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Gas-Phase Reactions of Fe^+ with Ketones and Ethers

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Abstract: A pulsed laser has been used in conjunction with an ion cyclotron resonance spectrometer to generate and study the gas-phase ion–molecule reactions of Fe^+ with simple carbonyl compounds and ethers. Oxidative addition reactions are observed, producing alkyl, acyl, and alkoxide intermediates which undergo intramolecular rearrangement by a β-hydride shift mechanism. Decarbonylation reactions are observed with only a few small ketones. The main reaction channel is dehydrogenation for unbranched ketones and reductive elimination of methane for those branched at the α carbon. Reactions of Fe^+ with diisopropyl ketone, cyclohexanone, cyclopentanone, and tetrahydrofuran suggest the existence of intermediate and stable π-allyl complexes resulting from sequential β-hydride shifts.

To a solution chemist the direct cleavage of carbon–carbon bonds by transition metals is not as common a process as carbon–carbon bond formation. To the gas-phase ion–molecule chemist, however, carbon–carbon bond cleavage by atomic metal ions and metal-ion complexes may be a more common occurrence. The reason for this is that the collision complex formed in an ion–molecule collision is activated with an excess internal energy that can be as much as 40–60 kcal. That energy plus the metal–carbon bond energy may be sufficient to allow for the oxidative addition across a carbon–carbon bond. This general process has been observed in the decarbonylation of aldehydes by $CpNi^+$[1] and the reactions of Ni^+, Cr^+, Fe^+, and Co^+ with a few simple alkanes.[2,3] Furthermore, oxidative addition across carbon–hydrogen,[3,4] carbon–oxygen,[4,5] and carbon–halogen[6,7] bonds has also been reported. The prediction of reaction intermediates and mechanisms has been a major emphasis of these studies.

An excellent report by Allison and Ridge[4] involving the reactions of a variety of alkali and transition-metal ions with alkyl halides and alcohols revealed significant differences in the mechanisms and energetics of the reactions of these two classes of metal ions. For alkali ions, the interaction is mainly electrostatic with a small amount of covalency. Transition-metal ions typically bond in a covalent fashion, and therefore give rise to a richer chemistry. Rearrangement processes involving β-hydride elimination, for example, so far have only been observed for the transition-metal ions, but not for the alkali ions.

In an earlier paper we reported the reactions of Cu^+ with ketones.[8] The major mechanism appeared to involve the metal-induced enolization of the ketone, with rearrangement by sigmatropic shifts on the organic moiety rather than ligand migration to the metal atom. In this paper we report the reactions of Fe^+ with a series of ketones and ethers. The emphasis here is to formulate basic mechanisms for these simple coordinatively unsaturated organometallics and to compare them with related gas- and condensed-phase metal-ion systems.

Experimental Section

All experiments were performed on a modified V-5900 series ion cyclotron resonance spectrometer manufactured by Varian Associates.[9] The open-ended cell was provided with an end plate made of high-purity iron. Iron ions were generated by focusing the beam from an International Laser Corporation pulsed Nd:YAG laser through a sapphire view port onto the end plate target (spot size ~0.5 mm in diameter). Pulse characteristics are typically 100 mJ for 30 ns at a repetition rate of 5 Hz, thus providing a power density of about 10^8 W/cm^2. The output of the laser had a peak-to-peak reproducibility of ±10%.

The iron plasma consists of monatomic ionic and neutral species under the relatively low power density utilized in these experiments. Neutral iron atoms condense immediately on the walls of the cell and, therefore, do not participate in any observable ion–neutral processes. Operating pressures typically ranged from 1×10^{-7} to 2×10^{-6} torr. The target plate was grounded to avoid sporadic charging of the surface. We routinely keep the ion-trapping voltage at ~0.2 V which serves to minimize the containment of kinetically hot ions and maximize peak resolution. Even at very low pressures, however, the spectral peaks are much broader than those usually observed under electron impact ionization conditions. This effect has made it difficult to access accurate mass measurements above 160 amu and, therefore, we have omitted much of the chemistry of the secondary ions that is unquestionably occurring to produce ions in and above this mass region. The broadening may be due to an energy and/or spatial distribution of ions within the cell. Experiments are underway to analyze this problem by employing a different optical/target geometry so that ion trajectories can be focused and directed parallel to the magnetic field vector. In this way the laser-generated ions are only constrained by the trapping-plate potentials. By maintaining low trapping potentials, high-energy ions will be selectively annihilated on the trapping plates.

Reaction pathways were identified by observing changes in reactant- and product-ion signals as a function of time and by the double-resonance technique.[10,11] Measured product ratios are obtained with an absolute error of ±15%. Therefore, the product-ion-branching ratios reported in Tables I and II should only be interpreted in a qualitative sense due to the fluctuations in ion intensity arising from pulse-to-pulse variations in ion concentration and in ion spacial distributions within the cell.

Each of the chemicals used was a commercial sample of high purity. The deuterated ketones were synthesized according to the procedure of McNesby, Drew, and Gordon[12] by refluxing 10.0 mL of the pure ketone in 9.0 mL of D_2O containing 0.1 g of K_2CO_3 for 8–16 h in a closed system. Saturation of the water layer with K_2CO_3 is then followed by separation of the ketone layer, and the procedure is repeated at least 6 times. Mass spectrometric analysis showed about 94% α,α'-2-butanone-d_5 and 6% of the tetradeuterio compound, 91% α,α'-2-pentanone-d_5 and 8% of the tetradeuterio and 1% of the trideuerio compound, 95% α-3,3-dimethyl-2-butanone-d_3 and 5% of the dideuterio compound, and 79% α,α'-cyclohexanone-d_4 and 16% of the trideuterio and 5% of the dideuterio compound. Acetone-d_6 was obtained from Aldrich (99.5 atom % D). All the chemicals were degassed by multiple freeze–pump–thaw cycles prior to their use.

Results and Discussion

The initial interaction between Fe^+ and RCOR′ generates a chemically activated species, $[Fe(RCOR')^+]^*$, whose internal energy is available for the three sequential processes: oxidative addition, rearrangement, and reductive elimination. This behavior was previously observed with ICR for the decarbonylation of aldehydes by $CpNi^+$.[1] Interestingly, with $CpNi^+$ decarbonylation of acetone was not observed nor were reactions with other ketones

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[1] R. R. Corderman and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 5700 (1976).

[2] R. B. Freas and D. P. Ridge, *J. Am. Chem. Soc.*, **102**, 7129 (1980).

[3] (a) J. Allison, R. B. Freas, and D. P. Ridge, *J. Am. Chem. Soc.*, **101**, 1332 (1979); (b) P. B. Armentrout and J. L. Beauchamp, *ibid.*, **102**, 1736 (1980).

[4] J. Allison and D. P. Ridge, *J. Am. Chem. Soc.*, **101**, 4998, (1979).

[5] J. Allison and D. P. Ridge, *J. Am. Chem. Soc.*, **100**, 163 (1978).

[6] J. Allison and D. P. Ridge, *J. Am. Chem. Soc.*, **98**, 7445 (1976).

