Reactions with $Fe(CO)_5$ (298 K)[a]

cluster ion $X(XH)_n^-$	n	$-\Delta H_{0,n}$[b]	$-\Delta S_{0,n}$[b]	$D[(CO)_4FeC(O)-X^-]$[c]	$\Delta H(6)$	$\Delta S(6)$[d]	$\Delta G(6)$
$NH_2(NH_3)_n^-$	0			60.4	-60.4	-31.2	-51.1
	1	11.9[e]	20.0[f]		-48.5	-11.2	-45.1
$OH(H_2O)_n^-$	0			$53.1 \leq x \leq 60.3$	-53.1	-32.8	-43.3
	1	25.0	20.8		-28.3	-12.0	-24.7
	2	42.9	42.0		-10.4	-9.2	-13.1
	3	58.0	66.8		4.7	34.0	-5.4
	4	72.2	96.3		18.9	63.5	≤0.0
$CH_3O(CH_3OH)_n^-$	0			45.7	-45.7	-32.2	-36.1
	1	21.8	21.8		-23.9	-10.4	-20.8
	2	(37.4)	(44.0)		-8.3	11.8	-11.8
	3	(50.6)	(70.0)		4.9	37.8	-6.4
$CH_3CO_2(CH_3CO_2H)_n^-$	0			24.0	-24.0	-34.6	-13.7
	1	27.0	26.2		3.0	-8.4	5.5

[a] Energies in units of kcal mol^{-1}; entropies in eu. [b] Solvation enthalpies and entropies taken from ref 38 and 47. Estimated values in parentheses; see text. [c] Estimated with eq 7; see ref 47. The values for OH^- are the experimentally determined limits. [d] Entropy changes for anion attachment to $Fe(CO)_5$ estimated from $\Delta S_{trans} + \Delta S_{rot}$: NH_2^- (-31.2 eu), OH^- (-32.8 eu), CH_3O^- (32.2 eu), $CH_3CO_2^-$ (-34.6 eu). $\Delta S(6)$ is given by the difference between these values and the corresponding $\Delta S_{0,n}$ in column four. [e] HF/4-31+G//4-31G. [f] Estimate based on known values for other homoconjugate clusters.

efficiencies observed with the thiolate ion clusters are expected, since the nude reactions are *termolecular* additions which are effectively converted to *bimolecular* reactions by the presence of a "disposable" solvent molecule in the clusters.[24a] The decrease in efficiency which accompanies monosolvation of the remaining alkoxides RO^- (R = ^tBu, $MeOCH_2CH_2$, *tert*-amyl, *sec*-Hex) is most likely due to a diminishing reaction exothermicity. In these reactions, ion transfer from the cluster to $Fe(CO)_5$ is estimated to be near thermoneutral (vide infra). Additional solvation further reduces the exothermicity for ion transfer, resulting in a successively decreasing reactivity for most of the larger clusters. The reactions involving $CF_3CH_2O(CF_3CH_2OH)_n^-$ ions most clearly illustrate this trend in that a nearly sixfold drop in reaction efficiency occurs between the bare ion and the second cluster.

It is noteworthy that many of the measured efficiencies were near unity (ca. 0.5). This suggests that once ion transfer from the cluster to $Fe(CO)_5$ occurs, reaction will go on to completion. Unsuccessful (nonreactive) collisions which are responsible for reduced reaction efficiencies in some cases probably derive from back dissociation of complex I, as opposed to reversion of complex III. It is unlikely that redissociation of the iron acyl ion in III followed by "reassembly" of the original cluster ion within the collision complex would occur because of the unfavorable entropy requirements of such a process. This hypothesis is substantiated by our earlier report[30] that $H^{18}O(H_2{}^{18}O)_n^-$ ions do *not* exchange oxygens with $Fe(CO)_5$, since this would require reversible $^{18}OH^-$ addition to CO (with intramolecular proton transfer) prior to expulsion of water molecules from the collision complex. Summarizing Scheme I, strong electrostatic forces between $Fe(CO)_5$ and a cluster ion can act to partially desolvate the core ion and facilitate its transfer to a carbonyl ligand. If the strength of the nascent covalent bond exceeds the total solvation energy of the anion, then complete ion transfer to $Fe(CO)_5$ will occur with the reaction exothermicity being dissipated by solvent "boil-off".

