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Generation, Fragmentation, and Interconversion Processes of $[Fe,C_6,H_6,O]^+$ Isomers Relevant for the Oxygenation of Aromatic Hydrocarbons[†]

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Abstract: The gas-phase potential energy surface of $[Fe,C_6,H_6,O]^+$ isomers is examined by collisional activation using a large-scale tandem mass spectrometer, as well as ion/molecule reactions employing the conditions of ion cyclotron resonance mass spectrometry. In addition to the (phenol)Fe^+ complex (**1**), five other isomers could be distinguished and characterized: $(C_6H_5)Fe^+(OH)$ (**2**), $(C_6H_4)Fe^+(OH_2)$ (**3**), (2,4-cyclohexadienone)Fe^+ (**4**), (c-C_5H_6)Fe^+(CO) (**5**), and $(C_6H_6)FeO^+$ (**6**). The collision-induced fragmentation patterns of these isomers, the results of H/D exchange reactions with C_2D_4 and D_2O, as well as thermochemical estimates, using a simple additivity scheme, permit the construction of a qualitative potential energy surface for $[Fe,C_6H_6,O]^+$. On the basis of these findings, new insight is provided into the reaction mechanisms of and the intermediates formed in the oxidation of benzene and ethylbenzene by "bare" FeO^+. Furthermore, the dissociation of the Fe^+ complex of the valence tautomers benzene oxide $\rightleftarrows$ oxepin is demonstrated to proceed via (phenol)Fe^+ (**1**) rather than (2,4-cyclohexadienone)Fe^+ (**4**), and evidence is presented for the existence of an additional mechanism for the oxygenation of arenes by iron oxenoids in the gas phase.

Introduction

Nearly all conceivable aspects of the keto–enol tautomerism of carbonyl compounds have been studied with special emphasis on the energetics and mechanisms of this fundamental equilibrium. Whereas for simple aliphatic carbonyl compounds the keto forms are thermodynamically more stable by as much as 12 kcal/mol than the corresponding enols, conjugated double bonds increase the stabilities of the enol forms, e.g. 1,3-diones.[1] In the case of phenol, the equilibrium concentration of the keto form, i.e. 2,4-cyclohexadienone, is extremely low at room temperature.[2] The barriers associated with the unimolecular interconversion of keto–enol pairs via an intramolecular 1,3-hydrogen shift are quite high in general, demanding activation energies of ca. 50 kcal/mol, if not more;[3] however, in solution the bimolecular, acid/base-catalyzed isomerization is facile and occurs rapidly.[4] Interestingly, the stability order between the keto and the enol forms of simple alkanones reverses upon single-electron oxidation to the corresponding radical cations.[5]

Coordination of transition metal fragments is known to affect the keto–enol tautomerism in the condensed phase.[6] Most recently, simple methods for the transition metal-catalyzed isomerization of allyl alcohols to the corresponding enols have been reported, which allow the generation of pure enols on a preparative scale.[7] In the dilute gas phase, bi- or termolecular reactions and/or interactions with additional ligands, counter ions, and solvents can be excluded; consequently, the intrinsic effects of transition metal fragments or "bare" atoms on the keto–enol tautomerism can be studied. In addition, the gas-phase studies permit the probing of the transition metal ion mediated CH and CC bond activation, a topic which has attracted considerable attention in the last decade.[8] The effect of coordination of bare Fe^+ ions on the keto–enol equilibrium of phenol and the study of $[Fe,C_6,H_6,O]^+$ isomers deserve interest for several reasons:[9,10] (i) Does the metal cation change the relative stability order of keto–enol tautomers? (ii) Is the intramolecular interconversion affected by the presence of a metal ion? (iii) What are the major fragmentation pathways of the cationic complexes? (iv) In addition, a knowledge of the structures and energetics of $[Fe,C_6,H_6,O]^+$ isomers is of prime interest for an understanding of the oxygenation of arenes, which constitutes a crucial step in the metabolism of aromatic hydrocarbons by the iron-centered cytochrome P450 and related enzyme systems.[11] In this respect it is worthy of note to mention that we have shown recently that benzene as well as its monoalkyl derivatives can be oxidized efficiently in the gas phase by "bare" FeO^+ cations.[12]

In this article we report the generation of different cyclic $[Fe,C_6,H_6,O]^+$ isomers and their characterization by means of

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[†] Dedicated to Professor Hans Gross, Centre for Selective Organic Synthesis, Berlin-Adlershof, on the occasion of his 65th birthday.