[7] J. S. Uppal and R. H. Staley, *J. Am. Chem. Soc.*, **102**, 4144 (1980).

[8] R. C. Burnier, G. D. Byrd, and B. S. Freiser, *Anal. Chem.*, **52**, 1641 (1980).

[9] T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectrometry", Wiley-Interscience, New York, 1976.

[10] L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

[11] B. S. Freiser, T. B. McMahon, and J. L. Beauchamp, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 249 (1973).

[12] J. R. McNesby, C. M. Drew, and A. S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955).

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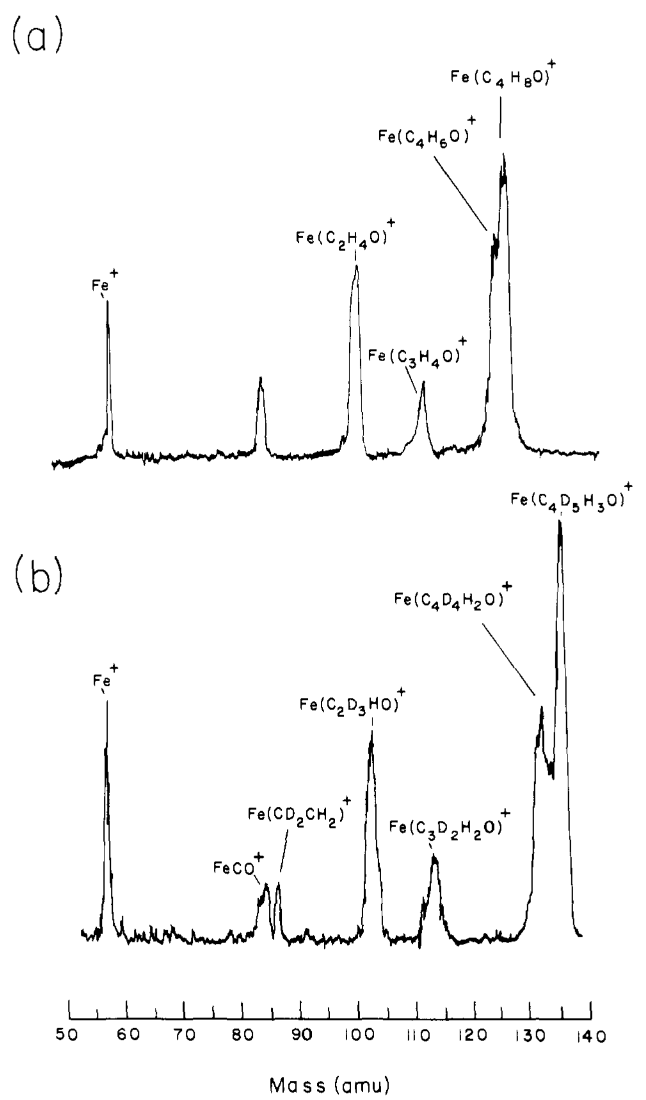
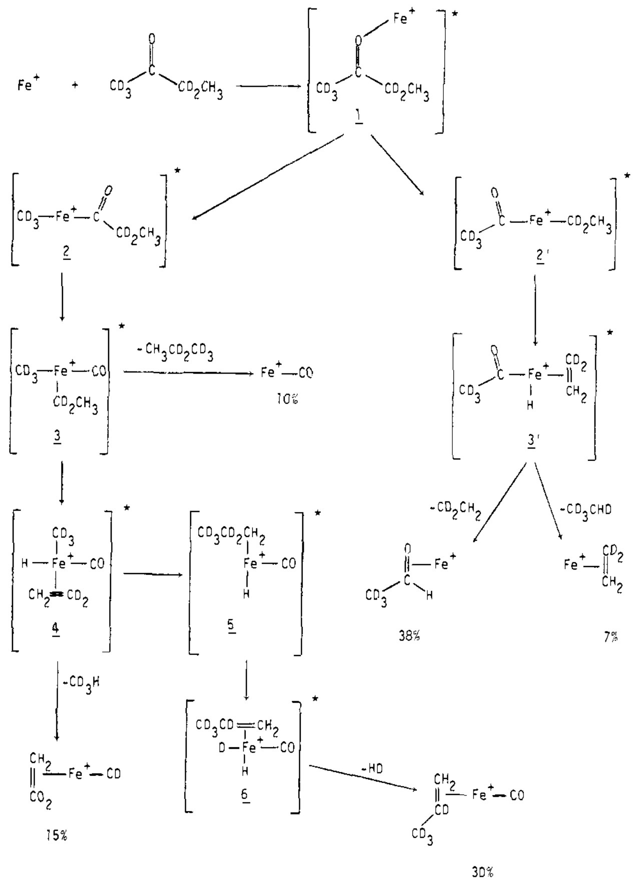


Figure 1. Single-resonance mass spectrum arising from laser emission of Fe^+ from an iron ICR end plate in the presence of (a) 2-butanone and (b) α,α'-2-butanone-d_5 at approximately 2×10^{-7} torr and a trapping time of 140 ms.

Scheme I



reported. Fe^+ appears to be more chemically active in this regard, since it readily decarbonylates small ketones and aldehydes. ($CpFe^+$, therefore, might also decarbonylate ketones, although this has yet to be borne out by experiment.)

The reactions of Fe^+ with ketones are summarized in Table I. As an example, Figures 1a and 1b show mass spectra of Fe^+ reacting with 2-butanone and α,α'-2-butanone-d_5, respectively, taken at a pressure of 2×10^{-7} torr and a trapping time of 140 ms. A comparison of the two spectra reveals that the peak at m/e 84 is unresolved in the undeuterated spectrum and actually consists of the two distinct species, $Fe(CO)^+$ and $Fe(C_2H_4)^+$. In addition, the ion at m/e 100 is shifted by three mass units to give m/e 103 for the deuterated product. This unequivocally indicates that the ion has the empirical formula FeC_2H_4O rather than FeC_3H_8.

Scheme I illustrates a proposed mechanism for the reaction of Fe^+ with deuterated 2-butanone. The initial interaction is envisioned to be with the more basic site on oxygen forming intermediate **1**. This type of intermediate, however, probably becomes less important with larger ketones as evidenced by the observation that Fe^+ reacts similarly with alkanes.[3a] Both oxidative addition and alkyl migration are involved. The final result for the deuterated 2-butanone shown in Scheme I is the competitive elimination of $CH_3CD_2CD_3$ from **3**, of CD_2CH_2 and CD_3CHO from **3'**, and of CD_3H from **4**. Another reaction channel observed is the elimination of HD. The addition/reelimination step to produce **6** could reasonably account for this, yet an alternative mechanism is shown in Scheme II, where oxidative addition into the C–H bond is the initially preferred route and generation of the unsaturated ketone bonded to the metal results. This is a more attractive mechanism since olefin insertion reactions involving a methide shift are rare.

