Organometallics **1993,** *12,* 1079–1085

Functional Group Interactions in the Fe^+-Mediated Degradation of Phenols and Their Methyl Ethers[†]

Detlef Schröder, Waltraud Zummack, and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin,
Strasse des 17. Juni 135, W-1000 Berlin 12, Germany

Received November 10, 1992

The unimolecular reactions of organometallic complexes generated from oxygenated arenes and bare iron cations were studied in the gas phase by means of tandem-mass spectrometry and extensive deuterium-labeling experiments. The transition-metal ion Fe^+ mediates dehydration and decarbonylation of phenol; the latter process requires a metal-induced interconversion of phenol in its corresponding keto form. Replacement of the OH group of phenol by a methoxy functionality results in the loss of formaldehyde and dihydrogen from the corresponding Fe^+ complexes. For the Fe^+ complexes of dihydroxylated arenes and their *O*-methyl derivatives we observe regiospecific fragmentation pathways. For example, the ortho-compounds lead to the almost exclusive formation of the iron catecholate cation, whereas the reactions of the meta-complexes resemble the chemistry of the parent compounds phenol and anisole; interaction of both functionalities is of minor importance in the meta-isomers. The Fe^+ complexes of the para-disubstituted arenes react similarly to the meta-compounds; however, in addition metal-induced rearrangements as well as charge transfer allow a clear-cut distinction of both sets of isomers. The combination of the reactivity trends in conjunction with isotopic labeling studies point to a rate-determining C–O insertion in the Fe^+-mediated degradation of methoxyarenes.

Introduction

Dihydroxybenzenes and their derivatives play an important role in biochemistry as well as serve as ligands in organometallic chemistry. For example, in many biological processes dioxygenated arenes serve as active species for single- and multiple-electron transfer. In addition, the ortho-isomers are of relevance for the transportation and storage of iron in living systems.[1]

In 1989, Bjarnason et al. reported a straightforward method for the previously difficult mass-spectrometric distinction between isomeric disubstituted benzenes by means of ion/molecule reactions of bare iron cations.[2] The pronounced spectroscopic differences were accounted for in terms of ortho-effects[3] in the course of which specific reactions of the metal ion with the two substituents take place. As demonstrated repeatedly, gas-phase studies of bare metal cations provide insights into general aspects of transiton-metal-mediated CH- and CC-bond activation.[4] Furthermore, in the gas phase, intrinsic properties of metal complexes can be examined in the absence of complicating effects which result from the presence of ligands, counterions, aggregation phenomena, or solvation spheres. Albeit the reactions of bare metal ions with arenes have received considerable attention in the past, no detailed studies have been undertaken on this class of compounds as far as the elucidation of reaction mechanisms and the determination of product ion structures are concerned.[5]

Here we present an account of the study of unimolecular reactions of mass-selected Fe^+ complexes of disubstituted benzenes which were probed by means of isotopic labeling and advanced mass spectrometric experiments.

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector), which has been described in detail previously.[6] Briefly, $Fe(CO)_5$ was admitted to the ion source via the heated septum inlet system; the corresponding benzene derivatives were introduced either together with $Fe(CO)_5$ or via the cooled solid probe inlet system. The mixture was subsequently ionized by a beam of electrons (50–100 eV) in a chemical ionization source (repeller voltage ca. 0 V). The ions of interest were accelerated to 8 kV and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m = 3000$. Unimolecular fragmentations occurring in the field-free region

---

[†] Dedicated to Prof. Herbert Budzikiewicz on the occasion of his 60th birthday.

(1) Kaim, W.; Schwederski, B. *Bioanorganische Chemie*; Teubner: Stuttgart, 1991; pp 153.

(2) Bjarnason, A.; Taylor, J. W.; Kinsinger, J. A.; Cody, R. B.; Weil, D. A. *Anal. Chem.* **1989**, *61*, 1889.