Energetics. The results of our previous investigation of anion binding energies to $Fe(CO)_5$[47] permit us to evaluate the energetic consequences of partial ion solvation in the cluster ion reactions. It was shown that heterolytic bond energies for iron tetracarbonyl acyl ions, $D[(CO)_4FeC(O)-X^-]$ form a good linear correlation with the proton affinity of the negative ion, $PA(X^-)$ (eq 7). As

$$D[(CO)_4FeC(O)-X^-] = 0.66PA(X) - 206 \text{ kcal mol}^{-1} \quad (7)$$

outlined in our recent study of nucleophilic additions,[29] the anion binding energies derived from eq 7 provide a measure of the amount of excess internal energy deposited in an iron tetracarbonyl acyl anion when a bare negative ion attaches to $Fe(CO)_5$. Furthermore, from the observed threshold for appearance of CO-loss products from a series of negative ion reactions with $Fe(CO)_5$, an estimate for the first Fe–CO bond dissociation energy in iron tetracarbonyl acyl ions of ca. 34 kcal mol^{-1} was derived. The main thermochemical influence of reactant ion solvation in the present context is that it will act to decrease the energy of anion attachment to $Fe(CO)_5$ by an amount equal to the total solvation energy in the cluster. If the excess energy remaining from ion transfer between the cluster and $Fe(CO)_5$ exceeds approximately 34 kcal mol^{-1}, then CO loss from the metal acyl ion may accompany solvent boil-off from the product complex. If the overall exothermicity is less than 34 kcal mol^{-1}, then only $(CO)_4FeC(O)X^-$ will be produced. Therefore, with a knowledge of ion solvation energies, anion affinities of $Fe(CO)_5$ (eq 7), and the estimated 34-kcal mol^{-1} barrier for CO loss from an iron tetracarbonyl acyl ion, we may rationalize the observed cluster ion reactivity patterns shown in Table II. Table III provides a summary of the calculated thermochemistry for four representative cluster-ion reactions for which the relevant solvation data are known, or estimable. The hydration energies and entropies of OH^- were measured by Kebarle and co-workers using high-pressure mass spectrometry,[38] as were $\Delta H_{0,1}$ and $\Delta S_{0,1}$ for $CH_3O(CH_3OH)^-$ and $CH_3CO_2(CH_3CO_2H)^-$.[48] The additional solvation energies listed for the methanol clusters are based on an estimation procedure described previously,[47] while the data for $NH_2(NH_3)^-$ are derived from the ab initio MO calculations outlined in the Experimental Section. The $Fe(CO)_5$ binding energies of NH_2^-, CH_3O^-, and $CH_3CO_2^-$ listed in column five were obtained with eq 7, using $PA(NH_2^-)$ = 403.6 kcal mol^{-1},[49] $PA(CH_3O^-)$ = 381.4 kcal mol^{-1},[50] and $PA(CH_3CO_2^-)$ = 348.5 kcal mol^{-1}.[49] The limits listed for $D[(CO)_4FeC(O)-OH^-]$ represent the experimentally determined range reported earlier.[47] Calculated enthalpies, entropies, and free energies for eq 6 are tabulated for each cluster in the last three columns. One of the most significant features exhibited in the data in Table III is that the observed reactions of the higher methanol and water clusters (n = 3, 4) correspond to positive enthalpy changes ($\Delta H(6) > 0$) which are offset by large enough entropy terms to render the overall free energy changes negative ($\Delta G(6) < 0$). That is, these particular reactions would appear to be "entropy-driven", occurring by virtue of the substantial entropy increase which attends desolvation of the product metal ion complex. The influence of entropy in the occurrence of fast, endothermic electron- and proton-transfer reactions has been demonstrated convincingly by Mautner and Sieck,[51] and additional examples of "entropy-driven reactions" have been encountered recently in other laboratories.[52,53] Nevertheless, the subject is still a matter of some debate. The present results can be interpreted in several ways. First of all, it is important to note that