The decarbonylation of acetone to yield $Fe(CO)^+$ and an ion corresponding to either $Fe(CH_3)_2{}^+$ or $Fe(C_2H_6)^+$ may be compared to that observed for 2-butanone. The calculated enthalpy change for both reactions 1 and 3 is −56 kcal/mol.[13] A small

$$Fe^+ + CH_3COCH_3 \rightarrow Fe(CO)^+ + C_2H_6 \qquad (1)$$

$$Fe^+ + CH_3COCH_3 \rightarrow Fe(C_2H_6)^+ + CO \qquad (2)$$

$$Fe^+ + C_2H_5COCH_3 \rightarrow Fe(CO)^+ + C_3H_8 \qquad (3)$$

abundance of $Fe(C_2H_6)^+$ is generated by reaction 2, whose counterpart, $Fe(C_3H_8)^+$, unexpectedly is not seen with 2-butanone. Therefore, it would appear that the reaction channel shown as a β-hydride shift in step **3** to **4** of Scheme I (not available for acetone, although one could envision the generation of an intermediate carbene complex by α-elimination) accounts for the reduction in overall yield of $Fe(CO)^+$ from 2-butanone and suggests that elimination of CO from acetone arises from $[Fe(CH_3)_2(CO)^+]^*$ rather than $[Fe(C_2H_6)(CO)^+]^*$. (Although the Fe^+–CH_3 bond energy in $Fe(CH_3)_2(CO)^+$ is unknown, $D(Fe^+–CH_3)$ lies somewhere between 56 and 68 kcal/mol[3a] and is comparable in energy to 62 kcal/mol[14] that has been measured for $D(Fe^+–CO)$.) Similarly, the absence of $Fe(C_3H_8)^+$ with 2-butanone follows from the above argument, since a facile β-hydride shift can compete effectively with alkyl recombination.

Upon going from 2-butanone to 3-methyl-2-butanone and 3,3-dimethyl-2-butanone, we observe that elimination of CH_4 becomes the dominating reaction, with no elimination of aldehyde or olefin. Only CH_4 is eliminated from $CD_3COC(CH_3)_3$ indi-

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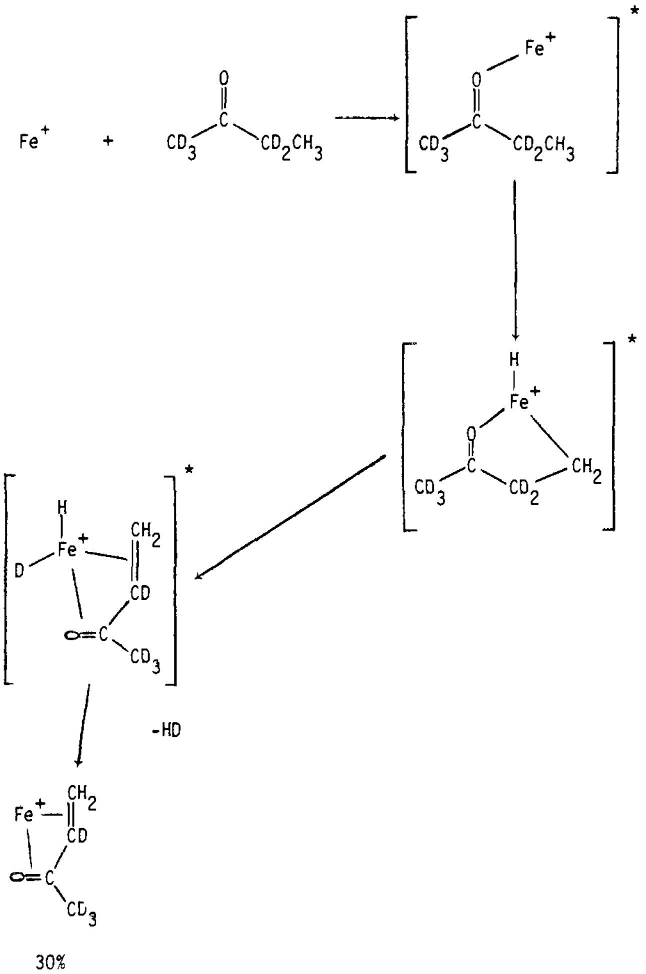
(13) Based on heats of formation of neutrals in H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, **6** (1977), and on $D(Fe^+–CO)$ = 62 kcal/mol in ref 14.

(14) G. Distefano, *J. Res. Natl. Bur. Stand., Sect. A*, **74**, 233 (1970).