(3) (a) For a recent examination of ortho-effects in the fragmentation of closed-shell aromatic ions, see: Donovan, T.; Brodbelt, J. *Org. Mass Spectrom.* **1992**, *27*, 9. (b) Review on ortho-effects: Schwarz, H. *Top. Curr. Chem.* **1978**, *73*, 231. (c) For recent studies on the electron-impact ionization of substituted resorcinols and dimethoxyarenes, see: Weisz, A.; Andrzejewski, D.; Mandelbaum, A. *Org. Mass Spectrom.* **1992**, *27*, 891. Nakata, H.; Jitsukawa, F.; Toyama, H.; Kato, Y.; *Org. Mass Spectrom.* **1992**, *27*, 720.

(4) (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Ephritikhine M. *Nouv. J. Chem.* **1986**, *10*, 9. (d) Dahlenburg, L. *Nachr. Chem., Techn. Lab.* **1988**, *36*, 899. (e) Hill, C. L. (Ed.) *Activation and Functionalization of Alkanes*; Wiley: New York, 1989. (f) Davies, J. A.; Watson, L.; Greenberg, A.; Liebman, J. F. (Eds.) *Selective Hydrogen Activation*; VCH: Weinheim, 1990. (g) For a recent, comprehensive review of gas-phase transition-metal chemistry, see Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(5) (a) Dietz, T. G.; Chatelier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 4905. (b) Jacobson, D. B.; Bryd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553. (c) Stepnowski, R.; Allison, J. *J. Am. Chem. Soc.* **1989**, *111*, 449. (d) Bjarnason, A.; Taylor, J. W. *Organometallics* **1989**, *8*, 2020; **1990**, *9*, 1493. (e) Huang, Y.; Freiser, B. S. *Inorg. Chem.* **1990**, *29*, 2053. (f) Chen, L.-Z.; Miller, J. M. *Org. Mass Spectrom.* **1992**, *27*, 19. (g) See also: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1159. (h) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 2387; **1990**, *112*, 1682.

(6) (a) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 368. (b) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970.

0276-7333/93/2312-1079$04.00/0

preceding the second magnet were recorded by scanning B(2); the mass spectra obtained by using this scan mode will be referred to as metastable ion (MI) spectra. For collisional activation (CA) experiments the fast moving ions were collided with helium (80% transmission, this corresponds to an average of 1.1–1.2 collisions[7]). For MS/MS/MS experiments, the precursor ions of interest were mass-selected by means of B(1)/E(1) and the fragment ions originating from unimolecular dissociation within the field-free region preceding the second magnet B(2) were selected using this analyzer; collisional activation of the daughter ions was performed in the field-free region between B(2) and E(2), and the resulting product ions of these MI/CA experiments were recorded by means of E(2). In order to enhance the fragment ion resolution, some MS^n experiments were performed using B(1) only for the mass selection of the parent ion, selecting the fragment ion with E(1), subjecting it to collisional activation in the field-free region preceding B(2), and recording the products by scanning B(2). If the mass differences between fragment ions are too small (e.g. parent ion and H_2 loss from **2**/Fe$^+$, or combined HDO and D_2O losses from **3a**/Fe$^+$), mass-selection of the fragment ions was achieved under high resolution using both E(1) and B(2), followed by collisional activation in the field-free region preceding E(2).[8] All spectra were accumulated and on-line processed with the AMD-Intectra data system; 5–20 scans were averaged to improve the signal-to-noise ratio. Kinetic isotope effects were derived from the average of at least three independent measurements; if not stated otherwise, the experimental error of these figures amounts to +/−5%.

All chemicals were synthesized by standard laboratory procedures, purified by preparative gas chromatography, and characterized by spectroscopic means.[9] The [OD]-labeled phenols were prepared by repetitive evaporation of their solutions in [OD]methanol (Janssen Chimica, 99.5 atom % D). Due to an inevitable intermolecular self-exchange of ring and hydroxyl protons,[9] the [OD]-labeled phenols cannot be stored for long periods and were measured immediately after their preparation. However, even with these precautions, the [$(OD)_2$]-labeled resorcin **4a**, which has a labile aromatic hydrogen atom at C(2), contained significant amounts of **4** labeled at C(2) and one hydroxy group. The data of **4a**/Fe$^+$ were corrected for this imperfect labeling.