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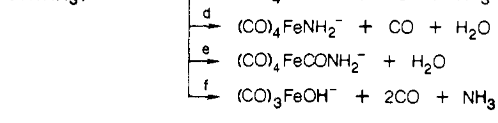
the measured efficiencies for the endothermic reactions in question greatly exceed $\exp(-\Delta H(6)/RT)$. Therefore, their occurrence is not simply a manifestation of the "high-energy tail" of the Boltzmann distribution for the reactants.[51] Unfortunately, uncertainty regarding the true primary product distribution for these solvated ion reactions, i.e., whether the water molecules in the $OH(H_2O)_{3,4}^-$ reactions are initially produced in associated (trimeric, tetrameric) forms or as separate entities, obscures the role of entropy. High-level ab initio calculations for $(H_2O)_3$ and $(H_2O)_4$ clusters provide estimates of the total solvation energies relative to separated water molecules of 12 and 20 kcal mol^{-1}, respectively.[54] Association energies of this magnitude are sufficient to overcome the endothermicities for the $HO(H_2O)_{3,4}^-$ reactions given in Table III. However, even if water trimers and tetramers were produced initially, they would rapidly succumb to thermal dissociation at room temperature in the flow tube at 0.4 torr. In this sense, the overall reaction taking place would still be that as written in eq 6, the only difference being the necessity for thermal coupling between the system (reactants and products) and the surroundings (the helium bath gas). A related mechanism with this same requirement is for complete solvent retention to take place in the initially formed metal ion "product" (e.g., $[(CO)_4FeCOOH^-\cdot 4H_2O]$) wherein the *sum* of all the H_2O binding energies to the ion is sufficient to overcome the endothermicity for hydroxide transfer from the cluster to the carbonyl. However, each of the individual H_2O binding energies are small, so rapid sequential dissociation of solvent would occur as the "product" thermalizes within the helium bath gas. While it does not seem possible to distinguish between these two mechanistic possibilities experimentally, the overall outcome is the same (eq 6). The important point here is that a coupling must exist between the thermal reservoir of the bath gas and the products, reactants, and "intermediates" (i.e., $[(CO)_4FeCOOH^-\cdot 4H_2O]$ or $((CO)_4FeCOOH^- + (H_2O)_4)$ in order for the large positive entropy changes to "drive" these reactions. The implication is that the "intermediates" such as I–III shown in Scheme I must persist long enough to achieve thermal equilibrium with the buffer gas throughout the course of the overall reaction. This is actually not unlikely with the present systems since we showed earlier[29] that certain of the nude ion reactions with $Fe(CO)_5$ exhibited pressure-dependent *bimolecular* product distributions, and, therefore, the corresponding reactive intermediate complexes must have had lifetimes on the order of the ion–He collision frequency at 0.3–0.9 torr (ca. 10^{-7} s). Even longer lifetimes for the solvated ion reaction intermediates (I–III) are likely owing to their increased sizes. Suffice it to state at this point that the computed *free-energy* changes for the solvated ion reactions are in good accord with our experimental observations and appear to be better indicators for the occurrence of reaction under flowing afterglow conditions than the enthalpy changes. For example, a positive $\Delta G(6)$ is derived for the unreactive $CH_3CO_2(CH_3CO_2H)^-$ ion, while negative $\Delta G(6)$ values are associated with each of the reactive clusters. We can also note in support of this our earlier observation that $Cl(H_2O)^-$ does not react with $Fe(CO)_5$.[47] Here, the enthalpy and free energy for Cl^- transfer from the cluster are 0.5 and 4.9 kcal mol^{-1}, respectively.