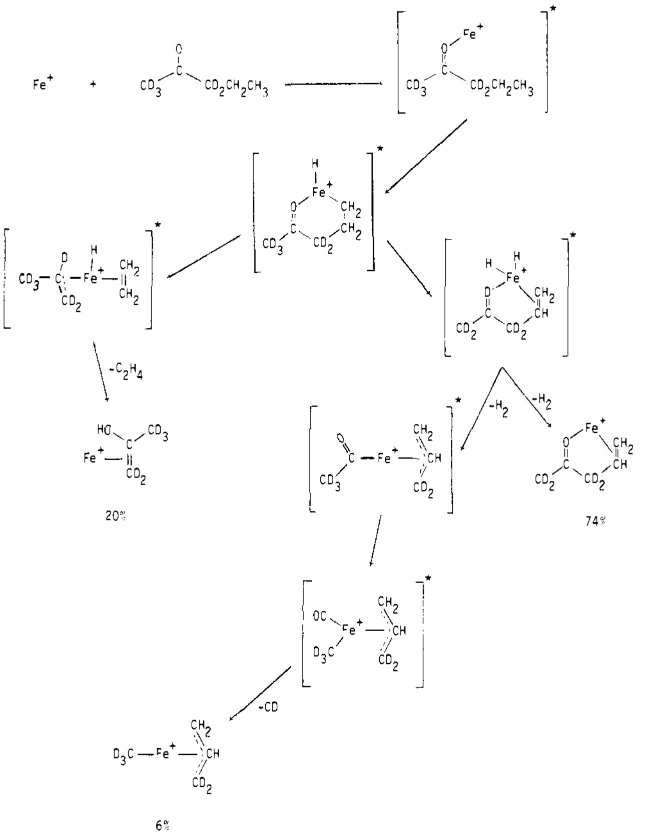
Scheme II



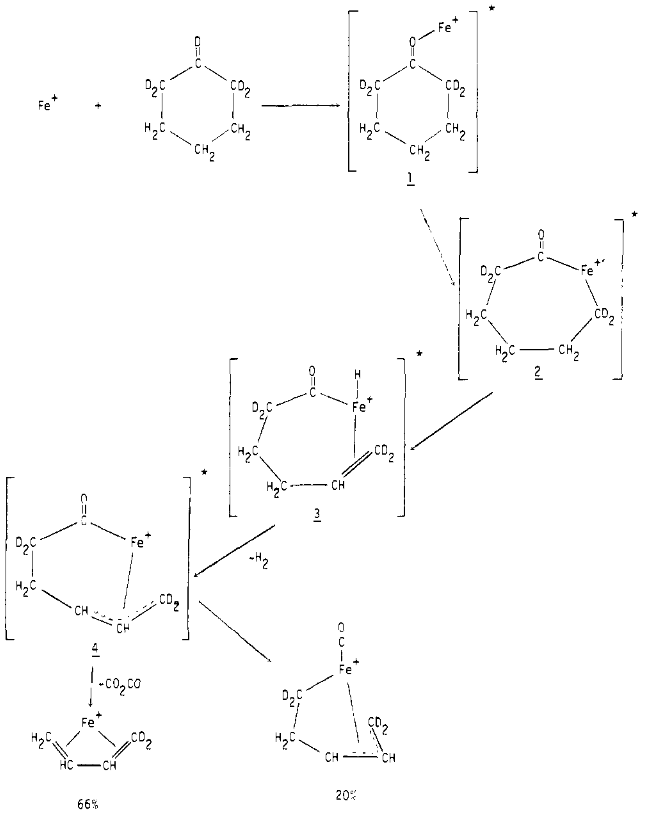
cating that β C–C bond cleavage or C–H bond cleavage is competitive with α C–C bond cleavage. This preference for the β position would explain the absence of any reductive elimination of H_2 by the mechanism in Scheme I. Although loss of H_2 from $CD_3COC(CH_3)_3$ by the mechanism in Scheme II is not possible since no β hydrogen is available, one cannot rule out the possibility of oxidative addition across the C–H bond followed by a methide shift. Support for the type of mechanism portrayed in Scheme II comes from the reactions of Fe^+ with alkanes,[3a,15] which demonstrate that insertion into C–H bonds will occur. This indicates the possibility for insertion of Fe^+ into the C–H bond on the extended alkyl chain of a ketone.

Since a number of competitive initial dissociation processes may occur, some difficulty in predicting the chemistry with larger aliphatic ketones is expected. In fact, perhaps no all-inclusive mechanism for these reactions exists. Comparing the chemistry of 2-pentanone and 2-butanone illustrates this point. The combined results for 2-pentanone and α,α'-2-pentanone-d_5 suggest the mechanism shown in Scheme III. An alternative mechanism involving α or β C–C bond cleavage similar to that in Scheme I is also possible but indistinguishable by any labeling experiment. Neither CH_4 nor CH_3CHO are neutral products of the reaction, but rather extensive (75%) dehydrogenation occurs suggesting the mechanism in Scheme III involving addition at the γ C–H bond. The overall sequence is analogous to that shown in Scheme II. The elimination of C_2H_4 via C–C fission at the β position, however, also becomes feasible.[16] In addition, ions observed at m/e 112 and 117, corresponding to a total neutral loss of 30 amu for both the unlabeled and labeled ketone, are difficult to explain by any mechanism other than one involving a sequential loss of H_2 and

Scheme III



Scheme IV



CO (elimination of C_2H_6 is not possible with the deuterated 2-pentanone). The reductive elimination of methane and/or acetaldehyde would probably occur if initial cleavage at the α carbon were involved. Therefore, the reaction appears more likely to proceed via an allyl intermediate as shown in Scheme III. The generation of the complex, $Fe(CO)_3(C_3H_5)^+$, in the reaction of

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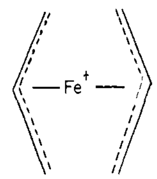
[15] G. D. Byrd, R. C. Burnier, and B. S. Freiser, unpublished results.

[16] This mechanism was suggested first by the authors in ref 18.

$Fe(CO)_5$ with $C_3H_7^+$[4] supports the contention that an allyl intermediate is probably involved.

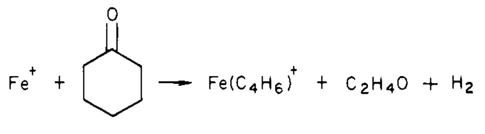
The formation of the species $Fe(C_4H_6)^+$ in low yield by the reaction of Fe^+ with 2-hexanone also is strongly indicative of a π-allyl intermediate. The sequential migration of three hydrogen atoms from the *n*-butyl group makes possible the elimination of H_2 and CH_3CHO, in contrast to the case of 2-pentanone where only two hydrogens are accessible and no neutral loss of aldehyde occurs. Allyl acetone, on the other hand, requires a shift of only one hydrogen to form the diene, and now this becomes the dominant reaction pathway. Furthermore, as a result of this, no H_2 elimination occurs. If initial attack is on the unsaturated portion of the molecule, rearrangement to an allyl intermediate is not unreasonable. Alternatively, one cannot rule out the possibility that initial cleavage is occurring adjacent to the carbonyl group. In this case, iron bound to the diene through only one π bond would result.

The isomeric compounds diisopropyl ketone and 4-heptanone also give products suggesting π-allyl intermediates. In fact, the sequential elimination of $2H_2$ and CO from diisopropyl ketone produces an ion most likely having the bis(trihapto) allyl structure:[17]

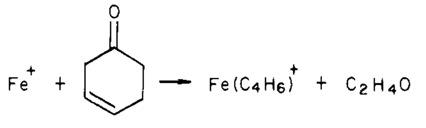


Interestingly, this species is not produced (or produced in very small yield) with 4-heptanone, implying that dehydrogenation is less facile or occurs by a different mechanism. It is also observed that the dominant reaction of diisopropyl ketone is the elimination of methane, again suggesting oxidative addition at the β position.

The above analysis may also be extended to the reactions of Fe^+ with cyclic ketones. The reactions of cyclohexanone and cyclohexenone with Fe^+ were first reported by Ridge and Allison.[18] Since cyclohexenone forms the same ionic product as cyclohexanone, it was assumed that reaction 4 began with H_2 elimination via a metal-insertion hydrogen-atom shift mechanism. This forms a cyclohexenone metal complex which can undergo a reverse Diels–Alder reaction to eliminate a ketene molecule, thus forming the diene complex. We postulate a somewhat different mechanism (Scheme IV) based on our interpretation of the results obtained for the acyclic aliphatic ketones. In this scheme a seven-membered metallocycle is initially produced by oxidative addition at the α C–C bond. Elimination of H_2 by sequential β-hydride shifts affords the 1,3-diene and ketene fragments via a π-allyl intermediate. This type of transformation is fundamental to the understanding of catalytic processes accompanying diene oligomerization.[19] The dissociative mechanism we are proposing here in many ways resembles the reverse of addition reactions of acyl metal complexes to olefinic compounds.[20] For instance, the 5-hexenoylcobalt complex, $CH_2{=}CH(CH_2)_3COCo(CO)_4$, undergoes internal addition of the acyl group to the double bond, releasing CO, and ultimately forming five- and six-membered cyclic ketones. An intermediate olefin π complex is suggested. Moreover, 2-cyclohexenone has been synthesized[21] by irradiating vinylcyclopropane in the presence of $Fe(CO)_5$, which gave I as the isolated precursor to the 2-cyclohexenone product. Only under the influence of air or 20 atm of CO, however, was the 2-cyclohexenone obtained; milder conditions gave II as the decomposition product.