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Table 1. Mass Differences and Characteristic Neutral Fragments in the CA Mass Spectra (He 80% Transmission) of $[Fe,C_6,H_6,O]^+$ Ions Derived from Different Precursor Systems (Intensities Relative to the Base Peak = 100%)[a]

		Δm (in amu) and neutral(s)[b]										
	$Fe(CO)_5/[C_6,H_6,O]$	16 O	17 $OH^\bullet$	18 H_2O	19 $(H_3O)^\bullet$	28 CO	29 $(CHO)^\bullet$	56 Fe	73 FeOH	77 $C_6H_5^\bullet$	78 C_6H_6	94 C_6H_6O
I	C_6H_5OH		3	100	45	15	25	10		8		55
II	C_6H_5COOH		35	100	30	7	8	3	2	25		45
III	C_6H_5Cl/H_2O		3	100	5	12	4	3		3		7
IV	$C_6H_5OC_2H_5$			8	2	100	15	2		1		20
V	c-C_5H_6					100	45	1				2
VI	C_6H_6/N_2O	8		45	5	100	35	3	2	5	5	30
VII	benzene oxide/oxepine		3	100	40	20	22	8		10		50
VIII	$C_6H_5C_2H_5/N_2O$		35	100	30	18	8	3	3	18	1	75

[a] For the sake of simplicity, intensities <1% are omitted. [b] The neutrals assigned to some entries may contain contributions from isobaric molecules; for example, $\Delta m = 56$ amu may also correspond to C_3H_4O, and species such as $(H_3O)^\bullet$ and $(CHO)^\bullet$ may be due to consecutive losses of $H^\bullet/H_2O$ and $H^\bullet/CO$, respectively.

collisional activation (CA) and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Furthermore, the relative stabilities as well as intramolecular interconversion processes of these isomers will be discussed.

Experimental Details

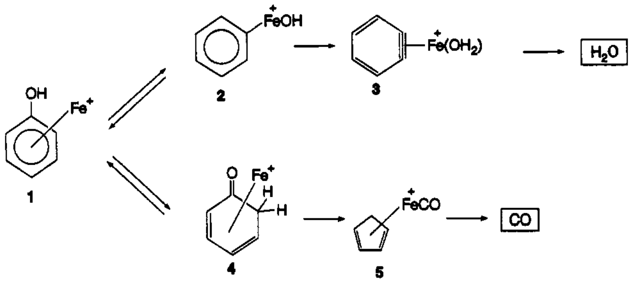
Most of the experiments were performed with a modified ZAB/HF/AMD 604 tandem mass spectrometer of *BEBE* configuration (*B* stands for a magnetic and *E* for an electric sector), which has been described previously.[13] In brief, $[Fe,C_6,H_6,O]^+$ ions were generated by electron bombardment (50–100 eV) of mixtures of $Fe(CO)_5$ and the appropriate organic precursors (vide infra) in a chemical ionization source (repeller voltage ca. 0 V). For the collisional activation experiments an 8-keV beam of ions of interest was mass-selected by means of $B1/E1$ at a resolution of $m/\Delta m \approx 2$–5000, collided with helium (80% transmission) in the field-free region preceding $B2$, and the ionic fragments were monitored by scanning $B2$; the fourth sector $E2$ was not used in the present study. All spectra were accumulated and on-line processed with the AMD Intectra data system; 5–40 spectra were averaged to improve the signal to noise ratio.

Additional experiments were performed with a Spectrospin CMS 47X FTICR mass spectrometer.[14] In brief, Fe^+ ions were formed via laser desorption/ionization of a stainless steel target in the external ion source, transferrred into the analyzer cell by a system of electric potentials and lenses, and trapped in the magnetic field of a superconducting magnet (max field strength 7.05 T). The $^{56}Fe^+$ isotope was isolated using the FERETS technique[15] and collisional cooled by pulsed-in argon gas (ca. 250 collisions). Reagent gases were introduced via either pulsed or leak values. The $[Fe,C_6,H_6,O]^+$ ions studied in the FTICR were generated from isolated $^{56}Fe^+$ by the two following methods: (i) reaction of Fe^+ with propane to afford a mixture of $(C_2H_4)Fe^+$ and $(C_3H_6)Fe^+$;[8a] these ions undergo ligand exchange reactions with phenol to yield the corresponding Fe^+ adduct;[16] and (ii) reaction of bare Fe^+ with phenetol (ethoxybenzene), in which $[Fe,C_6,H_6,O]^+$ is formed by loss of ethene from the encounter complex.[17] Due to their low vapor pressure, phenol and phenetol were introduced via a leak valve. All subsequent isolations and manipulations of the ions were performed using FERETS.