It can be seen in Table III that the presence of the first solvent molecule in $OH(H_2O)_n^-$ and $CH_3O(CH_3OH)_n^-$ drops the overall exothermicity ($\Delta G(6)$ and $\Delta H(6)$) for OH^- or CH_3O^- attachment to $Fe(CO)_5$ to a value below the estimated 34-kcal mol^{-1} barrier for CO loss from the product acyl anions. As a result, no CO-loss products are observed. In contrast, for the $NH_2(NH_3)^-$ cluster $\Delta G(6)$ and $\Delta H(6)$ *exceed* the CO dissociation barrier by more than 10 kcal mol^{-1}. This is consistent with the appearance of $(CO)_3FeNH_2^-$ and $(CO)_4FeNH_2^-$ in addition to $(CO)_4FeC(O)NH_2^-$ as primary products from this reaction. We can best illustrate the consequences of reactant ion monosolvation on the product distributions with semiquantitative energy profiles similar to those which we presented previously[29] for the bare ion reactions. Figure 1 shows two such profiles for the $OH(H_2O)^-$ and $NH_2(NH_3)^-$ reactions. Here, the energy profiles are formulated in terms of enthalpy since the estimated 34-kcal mol^{-1} CO-loss barrier for iron acyl ions is formally an enthalpy term[29] and, furthermore, $\Delta G(6)$ and $\Delta H(6)$ for $HO(H_2O)^-$ and other *mono*solvated ions are quite similar in magnitude (Table III). In constructing these profiles the interaction energies between the neutral solvent molecules (H_2O or NH_3) and each of the intermediate metal ion complexes are assumed to be negligibly small (vide supra). The bare OH^- energy profile (Figure 1A) is similar to the one presented previously,[29] except for inclusion of a free H_2O molecule for internal consistency. It is evident in the figure that association of OH^- with H_2O drops the total energy of the reactants below the top of the barrier for CO loss from the initially formed adduct ($(CO)_4FeCOOH^-$) by approximately 6 kcal mol^{-1}. Therefore, CO loss does not occur. In Figure 1B, the lesser solvation energy in $NH_2(NH_3)^-$ and the stronger binding energy between NH_2^- and $Fe(CO)_5$ combine to produce a total energy for the reactants which is roughly 15 kcal mol^{-1} above the barrier for decarbonylation of the $(CO)_4FeC(O)NH_2^-$ intermediate. Accordingly, $(CO)_4FeNH_2^-$ and $(CO)_3FeNH_2^-$ are observed as products. The appearance of $(CO)_4FeNH_2^-$ is especially interesting since it did not appear at all in the bare NH_2^- ion reaction, even at the highest bath gas pressures which we could achieve.[29] Evidently, its formation in the $NH_2(NH_3)^-$ ion reaction with approximately 12 kcal mol^{-1} *less* excess internal energy than in the bare ion reaction increases its dissociation lifetime sufficiently to permit collisional stabilization and, thus, its observation as a product.

Reactive Solvent Participation. There are a few examples in the literature where bimolecular reactions of cluster ions involve reactive participation of otherwise inert solvent molecules in the overall mechanism.[14] For instance, sequential hydration of NO^+ in a flow reactor at 0.5–1.0 torr ultimately gives rise to $H_3O(H_2O)_2^+$ through expulsion of nitrous acid from the fourth association step (eq 8).[55] The heteroconjugate cluster ion, $HO(NH_3)^-$, exhibits reactivity with $Fe(CO)_5$ which similarly suggests a nonpassive role of the ammonia solvent molecule. By adding a relatively high concentration of NH_3 ($P \approx 10^{-2}$ torr) to OH^- formed at the ion source, slow clustering to produce $OH(NH_3)^-$ (m/z 34) can be observed at 0.4 torr total flow tube pressure. Downstream addition of $Fe(CO)_5$ results in rapid decay of the $OH(NH_3)^-$ signal ($k = 1.8 \times 10^{-9}$ cm^3 s^{-1}, eff = 0.8) and appearance of at least five different primary metal ion products (eq 9). Because of the unavoidable presence of unclustered OH^- in this experiment, we are unable to determine an accurate product distribution for this reaction. That is, the large signal due to $(CO)_3FeOH^-$ which is observed (eq 9f) could arise from either the cluster ion or free OH^-. The first five products in eq 9 are listed in order of their decreasing relative yields (11:8:4:2:1).[56]

$$NO^+ \xrightarrow[\mathrm{He}]{H_2O} NO^+(H_2O) \xrightarrow[\mathrm{He}]{H_2O} NO^+(H_2O)_2 \xrightarrow[\mathrm{He}]{H_2O} NO^+(H_2O)_3 \xrightarrow{H_2O} H_3O^+(H_2O)_2 + HONO \quad (8)$$