Results and Discussion

In this section, we will first present and discuss the unimolecular fragmentations of the Fe$^+$ complexes of phenol and anisole. This will then be followed by a section describing the other hydroxy- and methoxybenzenes (Chart I). Finally, we will discuss some trends in reactivity and will address the mechanism of Fe$^+$-mediated formaldehyde loss from methoxyarenes.

Chart I

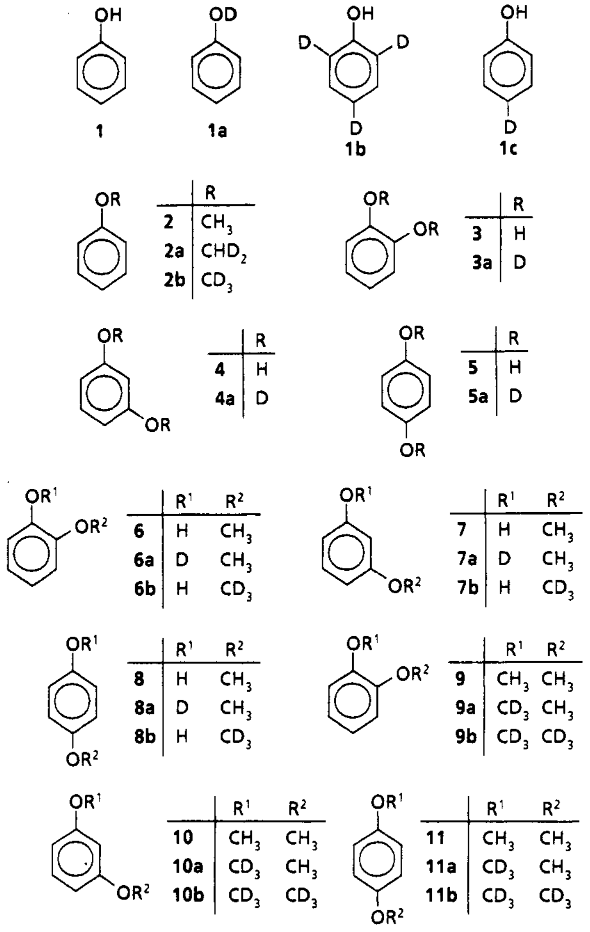


Table I. Metastable Ion Spectra of Fe$^+$ Complexes of Phenol and Anisole[a]

	1/Fe$^+$	1a/Fe$^+$	1b/Fe$^+$	1c/Fe$^+$	2/Fe$^+$	2a/Fe$^+$	2b/Fe$^+$
H_2					30	27	
HD						25	15
$CH_3\cdot$					2		
$CHD_2\cdot$						3	
$CD_3\cdot$							2
H_2O	100		3	100	1	1	
HDO		100	100		1	1	1
D_2O			4				
CO	15	15	65	20			
CH_2O					100		
CHDO						100	
CD_2O						77	100
FeOH					<1	<1	
FeOD						<1	<1
Ligand loss	25	25	95	25	1	1	1

[a] Data are given in percent relative to the base peak.

Monosubstituted Benzene Complexes. The unimolecular reactions of the metastable ion complexes (Table I) agree well with the previously reported[2,5c,d] reactivity of bare Fe$^+$ with phenol and anisole under ion cyclotron resonance (ICR) conditions.[10] The loss of the entire ligand from **1**/Fe$^+$ implies that the energy demand for the dehydration and the decarbonylation of phenol is of the same order of magnitude as is the binding energy of phenol to Fe$^+$.[11] Coordination of the iron cation in the vicinity of the oxygen functionality is evidenced by the relatively intense FeOH$^+$ fragment (10% of the base peak Fe$^+$) upon collisional activation of **1**/Fe$^+$; this interpretation is further supported by the significant loss of a methyl radical in the CA spectrum of **2**/Fe$^+$, leading to an iron phenolate cation (Figure 1b, which will be discussed further below).