C_2D_4 (MSD Isotopes, >99.5 atom % D) and D_2O (Janssen Chimica, >99.8 atom % D) were degassed by freeze–thaw cycles and introduced into the FTICR cell via leak valves. For experiments with D_2O the instrument was pretreated with D_2O for several hours, in order to equilibrate the adsorbed water on the stainless steel surfaces.[18]

The tautomeric mixture of benzene oxide $\rightleftarrows$ oxepine[19] was prepared by double dehydrobromination of 4,5-dibromocyclohexeneepoxide using diazabicyclo[5.4.0]undec-7-ene and purified by bulb-to-bulb distillation.[20] All glassware and the heated septum inlet system of the mass spectrometer were pretreated with aqueous ammonia and subsequently dried at 120 °C in order to avoid the acid-catalyzed isomerization of benzene oxide $\rightleftarrows$ oxepine to the more stable phenol;[19b,21] according to 400-MHz ^{1}H-NMR, the freshly prepared benzene oxide $\rightleftarrows$ oxepine samples did not contain any phenol impurities. WARNING: Benzene oxide is suspected to be the carcinogenic principle of benzene;[22] thus, appropriate safety precautions are indicated.

Scheme 1



Results and Discussion

In the chemical ionization source, different $[Fe,C_6,H_6,O]^+$ ions[23] were generated using the precursor mixtures described in Table 1.

The CA mass spectrum (Table 1) of system I is in accordance with the generation of a genuine phenol complex **1**.[12a] Both ligand loss leading to bare Fe^+ (55%) and dehydration (100%) are observed as major fragmentation paths, whereas decarbonylation is less prominent (15%). This indicates that (i) the activation barrier for dehydration is of the same order of magnitude as is the ligand-binding energy in **1** (vide infra),[10] and (ii) the extent of isomerization of **1** to the corresponding keto form **4**, which serves as an intermediate en route to decarbonylation, is of minor importance. Water loss occurs as an almost exclusive 1,2-elimination process via **2** and **3** to yield (benzyne)Fe^+ (Scheme 1), as has been demonstrated previously.[10,12a]

The fragmentation pattern of the $[Fe,C_6,H_6,O]^+$ ion derived from system II by decarbonylation is not too different from that of **1**, with the exception that the amount of $OH^\bullet$ loss increases significantly. We interpret this is an indication for the formation

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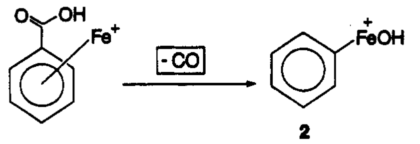
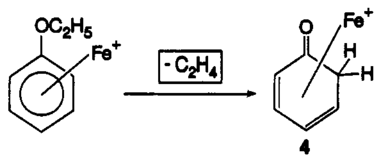
Scheme 2



Scheme 3



of the inserted structure **2** in the course of the reaction (Scheme 2). This assignment is also in keeping with the enlarged intensity of the $FeOH^+$ fragment (loss of $C_6H_5^\bullet$), in system II, as compared to the other spectra,[12,24] and the elimination of neutral FeOH. However, the overall similarity of the CA spectra of systems I and II with respect to the other fragmentation channels implies that the barrier separating **1** and **2** is not unsurmountably high.

Dehydrohalogenation of halobenzenes by bare metal cations is a convenient means to generate the corresponding benzyne complexes;[25] thus, upon chemical ionization of system III, the benzyne/water complex **3** may be formed. The CA spectrum is in line with this proposal: Water loss is the dominating fragmentation channel, whereas decarbonylation as well as complete ligand evaporation are less intense, as compared to other systems. Thus, we conclude that the collision-induced interconversion **3** → **2**, due to the existence of a barrier, is relatively inefficient as compared to the direct loss of the H_2O ligand from **3**. This conjecture is in line with the earlier observation[10,12a] that H/D exchange processes in the dehydration of specifically labeled ions **1** are almost negligible.