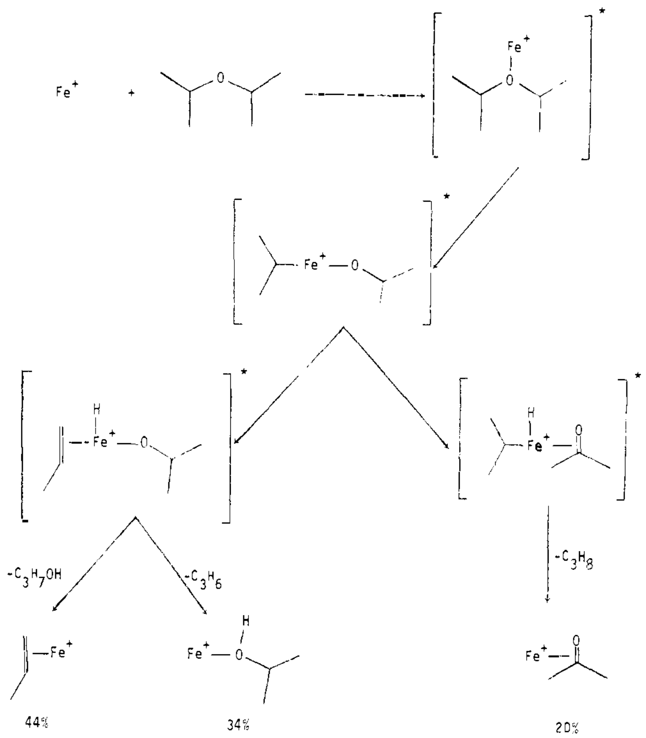


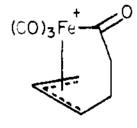
(4)



(5)

Scheme V





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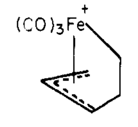
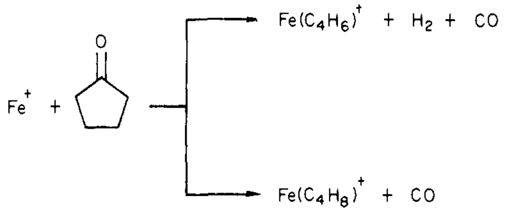


II

We believe the coordinative unsaturation and chemical activation of the intermediate complex, **4**, in Scheme IV would provide a driving force away from cyclohexenone formation to give the Fe^+–butadiene complex. Therefore, about 20% of the total reaction giving rise to dehydrogenation presumably generates a stable π-complex metallocycle rather than cyclohexenone bound as a ligand to Fe^+. $Fe(C_4H_6)^+$, produced in reaction 6, can be interpreted in the same manner. In this case, however, it is difficult to rationalize a reverse Diels–Alder reaction. In addition, $Fe(C_4H_8)^+$, produced by reaction 7, most likely exists initially as a metallocyclopentane with subsequent conversion to $Fe(C_2H_4)_2^+$ by a symmetry-allowed reverse oxidative cyclization step. This structure is suggested by the ligand-substitution reaction 8 with cyclopentanone.



(6)

(7)

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[17] (a) This structure can be found in condensed phase cyclic and acyclic bis(η^3-allylic)carbonyliron derivatives, with only one example of the latter: A. N. Nesmeyanov and I. I. Kritskaya, *J. Organomet. Chem.*, **182**, 903 (1968); (b) see also R. B. King, "The Organic Chemistry of Iron", Vol. 1, E. A. Koener Von Gustorf, F-W Grevels, and I. Rischler, Eds., Academic Press, New York, 1978, pp 463–526.

[18] D. P. Ridge and J. Allison, "26th Annual Conference on Mass Spectrometry and Allied Topics", 1978, p 224.

[19] For example, see P. W. Jolly and J. Wilke "The Organic Chemistry of Nickel", Academic Press, New York, 1975, Chapters I and II.

[20] (a) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974, pp 226–8; (b) J. A. Bertrand, C. L. Aldridge, S. Husebye, and H. B. Jonassen, *J. Org. Chem.*, **29**, 790 (1964).

[21] R. Aumann, *J. Am. Chem. Soc.*, **96**, 2631 (1974).

Table I. Reactions of Fe$^+$ with Ketones and Aldehydes

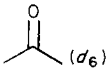
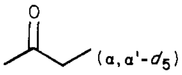
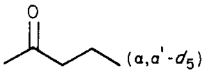
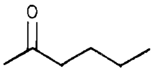
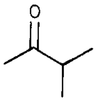
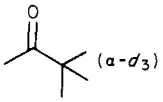
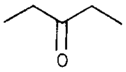
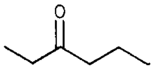
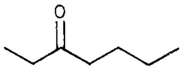
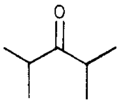
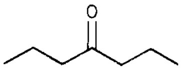
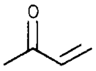
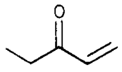
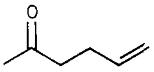
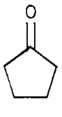
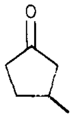
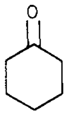
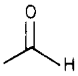
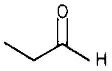
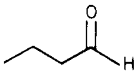
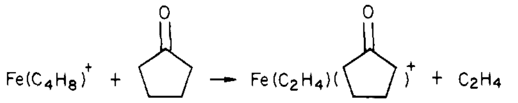
	reaction	% of total reaction
Fe$^+$ + 	→ $Fe(CO)^+ + C_2D_6$	93
	→ $Fe(CD_3)_2^+ + CO$	7
Fe$^+$ + 	→ $Fe(CO)^+ + C_3D_5H_3$	10
	→ $Fe(CD_2CH_2)^+ + CD_3CHO$	7
	→ $Fe(CD_3CHO)^+ + CD_2CH_2$	38
	→ $Fe(CO)(CD_2CH_2)^+ + CD_3H$	15
	→ $Fe(C_4D_4H_2O)^+ + HD$	30
Fe$^+$ + 	→ $Fe(CO)^+ + C_4D_5H_5$	}<1
	→ $Fe(C_2H_4)^+ + CD_3COCD_2H$	
	→ $Fe(C_4D_5H_3)^+ + H_2 + CO$	6
	→ $Fe(CD_3COCD_2H)^+ + C_2H_4$	20
	→ $Fe(C_5D_5H_3O)^+ + H_2$	74
Fe$^+$ + 	→ $Fe(CO)^+ + C_5H_{12}$	} 4
	→ $Fe(C_2H_4)^+ + CH_3COC_2H_5$	
	→ $Fe(C_4H_6)^+ + H_2 + CH_3CHO$	11
	→ $Fe(CH_3COC_2H_5)^+ + C_2H_4$	21
	→ $Fe(C_6H_{10}O)^+ + H_2$	64
Fe$^+$ + 	→ $Fe(C_4H_6O)^+ + CH_4$	87
	→ $Fe(C_5H_8O)^+ + H_2$	13
Fe$^+$ + 	→ $Fe(CD_3\ COC(CH_3)CH_2)^+ + CH_4$	100
Fe$^+$ + 	→ $Fe(CO)^+ + C_4H_{10}$	} 15
	→ $Fe(C_2H_4)^+ + C_2H_5CHO$	
	→ $Fe(C_2H_4)_2^+ + H_2 + CO$	} 15
	→ $Fe(CO)(C_2H_4)^+ + C_2H_6$	
	→ $Fe(C_2H_5CHO)^+ + C_2H_4$	26
	→ $Fe(C_5H_8O)^+ + H_2$	29
Fe$^+$ + 	→ $Fe(C_5H_{10})^+ + H_2 + CO$	7
	→ $Fe(C_4H_8O)^+ + C_2H_4$	9
	→ $Fe(C_6H_{10}O)^+ + H_2$	84
Fe$^+$ + 	→ $Fe(CO)^+ + C_6H_{14}$	} 4
	→ $Fe(C_2H_4)^+ + C_5H_{10}O$	
	→ $Fe(C_4H_6)^+ + H_2 + C_2H_5CHO$	9
	→ $Fe(C_5H_{10}O)^+ + C_2H_4$	21
	→ $Fe(C_7H_{12}O)^+ + H_2$	66
Fe$^+$ + 	→ $Fe(C_3H_6)^+ + i\text{-}C_3H_7CHO$	3
	→ $Fe(C_4H_6)^+ + 2H_2 + CO + C_2H_4$	2
	→ $Fe(C_4H_8)^+ + C_2H_4 + CO + H_2$	5
	→ $Fe(C_5H_8)^+ + CH_4 + CO + H_2$	2
	→ $Fe(CO)(C_3H_6)^+ + C_3H_8$	1
	→ $Fe(C_3H_5)_2^+ + 2H_2 + CO$	36
	→ $Fe(i\text{-}C_3H_7COCH{=}CH_2)^+ + CH_4$	47
	→ $Fe(C_7H_{12}O)^+ + H_2$	3
Fe$^+$ + 	→ $Fe(C_4H_6)^+ + 2H_2 + CO + C_2H_4$	2
	→ $Fe(C_4H_8)^+ + C_2H_4 + CO + H_2$	2
	→ $Fe(C_4H_{10})^+ + C_2H_4 + CO$	4
	→ $Fe(C_5H_8)^+ + CH_4 + CO + H_2$	5
	→ $Fe(CO)(C_3H_6)^+ + C_3H_8$	2
	→ $Fe(C_6H_{12})^+ + H_2 + CO$	48
	→ $Fe(C_7H_{12}O)^+ + H_2$	37
Fe$^+$ + 	→ $Fe(C_2H_2)^+ + CH_3CHO$	28
	→ $Fe(C_3H_6)^+ + CO$	36
	→ $Fe(CO)(C_2H_2)^+ + CH_4$	36