As far as the unimolecular reactions of **1**/Fe$^+$ are concerned, the investigation of the labeled complexes **1a**/Fe$^+$, **1b**/Fe$^+$, and **1c**/Fe$^+$ reveals the following: (i) Dehydration can be described as a 1,2-elimination process

---

[7] Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

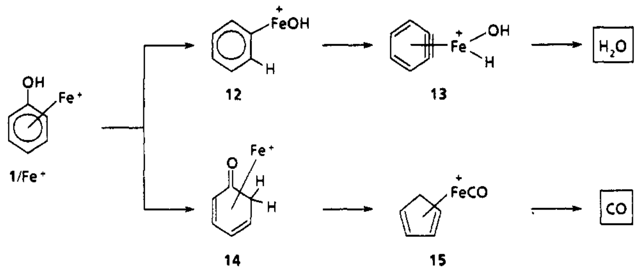
[8] In the case of small mass differences of the fragment ions, mass-selection using a single analyzer only was not sufficient for an unambiguous resolution of reasonable fluxes of these ions.

[9] For general aspects of the synthesis of deuterium-labeled phenols and H/D exchange in these substances, see: Thomas, A. F. *Deuterium Labeling in Organic Chemistry*; Appleton-Century-Crofts: New York, 1971; pp 204.

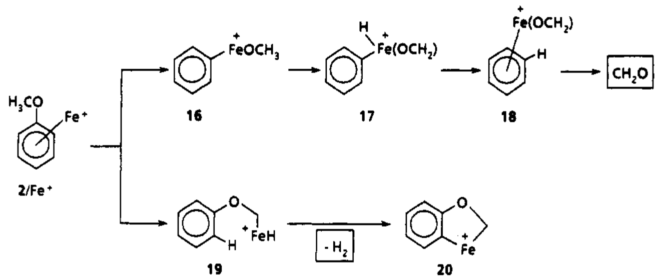
[10] For a comparison of ion/molecule reactions and unimolecular dissociations of metal-ion complexes, see: (a) Eller, K.; Zummack, W.; Schwarz, H.; Roth, L. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 833. (b) Schröder, D.; Eller, K.; Prüsse, T.; Schwarz, H. *Organometallics* **1991**, *10*, 2052.

[11] The binding energy of **1**/Fe$^+$ is not known; however, it will be at least as large as that of benzene/Fe$^+$ (55 kcal/mol): Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

Scheme I



Scheme II



resulting in the formation of benzyne/Fe$^+$; this is evidenced by the almost exclusive HDO elimination from **1a**/Fe$^+$ and **1b**/Fe$^+$ as well as the absence of HDO loss from **1c**/Fe$^+$. (ii) Activation of the aromatic CH bond preceding dehydration is associated with a substantial kinetic isotope effect; this is demonstrated by the increase of CO as well as ligand loss from **1b**/Fe$^+$ as compared to the other isotopomers. Assuming that ligand loss is almost independent of deuterium labeling, from the data of 1/Fe$^+$ and **1b**/Fe$^+$, an intermolecular kinetic isotope effect of k_H/k_D = ca. 4 can be derived for the CH-bond activation in the ortho-position.[12] (iii) A comparison with the ligand loss reveals that decarbonylation, leading to cyclopentadiene/Fe$^+$, is not affected by deuterium labeling of **1a**/Fe$^+$ and **1b**/Fe$^+$. These findings taken together suggest that, while in dehydration the β-H transfer (Scheme I: **12** → **13**) is rate determining, the Fe$^+$-mediated enol–keto tautomerism[13] (**1**/Fe$^+$ → **14**) preceding the CO loss is rapid on the μs time scale of the experiment. In contrast, the reversal of this tautomerism (**14** → **1**/Fe$^+$) must be very slow, since no H/D exchange of the hydroxyl group with the ring hydrogen atoms in **1a**/Fe$^+$ is observed. Most probably, decarbonylation (**14** → **15**) serves as a bottleneck for this reaction pathway.[14]