$$OH(NH_3)^- \xrightarrow{Fe(CO)_5} \begin{cases} \xrightarrow{a} (CO)_4FeCO_2H^- + NH_3 \\ \xrightarrow{b} (CO)_4FeH^- + CO_2 + NH_3 \\ \xrightarrow{c} (CO)_4FeOH^- + CO + NH_3 \\ \xrightarrow{d} (CO)_4FeNH_2^- + CO + H_2O \\ \xrightarrow{e} (CO)_4FeCONH_2^- + H_2O \\ \xrightarrow{f} (CO)_3FeOH^- + 2CO + NH_3 \end{cases} \quad (9)$$

The most interesting product is the metal hydride ion, $(CO)_4FeH^-$, which forms by loss of CO_2 and NH_3 as neutral fragments (eq 9b). This is the same ionic product which is produced in solution when $Fe(CO)_5$ is added to aqueous base, and it is believed to arise under these conditions from base-catalyzed

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[56] Relative yields are corrected for natural isotopic distributions of each product ion and all possible interference peaks.

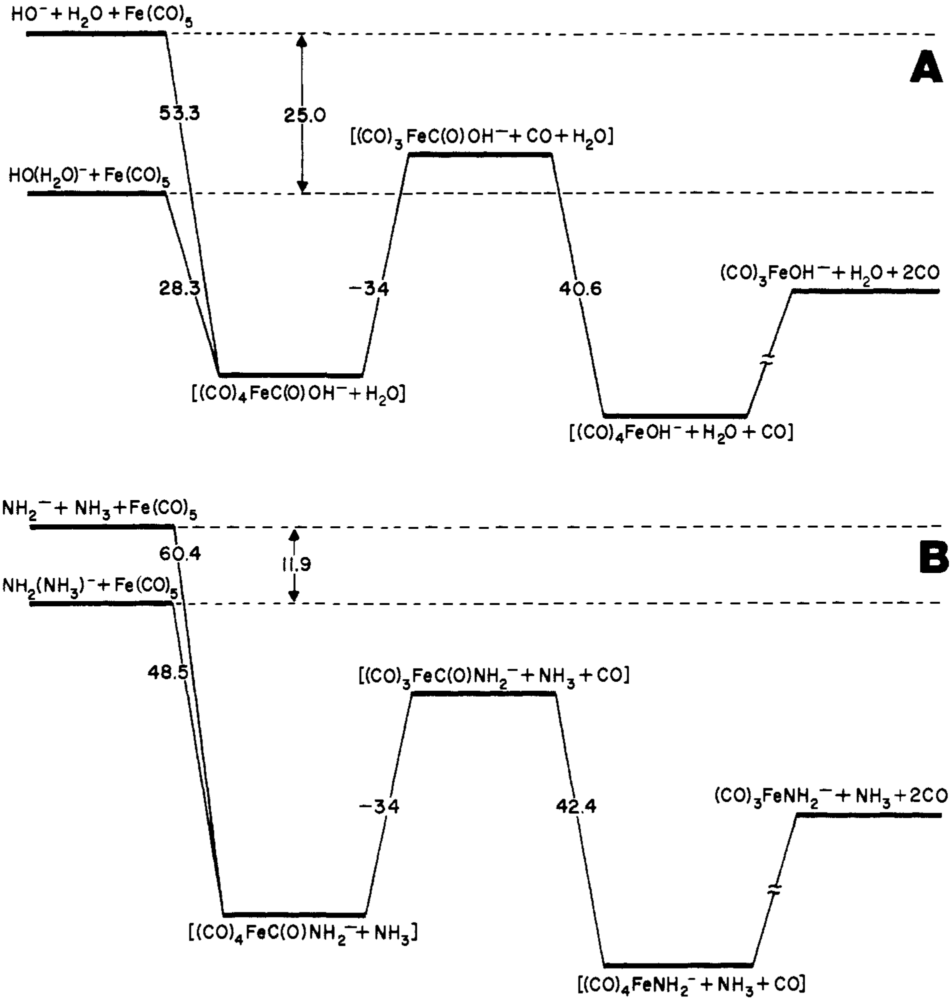


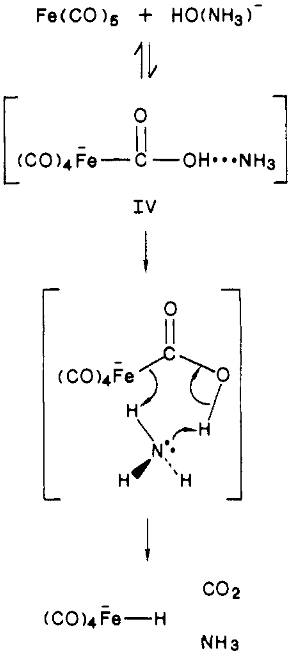
Figure 1. Semiquantitative energy profiles for reactions of Fe(CO)$_5$ with bare and monosolvated negative ions. See text for derivation of thermochemical data. (A) The OH(H$_2$O)$^-$ ion yields only the hydroxide transfer product. (B) CO loss accompanies amide transfer from NH$_2$(NH$_3$)$^-$.

decarboxylation of a transient (CO)$_4$FeCO$_2$H$^-$ intermediate.[57,58] In our earlier study of the (CO)$_4$FeCO$_2$H$^-$ ion formed in the gas phase, we showed that decarboxylation does *not* occur in the presence of high concentrations of NH$_3$ (eq 10), nor can it be

$$(CO)_4FeCOOH^- + NH_3 \rightarrow [(CO)_4\overset{-}{Fe}COOH\cdot NH_3] \nrightarrow (CO)_4FeH^- + CO_2 + NH_3 \quad (10)$$

induced by collisional activation.[30] The key difference in the OH(NH$_3$)$^-$ reaction is that the intermediate [(CO)$_4$FeCOOH$^-\cdot$NH$_3$] complex can be formed with a significantly greater amount of excess internal energy than the one depicted in eq 10. Scheme II summarizes our view of the mechanism for the NH$_3$-catalyzed