Table I (*Continued*)

	reaction	% of total reaction
Fe^+ + 	→ $Fe(C_2H_2)^+ + C_2H_5CHO$	4
	→ $Fe(CO)^+ + C_4H_8$	
	→ $Fe(C_2H_4)^+ + CH_2CHCHO$	23
	→ $Fe(C_2H_4)(C_2H_2)^+ + H_2 + CO$	47
	→ $Fe(CO)(C_2H_2)^+ + C_2H_6$	
	→ $Fe(C_2H_4)_2^+ + CO$	23
	→ $Fe(CO)(C_2H_4)^+ + C_2H_4$	
	→ $Fe(C_5H_6O)^+ + H_2$	3
Fe^+ + 	→ $Fe(CO)^+ + C_5H_{10}$	9
	→ $Fe(C_2H_4)^+ + CH_3COCHCH_2$	
	→ $Fe(C_3H_6)^+ + C_2H_4 + CO$	24
	→ $Fe(C_4H_6)^+ + CH_3CHO$	62
	→ $Fe(C_4H_6O)^+ + C_2H_4$	5
Fe^+ + 	→ $Fe(CO)^+ + C_4H_8$	2
	→ $Fe(C_2H_4)^+ + C_3H_4O$	
	→ $Fe(C_4H_6)^+ + H_2 + CO$	60
	→ $Fe(C_4H_8)^+ + CO$	35
	→ $Fe(C_5H_6O)^+ + H_2$	3
Fe^+ + 	→ $Fe(CH_2CO)^+ + C_4H_8$	32
	→ $Fe(C_4H_6)^+ + H_2 + CH_2CO$	38
	→ $Fe(C_5H_8)^+ + H_2 + CO$	8
	→ $Fe(C_5H_{10})^+ + CO$	4
	→ $Fe(C_5H_6O)^+ + CH_4$	6
	→ $Fe(C_6H_8O)^+ + H_2$	12
Fe^+ +  (α,α'-d_4)	→ $Fe(CO)^+ + C_5D_4H_6$	3
	→ $Fe(CD_2CO)^+ + C_4D_2H_6$	6
	→ $Fe(C_4D_2H_4)^+ + H_2 + CD_2CO$	66
	→ $Fe(C_5D_4H_4)^+ + H_2 + CO$	2
	→ $Fe(C_5D_4H_6)^+ + CO$	3
	→ $Fe(C_6D_4H_4)^+ + H_2$	20
Fe^+ + 	→ $Fe(CO)^+ + CH_4$	100
Fe^+ + 	→ $Fe(CO)^+ + C_2H_6$	81
	→ $Fe(C_2H_4)^+ + H_2CO$	
	→ $Fe(C_3H_4O)^+ + H_2$	19
Fe^+ + 	→ $Fe(CO)^+ + C_3H_8$	16
	→ $Fe(C_2H_4)^+ + CH_3CHO$	
	→ $Fe(C_3H_6)^+ + H_2CO$	5
	→ $Fe(C_3H_8)^+ + CO$	40
	→ $Fe(CH_3CHO)^+ + C_2H_4$	
	→ $Fe(C_4H_6O)^+ + H_2$	39

Interestingly, 3-methylcyclopentanone also yields $Fe(C_4H_6)^+$. In this case, though, a second β-hydride shift can dissociate the

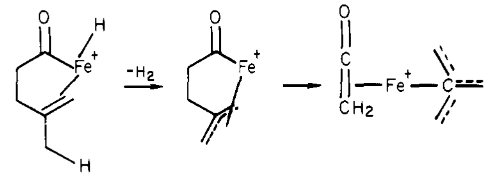


(8)

ketone into a trimethylenemethane and ketene fragment (a methallyl and ketene fragmentation is also possible). This is an example of stabilization of otherwise unstable species via metal complexation.[22]

The chemistry of Fe^+ with ethers is summarized in Table II.

In this system, oxidative addition across the C–O bond produces a metal alkoxide which then undergoes β-elimination with neutral alkane loss. Conversely, a β-hydride shift from the alkyl ligand



produces the corresponding alkene and alcohol metal complex. These reactions are illustrated in Scheme V for diisopropyl ether. A comparison of the chemistry of diisopropyl ketone and diiso-

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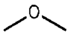
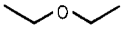
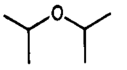
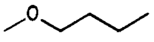
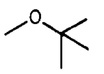
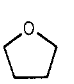
(22) J. M. Landesberg, ref 17b, pp 630–32.