O-Methylation of the phenol group suppresses both the Fe$^+$-induced 1,2-elimination process and the decarbonylation; rather, in the MI spectrum of **2**/Fe$^+$ the generation of molecular hydrogen and of formaldehyde prevails, thus pointing to a lower energy demand of the latter reactions. This conclusion is supported also by the almost negligible ligand loss from **2**/Fe$^+$ as compared to **1**/Fe$^+$. The CD_2O loss from **2b**/Fe$^+$ verifies the assumption made previously[2] that formation of formaldehyde occurs exclusively from the methoxy group (see Scheme II). Furthermore, from the finding that the MI/CA spectrum (Table II) of the corresponding product ion [**2**/Fe$^+$ – CH_2O] is identical with the CA spectrum of authentic[15] benzene/Fe$^+$, we conclude that the rearrangement (reductive elimination) of the intermediate phenyliron hydride cation (**17** → **18**) to yield eventually benzene/Fe$^+$ is rapid. As far as the loss of molecular hydrogen from **2**/Fe$^+$ is concerned, the exclusive formation of HD from **2b**/Fe$^+$ rules out conceivable reaction paths via intermediate carbene complexes. Such carbenoids have been reported in the gas-phase unimolecular dissociation of α,ω-dimethoxyalkane/Fe$^+$ complexes[16] as well as in the P-450-mediated degradation of catechol derivatives.[17] The activation of a ring proton, most probably from the ortho-position, implies the formation of the metallacycle **20** (Scheme II). However, due to the lack of other $[FeC_7H_6O]^+$ isomers, no structural assignment for mass-selected [**2**/Fe$^+$ – H_2] was possible on the basis of a comparative MI/CA experiment (Table II). Indeed, decarbonylation predominates the MI/CA spectrum of this ion, which may point to the (perhaps collisional induced) formation of a more stable benzaldehyde/Fe$^+$ complex.[18] In addition to the unimolecular H_2 and CH_2O losses from **2**/Fe$^+$, we observe the elimination of methyl, water, and FeOH as very minor unimolecular fragmentation pathways. These reactions will not be discussed in the present context. We note, however, that dehydration as well as FeOH loss implies the occurrence of substantial rearrangement processes within the cationic complex.[14b]

Dihydroxybenzene Complexes. As in the case of the parent compound **1**/Fe$^+$, water loss constitutes also a major reaction for the Fe$^+$ complexes of the dihydroxybenzenes **3**–**5** (Table III). As evidenced by the data of the [OD]-labeled isotopomers **3a**/Fe$^+$, **4a**/Fe$^+$, and **5a**/Fe$^+$, water is not formed in a straightforward specific manner. More likely, partial H/D exchange processes precede fragmentation; however, the deuterium distribution in the resulting products is far from being statistical. For example, the isotope distribution for water loss from a statistically averaged $[H_4D_2]$ system would result in H_2O:HDO:D_2O = 6:8:1. This ratio is not observed experimentally. Rather, the low intensities of H_2O losses from the $[OD]_2$-labeled ions imply that the intact hydroxy group is activated without exchanging its hydrogen atom. We also note that the MI/CA spectra of the product ions (Table II) formed by dehydration of **3**/Fe$^+$, **4**/Fe$^+$, and **5**/Fe$^+$ are similar to each other, irrespective of the substitution pattern of the precursor.[18] This observation points to the formation of a single isomer from the three dihydroxybenzene complexes. The MI/CA spectra of the resulting $[M - H_2O]^+$ ions **21** (Scheme III) are dominated by intense decarbonylations and consecutive acetylene losses while dehy-

---

[12] For a general discussion of intra- and intermolecular kinetic isotope effects in mass spectrometry, see: (a) Collins, C. J.; Bowman, N. S. (Eds.) *Isotope Effects in Chemical Reactions*; ACS Monograph; Van Nostrand: New York, 1970. (b) Derrick, P. J.; Donchi, K. F. In *Comprehensive Chemical Kinetics* Bamford, C. H., Tipper, C. F. H. Eds.; Elsevier: Amsterdam, 1983; Vol. 24.

[13] For keto–enol tautomerism in organometallic systems, see: Zagorevskii, D. V.; Volkova, T. V.; Yakushin, S. O.; Antipov, B. G.; Nekrasov, Y. S. *Org. Mass Spectrom.* **1991**, *26*, 748.