decarboxylation mechanism. In a collision between OH(NH$_3$)$^-$ and Fe(CO)$_5$, transfer of OH$^-$ from the cluster to a carbonyl ligand occurs to produce the iron hydroxycarbonyl complex according to the mechanism outlined in Scheme I. This endows the resulting intermediate IV with ca. 44 kcal mol^{-1} excess internal energy, as given by the difference between the calculated OH(NH$_3$)$^-$ solvation energy (12.7 kcal/mol, Table I) and the OH$^-$/Fe(CO)$_5$ binding energy (D[(CO)$_4$FeC(O)–OH$^-$] ≈ 56.7 ± 3 kcal mol^{-1}, Table III). Loss of CO ligands may occur since the 34-kcal mol^{-1} decarbonylation barrier is exceeded (eq 9c,f). Moreover, direct expulsion of NH$_3$ followed by collisional deactivation may give rise to the observed (CO)$_4$FeCO$_2$H$^-$ product (eq 9a). Competing with these reactions is a NH$_3$-mediated decarboxylation via the proposed cyclic proton transfer shown in Scheme II. It is interesting to note that our mechanism requires that the hydrogen in (CO)$_4$FeH$^-$ is ultimately derived from the NH$_3$ solvent molecule. However, this would be inherently difficult to test by experiments with OD(NH$_3$)$^-$ or OH(ND$_3$)$^-$, since H/D exchange studies have suggested that all protons become scrambled in OH(NH$_3$)$^-$ ions.[59]

Scheme II



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The appearance of nitrogen-bearing metal ion products (eq 9d,e) is unexpected and implicates a partial "$NH_2(H_2O)^-$" character for the $OH(NH_3)^-$ reactant ion. However, our 4-31+G//4-31G calculations suggest that $[NH_2^-{\cdot}HOH]$ does *not* represent a minimum-energy structure on the proton-transfer potential surface; i.e., $OH(NH_3)^-$ is best represented by a single minimum potential. Therefore, the mechanism for NH_2^- transfer may involve a highly vibrationally excited $OH(NH_3)^-$ cluster ion which is "heated" by the large ion-induced dipole forces accompanying the collision with $Fe(CO)_5$.