In contrast to systems I, II, and III, collision-induced decarbonylation dominates the CA mass spectra of the ions derived from systems IV and V, thus pointing to the generation of different $[Fe,C_6H_6,O]^+$ isomers. There are further differences in the CA spectra of systems IV and V which indicate the existence of two isomers: Whereas system IV undergoes water loss, in system V this process is not observed at all and the loss of "C_6H_6O" decreases significantly. These findings can be explained by the formation of the 2,4-cyclohexadienone complex **4** in the course of ethene loss from (phenetol)Fe^+ (system IV, Scheme 3) and the generation of a carbonyl complex **5** from system V, respectively. The absence of water loss from the ion formed from system V indicates not only that CO loss from **5** is facile but, furthermore, that the isomerization **4** → **5** has to be irreversible within the microsecond time scale of the experiment. In contrast, the occurrence of both water and CO losses for system IV requires an interconversion **4** → **1** prior to fragmentation. However, in view of the different intensities of H_2O and CO losses from systems I and IV, we conclude that the isomers **1** and **4** are certainly not fully equilibrated; rather, a partial interconversion seems to occur after the energizing collisions.[26] We note that, in contrast to the results reported in a previous study,[17] **1** is not generated directly by the Fe^+-mediated elimination of C_2H_4 of phenetol (system IV) but by a consecutive isomerization **4** → **1**, from which water is lost via **2** and **3**.

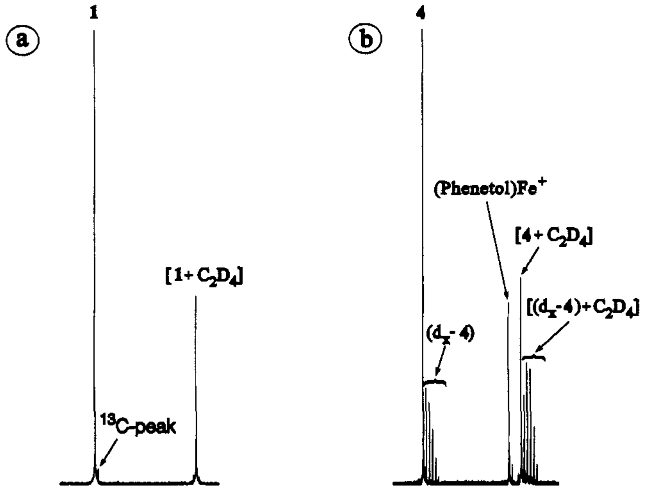


Figure 1. (a) Ion/molecule reactions of mass-selected $(C_6H_5OH)Fe^+$ (**1**) with C_2D_4 ($p \approx 9 \times 10^{-8}$ mbar) in the presence of C_6H_5OH ($p \approx 6 \times 10^{-9}$ mbar). Note the absence of any H/D exchange products. The presence of a ^{13}C peak is due to the thermoneutral ligand exchange of $(C_6H_5OH)Fe^+$ (**1**) with naturally ^{13}C-labeled phenol. (b) Ion/molecule reactions of mass-selected **4** with C_2D_4 ($p \approx 9 \times 10^{-8}$ mbar) and background phenetol ($p \approx 5 \times 10^{-9}$ mbar). At longer reaction times (not shown in this figure), all six hydrogen atoms of C_6H_6O are exchanged by deuterium.

Before we will address some qualitative aspects of the potential energy surface of cyclic $[Fe,C_6,H_6,O]^+$ isomers and discuss the intermediates involved in the reactions of bare FeO^+ with arenes, we will briefly describe the ion/molecule reactions of **1** and **4** with C_2D_4 and D_2O, respectively, under the conditions of FTICR mass spectrometry. In 1985, Jacobson and Freiser demonstrated that ion/molecule reactions with deuterated olefins can be used to determine the number of exchangeable hydrogen atoms in ionic transition metal complexes in the gas phase.[27] If **1** is reacted with C_2D_4, the formation of the corresponding adduct complex [**1** + C_2D_4] is observed exclusively (Figure 1a); however, in the reaction with D_2O a single hydrogen atom can be exchanged by deuterium, as expected for the hydroxy moiety in **1**. In contrast, for the isomer **4** the formation of the adduct [**4** + C_2D_4] is accompanied by the exchange of up to all six hydrogen atoms by deuterium (Figure 1b). The mechanism for the H/D exchange in complex **4** is probably similar to that described previously for the reactions of $(c\text{-}C_5H_6)Fe^+$ with deuterated reagents and in which also six H/D exchanges were observed.[27,28] These results are completely in line with the structural assignments based on the CA mass spectra of systems I and IV. In particular, they support our suggestion that the isomerization **1** ⇄ **4** is a high-energy, postcollisional process. Furthermore, from the absence of H/D exchange in the reaction of **1** with C_2D_4 we conclude that the energy gained upon complex formation of **1** with ethene (ca. 34 kcal/mol)[29] is not sufficient to overcome the activation barrier associated with the intramolecular interconversion process **1** ⇄