[14] (a) Schröder, D.; Schwarz, H. *Helv. Chim. Acta* **1992**, *75*, 1281. (b) Schröder, D.; Florencio, H.; Zummack, W.; Schwarz, H. *Helv. Chim. Acta* **1992**, *75*, 1792.

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

[16] Prüsse, T.; Fiedler, A.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 8335.

[17] Mansuy, D.; Battioni, J.-P.; Chottard, J.-C.; Ullrich, V. *J. Am. Chem. Soc.* **1979**, *101*, 3971.

[18] Although heats of formation of neither **20** nor benzaldehyde/Fe$^+$ are known in the literature, a simple thermochemical estimate, based on C–H and Fe$^+$–C bond strengths (ref 19), implies that benzaldehyde/Fe$^+$ is ca. 20 kcal/mol more stable than **20**. Note, however, that formation of tropolone/Fe$^+$ would also explain the collision-induced decarbonylation of the $[FeC_7H_6O]^+$ ions.

[19] Thermochemical data were taken from Lias et al.: 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.

Table II. Partial MI/CA Spectra of Mass-Selected Fragment Ions Generated from Different Precursors[a]

Δm	[**2**/$Fe^+ - CH_2O$]	[**2**/$Fe^+ - H_2$]	[**3**/$Fe^+ - H_2O$]	[**6**/$Fe^+ - CH_4$]	[**8**/$Fe^+ - CH_2O$]	[**8**/$Fe^+ - H_2O$]	[**9**/$Fe^+ - CH_3^\bullet$]	[**10**/$Fe^+ - CH_2O$]
2								40
15							100	30
18		5	5		100			
27	20							
28		100	100	100	20	100	10	
29		30	5	10	15			
30								100
43							10	5
52	5							
53	25							
54			10					
55		50						
56				70	5	10		
71							10	
82				20				
ligand loss	100	5	10	25	70	15	5	5

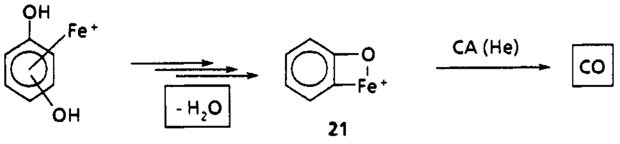
[a] See footnote *a* of Table I.

Table III. Metastable Ion Spectra of Dihydroxybenzene Complexes[a]

	3/Fe^+	**3a**/Fe^+	**4**/Fe^+	**4a**/Fe^+ [b]	**5**/Fe^+	**5a**/Fe^+
H_2	100					
HD		3				
D_2		100				
H_2O	40		100	2	100	2
HDO		20		15		100
D_2O		65		100		35
CO			2	3	3	4
Fe					5	8
ligand loss			1	1	3	6

[a] See footnote *a* of Table I. [b] The D_2 labeling is not entirely selective; see Experimental Section.

Scheme III

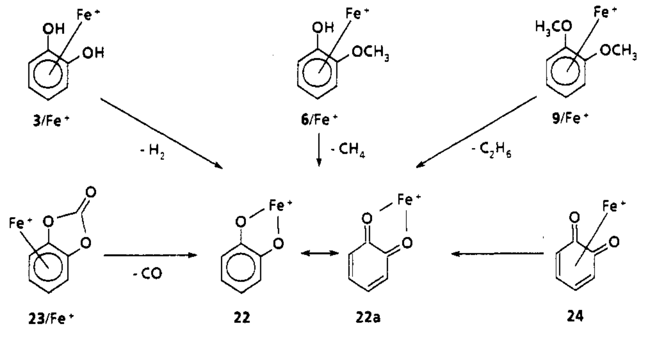


dration plays a minor role.[20] These findings can be explained by the less energy demanding formation of the benzometallacycle **21** rather than a hydroxybenzyne complex (analogous to **13**). This supposition rationalizes not only the intense D_2O losses from **3a**/Fe^+, **4**/Fe^+, and **5**/Fe^+, but also the absence of ligand loss from these ions as compared to the parent compound **1**/Fe^+.