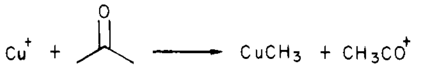
Table II. Reactions of Fe^+ with Ethers

reaction		% of total reaction
Fe^+ 	→ $Fe(CH_2O)^+ + CH_4$	100
Fe^+ + 	→ $Fe(C_2H_4)^+ + C_2H_5OH$	23
	→ $Fe(C_2H_4O)^+ + C_2H_6$	23
	→ $Fe(C_2H_5OH)^+ + C_2H_4$	47
	→ $Fe(C_4H_8O)^+ + H_2$	7
Fe^+ + 	→ $Fe(C_3H_6)^+ + i\text{-}C_3H_7OH$	44
	→ $Fe(C_3H_6O)^+ + C_3H_8$	20
	→ $Fe(i\text{-}C_3H_7OH)^+ + C_3H_6$	34
	→ $Fe(C_5H_{10}O)^+ + CH_4$	2
Fe^+ + 	→ $Fe(C_2H_4)^+ + C_3H_8O^+$	3
	→ $Fe(C_4H_6)^+ + H_2 + CH_3OH$	7
	→ $Fe(C_4H_8)^+ + CH_3OH$	34
	→ $Fe(C_4H_8O)^+ + CH_4$	2
	→ $Fe(C_5H_{10}O)^+ + H_2$	54
Fe^+ + 	→ $Fe(CH_3OH)^+ + i\text{-}C_4H_8$	60
	→ $Fe(i\text{-}C_4H_8)^+ + CH_3OH$	36
	→ $Fe(C_4H_8O)^+ + CH_4$	4
Fe^+ + 	→ $Fe(C_3H_6)^+ + CH_2O$	83
	→ $Fe(C_4H_6)^+ + H_2O$	17

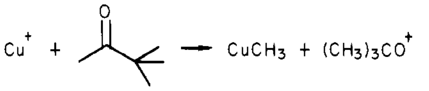
propyl ether shows that elimination of CH_4 via an initial C–C or C–H bond cleavage is preferred in the former but not the latter. The same kind of behavior persists even for *tert*-butyl methyl ether (compare 3,3-dimethyl-2-butanone), also indicating that formation of $[CH_3\text{-}Fe^+\text{-}OC(CH_3)_3]^*$ cannot result in CH_4 loss by a β-hydride shift. The implication is that in contrast to a σ-acyl complex, formation of the metal alkoxide bond is more facile, perhaps due to less steric hindrance by the isopropyl group on approach of Fe^+ to the oxygen atom than to the acyl carbon atom. On the other hand, Ridge et al. have shown evidence for little or no energy barrier for the concerted oxidative addition reactions of Fe^+, Co^+, and Ni^+.[2,4] Therefore, the relative stabilities of the initially formed ML_2^+ intermediates and/or the final product ions may be a more important factor influencing which reaction channel occurs.

Scheme VI illustrates that a cyclic ether can also be dissociated, and again the evidence strongly suggests that a η^3-allyl intermediate is the precursor of the observed product ions. There is no resemblance between the products obtained with tetrahydrofuran and its isomer butyraldehyde, implying that an Fe^+-induced isomerization of the cyclic ether to the aldehyde does not occur. In contrast, chlorotitanium ions do appear to induce this isomerization.[5]

The reactions of gas-phase Cu^+ provide an interesting comparison to those of Fe^+. For example, Cu^+ prefers to retain its +1 oxidation state when σ bonded to carbon atoms as illustrated by its propensity to abstract CH_3^- from ketones (eq 9 and 10).

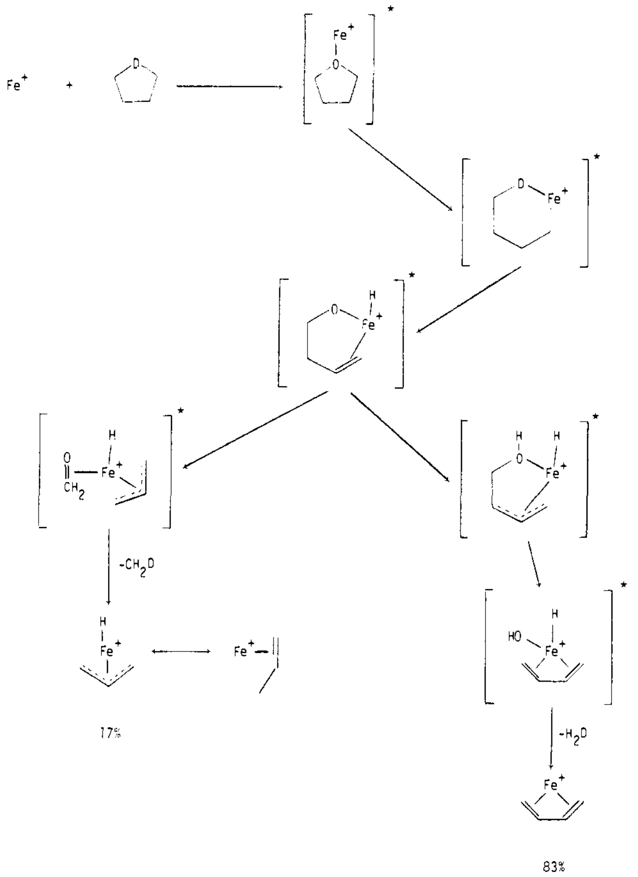


(9)



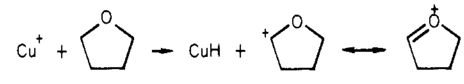
(10)

Scheme VI



Interestingly, oxidative addition of ketones to Cu^+ would involve the generation of the rather unstable Cu(III) oxidation state. In solution, copper(I) complexes undergo oxidative addition reactions in a special way. Their reactivity results from the tendency of cuprous complexes to associate forming, for example, in the Corey–Posner reaction,[23] dimeric lithium alkyl cuprate species.[24] Dimerization provides a one-electron metal oxidation path, thus bypassing the Cu(III) oxidation state. In the gas-phase system employed in our study, however, purely monomeric species are generated. This might explain the lack of Cu^+ insertion into the carbon framework of ketones by a concerted oxidative addition. Moreover, reactions of Cu^+ with diethyl ether and tetrahydrofuran produce solely CuH and the corresponding ether carbonium ion,[15] reactions 11 and 12. The affinity of Cu^+ for H^- and CH_3^- is

$$Cu^+ + C_2H_5OC_2H_5 \rightarrow CuH + CH_3\overset{+}{C}H\text{-}O\text{-}C_2H_5 \longleftrightarrow CH_3CH{=}\overset{+}{O}\text{-}C_2H_5 \tag{11}$$



(12)

understandable for such soft acid–soft base interactions and from the inability of these ligands to stabilize the Cu(III) state.[25]

As a further comparison, Ti^+ and $TiCl^+$ extract an oxygen atom from carbonyl compounds and cyclic ethers forming TiO^+ and $TiClO^+$ but are not observed to react with carbonyl compounds with more than five carbon atoms.[5] $TiCl_2^+$ and $TiCl_3^+$ are more difficult to oxidize and exhibit a chemistry similar to Cu^+. Moreover, gas-phase Li^+ has been found to electrostatically bond to carbonyl compounds and not to dissociate the neutral.[26] Clearly, the reducing power of the metal and its number of available sites for bonding are two important controlling factors.