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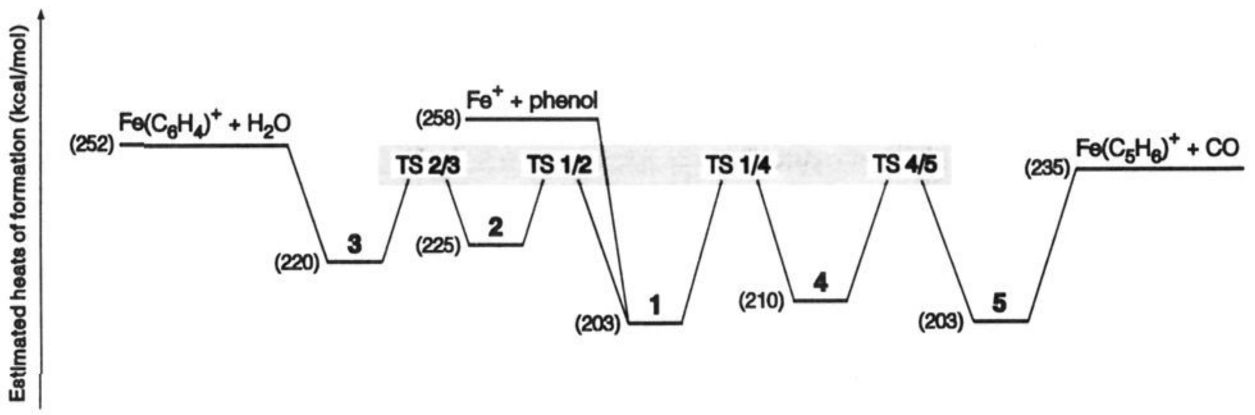
(29) $\Delta H_f(\mathbf{1}) = \Delta H_f(Fe^+) + \Delta H_f(\text{phenol}) - \text{BDE(phenol-Fe}^+)$,[30] $\Delta H_f(\mathbf{2}) = \Delta H_f(Fe^+) + \Delta H_f(\text{phenyl})\ \Delta H_f(OH) - \text{BDE(phenyl-Fe}^+)^{25e} - \text{BDE(HO-Fe}^+)$; $\Delta H_f(\mathbf{3}) = \Delta H_f(Fe^+) + \Delta H_f(\text{benzyne})^{33} + \Delta H_f(H_2O) - \text{BDE(benzyne-Fe}^+)^{25e} - \text{BDE}(H_2O\text{-}Fe^+)$,[34] $\Delta H_f(\mathbf{4}) = \Delta H_f(Fe^+) + \Delta H_f(\text{2,4-cyclohexadienone})^{3b} - \text{BDE(2,4-cyclohexadienone-Fe}^+)$,[35] and $\Delta H_f(\mathbf{5}) = \Delta H_f(Fe^+) + \Delta H_f(c\text{-}C_5H_6) + \Delta H_f(CO) - \text{BDE}(c\text{-}C_5H_6\text{-}Fe^+)^{28} - \text{BDE}(Fe^+\text{-CO})$.[36] If not noted otherwise, all thermochemical data were taken from the following: (a) Freiser, B. S. *Chemtracts: Anal. Phys. Chem.* **1989**, *65*, 1. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