Conclusion

In this work we have shown that $Fe(CO)_5$ reacts with a variety of partially solvated negative ions in the gas phase under flowing afterglow conditions at room temperature. Kinetic measurements, product distribution analyses, and thermochemical estimates for these reactions have exposed the following general trends. (i) Most all reactive cluster ions produce an iron tetracarbonyl acyl ion product, $(CO)_4FeC(O)X^-$, from which solvent molecules have been completely expelled. (ii) Compared to the bare ion reactions, addition of the first solvent molecule generally increases the overall efficiency of reaction, while further solvation slows the reaction down. (iii) The overall free-energy changes estimated for the solvated ion reactions with $Fe(CO)_5$ appear to be the best indicators for the occurrence or nonoccurrence of reaction under flowing afterglow conditions. (iv) If the energy of transfer of the negative ion from the cluster to $Fe(CO)_5$ is greater than -34 kcal mol^{-1}, then loss of CO ligands from the metal may accompany solvent expulsion. (v) Products observed in the reaction involving $OH(NH_3)^-$ expose reactive participation of the NH_3 solvent molecule in the ion-molecule encounter involving base-catalyzed decarboxylation of a $(CO)_4\ FeCO_2H^-$ intermediate.

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The Generation of Carbene Anion Radicals from Diazo Compounds. Factors Influencing the Unimolecular Decomposition of the Anion Radicals of Diazo Compounds in Solution

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Abstract: Anion radicals of two diazo compounds, azibenzil and diethyl diazomalonate, had previously been reported to undergo unimolecular decomposition in aprotic solvents to generate the corresponding carbene anion radicals. These processes have been examined in detail by transient electrochemical techniques. The rate constants for the loss of dinitrogen in DMF at 273.2 K are 407 and 125 s^{-1} for the anion radicals of diethyl diazomalonate and azibenzil, respectively. There is little difference in the rate constants in the two solvents. The activation enthalpies fall in the range 10.6-12.7 kcal/mol, and the entropies of activation are close to -6 cal/(K·mol). Hydrogen bonding to water (i) (K_i = 0.8 M^{-1}) facilitates unimolecular decomposition.

$$Ph(PhCO)C{=}N_2^{\bullet-} + HOH/CH_3CN \overset{K_i}{\rightleftharpoons} Ph(PhCO)C{=}N_2^{\bullet-}/HOH + CH_3CN \qquad (i)$$

The hydrogen bonded complex, $Ph(PhCO)C{=}N_2^{\bullet-}/HOH$, undergoes first-order decomposition with a rate constant in acetonitrile at 273.2 K equal to 1700 s^{-1}. This rate enhancement is attributed to the localization of charge away from nitrogen. The carbonyl group adjacent to the diazo function in both substrates also facilitates loss of dinitrogen. It is concluded that unimolecular loss of nitrogen is a more favorable process than previously thought, especially at higher temperatures and when the charge is delocalized.

The thermal decomposition of diazo compounds to yield carbenes is a well-established reaction.[1] Gas-phase studies suggested that diazoalkane anion radicals undergo unimolecular loss of dinitrogen to generate the corresponding carbene anion radicals.[2] Anion radicals of the carbenes, diphenylmethylene and fluorenylidene, have been suggested to be intermediates in the electrochemical reduction of the related diazoalkanes,[3,4] but detailed kinetic studies[5-10] provided powerful evidence to the contrary. Diazodiphenylmethane anion radical does indeed undergo first-order decomposition in acetonitrile and *N,N*-dimethylformamide (DMF). However, solvent deuterium kinetic isotope effects were observed in both solvents implicating reactions of the anion radicals with solvent before irreversible dinitrogen loss takes place.[5,6] The anion radical of 9-diazofluorene undergoes rate-determining dimerization initiating a complex sequence of reactions involving several intermediates before the final product, fluorenone azine, is formed.[9,10] Thus, in these cases more favorable reaction

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