In summary, we do not report here any evidence for the formation of metal carbene complexes by α-elimination. In general, the direct cleavage of C–C, C–H, and C–O bonds produces alkyl, acyl, and alkoxide Fe^+ intermediates whose kinetic labilities should be strongly influenced by the extent of coordinative saturation of the metal. Here the absence of other coordinating ligands

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(23) E. J. Corey and G. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1968).

(24) R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).

(25) Cu(III) is stabilized by very strong n-donor bases such as the triply deprotonated tetraglycine peptide: see J. S. Rybka, J. L. Kurtz, T. A. Neubecker, and D. W. Margerum, *Inorg. Chem.*, **19**, 2791 (1980), and references therein.

(26) R. V. Hodges and J. L. Beauchamp, *Anal. Chem.*, **48**, 825 (1976); R. L. Woodin, F. A. Houle, and W. A. Goddard III, *Chem. Phys.*, **14**, 461 (1976).

provides an ideal environment for β-elimination. This reaction appears to compete effectively with decarbonylation so that only small ketones react in the latter way. Larger straight-chain aliphatic ketones undergo extensive dehydrogenation while ketones branched at the α carbon prefer to eliminate methane. Whether or not this generalization may be extended to ketones containing secondary or tertiary β carbons still remains to be tested.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Department of Energy (DE-AC02-80ER10689). The authors also wish to express their appreciation to Dr. J. Kouba for his helpful discussions.

Photoprocesses in Cationic Microemulsion Systems[1]

S. S. Atik and J. K. Thomas*

Contribution from the Chemistry Department, University of Notre Dame, Notre Dame, Indiana 46556. Received January 30, 1981

Abstract: Photophysical methods are used to investigate the hexanol, dodecane, water, and cetyltrimethylammonium bromide (CTAB) microemulsion (μE), both as oil in water and water in oil systems. Several photochemical systems, e.g., the pyrene excimer formation, the pyrene–dimethylaniline exciplex and electron transfer system, and the ruthenium bipyridyl–methyl viologen electron system, are used to determine the particle radii and surfactant aggregation number. Fluorescence methods are used to investigate the site and environment of reactants in these systems. The effects of emulsion parameters, e.g., water content, nature of surface, etc., on electron-transfer reactions are studied and discussed.

There has been extensive photochemical studies on micellar systems and in particular CTAB.[2,3] As an extension of this work, we chose the CTAB-μE system (oil in water (O/W) and water in oil (W/O) for our present investigation. The objective of such an undertaking is to explore the influence of these structurally different molecular assemblies of the same surfactant molecule (CTAB) on a variety of photochemical and photophysical processes. A useful byproduct of this study is the elucidation of the fundamental basic structure of the host micellar or μE particles and water pools and the nature of their interaction with solutes.

Experimental Section

Fluorescence spectra were measured on a Perkin-Elmer MPF 44 spectrofluorimeter. Laser flash photolysis studies were carried out with the use of a Korad KIQ frequency doubled Q switch ruby laser: with 3471 Å; pulse width, 15 ns; and energy, 0.1 J. The transitory signals developed by the laser pulse were monitored on a Tektronix 7912AD transient capture device, while data processing was carried out on a Tektronix 4051 computer.

All chemicals were obtained from sources indicated previously, where the purification methods were also outlined.[4-6]

Results and Discussion

The results of this study will be described in two sections, the first one dealing with (O/W) CTAB-μE and the second one with W/O μE, where μE is an abbreviation for microemulsion.

Oil in Water (O/W) CTAB-μE. These μE particles are composed of CTAB, hexanol, and dodecane stabilized in an aqueous medium. These aggregate assemblies which are often referred to as swollen micelles are believed to consist of an oil droplet center coated with a mixed monolayer of surfactant and co-surfactant (hexanol) molecules with their ionic or polar groups directed outward in contact with the aqueous phase. The photochemical and photophysical studies presented in this paper are found to be consistent with this description.

The μE System. The composition of the μE used in this endeavor consisted of 8.37% CTAB, 0.5% hexanol, and 1.0% oil (dodecane) in water (or 0.01 M CTAB, 0.05 M hexanol, and 0.06 M dodecane). The solution formed from these components was very slightly bluish (light scattering) but otherwise perfectly clear. A useful ternary phase diagram for CTAB, hexanol, and water has already been reported by Friberg.[7]

Oil in Water (O/W) μE Size Determination. The average size of the μE particle was determined by the time-resolved pyrene excimer formation technique recently described by one of the authors.[8] The method relies on the assumption that solutes are distributed among the μE partilces according to Poisson statistics. According to this method the time-resolved fluorescence intensity is given by,

$$I_F(t) = I_F(0)e^{-\{k_1 t + \bar{n}(1-e^{-k_e t})\}} \qquad (1)$$

where $I_F(t)$ and $I_F(0)$ are the fluorescence intensities of excited pyrene at time t and $t = 0$, respectively, $\bar{n}$ is the average pyrene occupancy of a μE particle given by [P]/[μE], k_e is a first-order intra-μE excimer formation rate constant for a particle containing two pyrene molecules one of which is in its excited singlet state, and finally k_1 is the first-order rate of decay of P* solubilized in a particle that does not contain other pyrene molecules (i.e., the lifetime of P* under conditions where no excimer emission is observed at $\bar{n} \leq 0.1$).

For a certain $\bar{n}$ value ($\bar{n} \geq 0.2$) where Poisson law ($\alpha_n = \bar{n}^n e^{-\bar{n}}/n!$, α_n is the probability of finding a μE particle containing n probe molecules) predicts the existence of μE particles with two or more solubilized pyrene molecules, the fluorescence decay curve shows two components (as predicted by eq 1)—an initial fast one attributed to μE particles having solubilized two or more P molecules, and a limiting slow one corresponding to particles that contain only one P molecule.

At sufficiently long times when all the fluorescence eminating from multiply occupied μE particles has decayed completely (i.e., $e^{-k_e t} = 0$) the remaining fluorescence intensity can be ascribed

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(1) The authors would like to thank the NSF for support of this research via Grant CHE78-24867.

(2) J. K. Thomas, *Chem. Rev.*, **80**, 283 (1980).

(3) N. J. Turro, M. Grätzel, and A. M. Braun, *Angew. Chem.*, **19**, 675 (1980).

(4) M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **101**, 279 (1979).

(5) M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **102**, 188 (1980).

(6) S. Gregoritch and J. K. Thomas, *J. Phys. Chem.*, **84**, 149 (1980).

(7) S. Ahmad and S. Friberg, *J. Am. Chem. Soc.*, **94**, 5196 (1972).

(8) S. S. Atik and L. A. Singer, *Chem. Phys. Lett.*, **59**, 519 (1978); **66**, 234 (1979).

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