Scheme 4

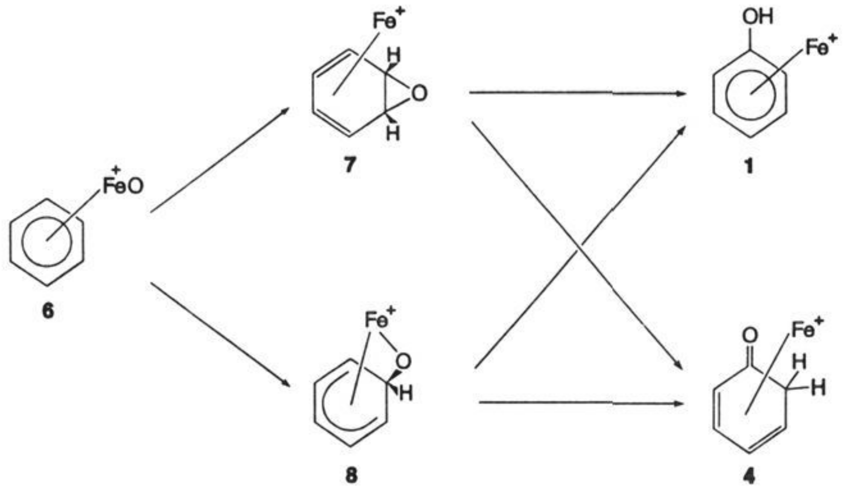


4. Thus, complexation of a bare Fe^+ cation to the phenol/2,4-cyclohexadienone system seems to facilitate the keto–enol tautomerization to a small extent only. However, when **4** is reacted with D_2O, one, and only one, H/D exchange reaction occurs; this clearly points to the irreversible conversion of **4** to **1**. Since ethene and water have similar binding energies to bare Fe^+,[29] the excess energies gained in the formation of the encounter complexes are similar; consequently, the water-induced rearrangement **4** → **1** implies that this isomerization does *not* involve a direct 1,3-hydrogen transfer; *rather, the water molecule is actively involved in the bimolecular isomerization process.* This situation resembles the ease of *intermolecular* keto–enol tautomerism in the condensed phase, and it demonstrates that a *single* water molecule is capabe of bridging the gas-phase and condensed-phase behavior of the phenol/cyclohexadienone system.

An attempt to combine the experimental findings to a schematic potential energy surface for cyclic $[Fe,C_6,H_6,O]^+$ isomers is presented in Scheme 4. Heats of formation of the individual species were estimated by using a simple additivity approach based on known ΔH_f values and bond dissociation energies (BDEs); more reliable thermochemical data are not available yet.[29] Although this approach neglects synergistic interactions of the ligands with the metal center, such an additivity scheme is expected to yield reasonable estimates for the comparison of the relative energies of the $[Fe,C_6,H_6,O]^+$ isomers within an error not exceeding ±8 kcal/mol.[12c]

Perhaps surprisingly, the $(C_5H_6)Fe(CO)^+$ complex **5** is as stable as the iron/phenol complex **1**. This finding reflects the favorable bonding situation in Fe^+/cyclopentadiene complexes,[28,37] which is further strengthened by the stabilizing effect of the additional CO ligand.[36] Interestingly, the energy difference between **1** and the keto isomer **4** does not seem to be perturbed by the presence of an iron cation when compared with the uncomplexed isomers:[3b] For both the neutral and the Fe^+-complexed systems the energy difference amounts to 7 kcal/mol in favor of the phenolic tautomer. The inserted complex **2** and the benzyne/water complex **3** are somewhat higher in energy, but well below the dissociation channels; this is in keeping with the collisional activation spectra of these isomers. With respect to the activation barriers we only can draw some very qualitative conclusions: The observation of dehydration and decarbonylation in the ion/molecule reaction of phenol with bare Fe^+ implies that the corresponding activaton barriers TS **1/2**, TS **2/3**, and TS **1/4** must be somewhat smaller than the energy of separated Fe^+ and phenol; however, since ligand loss from **1** competes with both dehydration and decarbonylation, the barriers toward isomerization must be in the range of the binding energy.[10] Similarly, while TS **2/3** is located below the exit channel for H_2O loss, it must be high enough to prevent the facile interconversion **1** ⇄ **2**. The occurrence of water loss from all isomers but **5** indicates that TS **4/5** is located between the exit channel for CO loss and TS **1/4**. A similar situation was found for the radical cations of phenol and 2,4-cyclohexadienone, in which decarbonylation is associated with a substantial kinetic energy release,[38] thus pointing to a reverse activation barrier.

Scheme 5



In the gas-phase oxidation of benzene by bare FeO^+, in which phenol is involved as a neutral product, several intermediates must be involved en route to products (Scheme 5). In a previous neutralization–reionization (NR) mass spectrometric study we proposed that chemical ionization of system VI leads to a mixture of three isomers, i.e. Fe^+ $(C_6H_5OH)^+$ (**1**), $FeO(C_6H_6)^+$ (**6**), and a third hitherto unidentified component.[12a] Collisional activation of $[Fe,C_6,H_6,O]^+$ ions produced from system VI supports this assignment: In addition to the abundant loss of H_2O and C_6H_6O, being characteristic for **1**,[39] the unusual elimination of an oxygen atom as well as of C_6H_6 strongly suggests the presence of structure **6**. With respect to the intense decarbonylation in system VI, we assign the previously unidentified third component to the

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(30) Upon collisional activation of the mixed bisligated complex $[(C_6H_6)Fe(C_6H_5OH)]^+$, generated from $Fe(CO)_5$, benzene, and phenol, both benzene and phenol losses occur in comparable intensities (10:8); thus, according to Cooks's kinetic method (ref 31), BDE(phenol-Fe^+) is similar to BDE(benzene-Fe^+); the latter amounts to 55 kcal/mol (ref 32).

(31) McLuckey, S. A.; Shoen, A. E.; Cooks, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 848. (b) Chen, L. Z.; Miller, J. M. *Org. Mass Spectrom.* **1992**, *27*, 883. (c) For a general discussion, see: Brodbelt-Lustig, J. S.; Cooks, R. G. *Talanta* **1989**, *36*, 225.

(32) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

(33) (a) Riveros, J. M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1991**, *113*, 1053. (b) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414.

(34) For recent values and leading references, see: (a) Fiedler, A.; Hrušák, J.; Schwarz, H. *Z. Phys. Chem.* **1992**, *175*, 15. (b) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1993**, *97*, 596.

(35) Upon collisional activation of the mixed bisligated complex $[(C_6H_6)Fe(C_6H_6O)]^+$, generated from $Fe(CO)_5$, phenetol, and benzene, C_6H_6O and benzene losses occur in comparable intensities (10:7); thus the BDE(2,4-cyclohexadiene-Fe^+) was estimated to be ca. 55 kcal/mol (ref 30). We note, however, that we cannot rigorously exclude a benzene-induced isomerization **4** → **1**, although—on the basis of the exchange experiments of **4** with C_2D_4 and D_2O—this is not likely to occur.

(36) The BDE(Fe^+-CO) is a matter of controversy; a recent value which is consistent with all previous findings amounts to 32 kcal/mol (Dalleska, N. F.; Armentrout, P. B. Private communication). For a discussion, see: Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

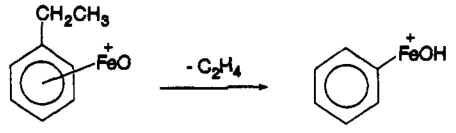
(37) (a) Dearden, D. V.; Beauchamp, J. L.; van Koeppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 1682. (b) Also see: McKee, M. L. *J. Phys. Chem.* **1992**, *96*, 1683. (c) Reference 8a.

(38) (a) Borchers, F.; Levsen, K.; Theissling, C. B.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1977**, *12*, 746. (b) Russell, D. H.; Gross, M. L.; van der Greef, J.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1979**, *14*, 474.

formation of **4** in the course of the oxidation process. Furthermore, as OH• loss is practically negligible, the inserted complex **2** is not generated under these conditions. This is in line with the absence of a rate-determining CH insertion in the overall reaction of FeO^+ with benzene.[12a] On the basis of these findings and results of *ab initio* calculations on neutral and cationic iron oxide,[40] we refine our previous conclusions[12a] such that the reionized parent ion in the NR mass spectrum of system VI may point to the formation of neutral **6**, rather than the analogue of neutral **2**. Since both the neutral and the cationic FeO exhibit significant charge transfer from the metal to the oxygen atom,[40] the benzene ligand in neutral **6** may still be bound by its interaction with the Fe^+O^- dipole of neutral iron oxide, thus giving rise to a recovery signal under the NR conditions.

Among the several mechanistic scenarios existing in the literature for the oxygenating of arenes by iron-centered enzymes in the condensed phase, the *arene oxide path*, involving **7**, deserved considerable attention,[41] although it has recently been questioned[42] to act as a dominant metabolic path for the hydroxylation of several arenes. With respect to the previously studied[12a] gas-phase reaction of FeO^+ and benzene, further insight into the hydroxylation process may be obtained from a collisional activation experiment of the corresponding benzene oxide ⇄ oxepine complex as derived from system VIII. We note, however, that the situation is complicated by the facile valence tautomerism of the precursor molecule, which will certainly be influenced by the coordination of an iron cation.[43,44] The CA spectrum of the $[Fe,C_6H_6,O]^+$ isomer derived from system VII is almost superimposable with that of system I. The latter gives rise to the formation of the Fe^+/phenol complex, **1**.[45] The marginal intensity difference with respect to decarbonylation of both ions must not necessarily be attributed to the existence of another isomer than **1** in the case of system VII but can also be rationalized in terms of a higher internal energy content in **1**, when derived from benzene oxide ⇄ oxepin.[46] Most likely, the Fe^+ cation induces a rapid isomerization of benzene oxide ⇄ oxepin system to the more stable phenol complex **1**. Indeed, **7** might not even correspond to a minimum on the potential energy surface, as has been demonstrated for oxygen-protonated benzene oxide.[21] Interestingly, the keto isomer **4** does not seem to be formed directly from system VII. Consequently, the isomerization process **7** → **1** (Scheme 5) may involved a direct 1,2-hydrogen transfer from a bridgehead carbon to the oxygen atom of benzene oxide, rather than a 1,2-hydrogen transfer between both bridgehead carbon atoms (**7** → **4**). If one considers the differences in the CA spectra from systems VI and VII, the arene oxide path cannot account exclusively for the oxygenation of benzene by bare FeO^+ and thus—at least in the gas phase—an additional mechanism must exist, which might involve the initial formation of the σ complex **8** in the course of the reaction.

Scheme 6



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Finally, we shortly address the oxidation of alkylbenzenes by bare FeO^+ in which $[Fe,C_6H_6,O]^+$ isomers also play a role; for example, if ethylbenzene is reacted with thermalized FeO^+ under FTICR conditions besides other ion/molecule reactions, loss of C_2H_4 occurs (Scheme 6).[12d,47] The CA mass spectrum of the corresponding $[Fe,C_6H_6,O]^+$ isomer stemming from system VIII is similar to that of the ion derived from system II, and thus we conclude that the inserted complex **2** serves as the major intermediate in the degradation of the alkyl chain of alkylbenzenes by bare FeO^+ *en route* to the formation of the products.

Conclusions

Collisional activation of cationic organic iron complexes can be used to differentiate six stable $[Fe,C_6H_6,O]^+$ isomers being generated by chemical ionization mass spectrometry, i.e. (phenol)-Fe^+ (**1**), $(C_6H_5)Fe^+(OH)$ (**2**), $(C_6H_4)Fe^+(OH_2)$ (**3**), (2,4-cyclohexadienone)Fe^+ (**4**), (c-C_5H_6)$Fe^+(CO)$ (**5**), and (C_6H_6)-FeO^+ (**6**). By a combination of thermochemical estimates with the experimental results of CA studies and H/D exchange reactions in a FTICR experiment, a qualitative potential energy diagram is developed, in which **1** and **5** correspond to the energetically most stable structures. The knowledge of the stabilities, fragmentation, and interconversion process permits the identification of intermediates in the gas-phase oxidation of arenes by bare FeO^+, and furthermore, the results indicate the existence of an alternative mechanism to the arene oxide path in the oxygenation of arenes by iron oxenoids in the gas phase. Although the analysis of collisional activation mass spectra of transition metal complexes is subject to various limitations,[48] the present study shows that CA is a well-suited and sensitive mass spectrometric tool for the characterization of structural isomers of organometallics.

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[39] In addition, the presence of **1** in the mixture is confirmed by the characteristically low abundance of hydrogen losses from the $C_6H_6O^{\bullet+}$ ion in the NRMS spectrum; see ref 4c, 12a, and the following: Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day: San Francisco, 1967.

[40] (a) Krauss, M.; Stevens, W. J. *J. Chem. Phys.* **1985**, *82*, 5584. (b) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Komornicki, A. *Theor. Chim. Acta.* **1990**, *77*, 263. (c) Fiedler, A.; Hrušák, J.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1993**, *211*, 242.

[41] Jerina, D. M.; Daly, J. W. *Science* **1974**, *185*, 573. For further references also see refs 11, 12a, and 22.

[42] Guengerich, F. P.; MacDonald T. L. *FASEB J.* **1990**, *4*, 2453 and references therein.

[43] The benzene oxide ⇄ oxepin valence tautomerism is also strongly solvent dependent (ref 19).

[44] Upon photolysis of $Fe(CO)_5$ in etheral benzene oxide ⇄ oxepin solution, 3% of (oxepin)$Fe(CO)_3$, but no corresponding benzene oxide complex, has been isolated in addition to large amounts of benzene and phenol: Aumann, R.; Averbeck, H.; Krüger, C. *Chem. Ber.* **1975**, *108*, 3336.

[45] From independent experiments we have evidence that the isomerization of the benzene oxide ⇄ oxepine system to phenol does not occur in the inlet system of the mass spectrometer.

[46] (a) Procter, C. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, *18*, 193. (b) Reference 26.

[47] Besides $Fe(C_6H_6O)^+ + C_2H_4$ (10%) the following reaction products were observed (ref 12d): $Fe^+ + C_8H_{10}O$ (45%), $Fe(C_8H_8)^+ + H_2O$ (40%), $C_8H_{10}^{\bullet+} + Fe$ (5%).

[48] Schröder, D.; Sülzle, D.; Hrušák, J.; Böhme, D. K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *110*, 145.