In contrast to the meta- and para-isomers, the ortho-complex **3**/Fe^+ predominantely loses molecular hydrogen. As evidenced by the almost exclusive loss of D_2 from **3a**/Fe^+, most of the hydrogen atoms originate from the hydroxy groups. This is in line with the formation of the iron catecholate cation **22** (vide infra).[21]

With regard to the minor products reported in Table III, we conclude the following: (i) Decarbonylation via isomerization to the corresponding keto forms is nearly negligible in the dihydroxybenzene complexes. This observation indicates that dehydration is facilitated by the presence of a second hydroxy group, thus lending further support for the formation of the metallacycle **21**. (ii) The loss of a neutral iron atom from **5**/Fe^+ reflects the relatively low ionization energy of the para-isomer as compared to the others [IE(**3**) = 8.15 eV, IE(**4**) = 8.2 eV, IE(**5**) = 7.95 eV, IE(Fe) = 7.87 eV[19]]. Nevertheless, the unimolecular reactivity of **5**/Fe^+ is far from being derived from that of the radical cation $\mathbf{5}^{+\bullet}$, from which water loss is negligible.[22]

Scheme IV



Methoxyphenol Complexes. The almost exclusive fragmentation pathways of the ortho-isomer **6**/Fe^+ corresponds to demethanation as reported previously.[2] Dehydration, decarbonylation, and loss of formaldehyde cannot compete with this process. The losses of CH_3D and CHD_3 from **6a**/Fe^+ and **6b**/Fe^+, respectively, confirm the extraordinarily high specific activation of both oxygen functionalities.[23] The suggested formation of the catecholate **22** (Scheme IV) is in agreement with the successive decarbonylations being observed in the MI/CA spectrum of [**6**/$Fe^+ - CH_4$] (Table II). This structural assignment is further confirmed by the fact that **22** can also be generated by dehydrogenation of **3**/Fe^+, decarbonylation of 1,3-benzodioxol-2-one/Fe^+ (**23**/Fe^+), deethanation of **9**/Fe^+ (vide infra), and even directly by chemical ionization of a mixture of *o*-quinone **24** and $Fe(CO)_5$. Interestingly, neutral iron catecholates have been proposed as central intermediates in the degradation of arenes by non-heme dioxygenases to yield eventually muconic acid.[24] However, the actual bonding situation in the cation can either be derived from the Fe(III)–catecholate **22** or the *o*-quinone complex **22a**, the latter with a formal Fe(I) cation.

---

[20] Due to the overall similarity of the spectra, the data for the ortho-compound will be given only. In the MI/CA spectrum of [**5**/$Fe^+ - H_2O$] the dehydration increases to 20% intensity with respect to the CO loss (100%).

[21] For other examples of O–H bond activation by transition-metal ions and further references, see: Blum, O.; Stöckigt, D.; Schröder, D.; Schwarz, H. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 603.

[22] In the MI spectrum of $\mathbf{5}^{+\bullet}$, decarbonylation dominates (100%); in addition, $C_3H_3O^+$ is formed (10%), and water loss is hardly observed (<1%); see also ref 3c.

[23] This is in distinct contrast to the reactions of aliphatic mono- and diols. See for example: (a) Prüsse, T.; Allison, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 553. (b) Prüsse, T.; Fiedler, A.; Schwarz, H. *Helv. Chim. Acta* **1991**, *74*, 1127 and references therein. (c) Seemeyer, K.; Schwarz, H., unpublished results.

[24] (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 44. (b) Cox, D. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 8085.

Table IV. Metastable Ion Spectra of Methoxyphenol Complexes[a]

	6/Fe^+	6a/Fe^+	6b/Fe^+	7/Fe^+	7a/Fe^+	7b/Fe^+	8/Fe^+	8a/Fe^+	8b/Fe^+
H_2				55	58		5	6	
HD						35			3
$CH_3^•$				2	2		3	4	
CH_4	100								
CH_3D		100							
CHD_3			100						
H_2O				6		7[b]	35		15[b]
HDO					6	1		38	14
CH_2O	1	1		100	100		100	100	
CD_2O			1			100			100
Fe							4	5	5

[a] See footnote *a* to Table I. [b] These signals may contain minor contributions due to loss of $CD_3^•$ (isobaric with H_2O).

Table V. Metastable Ion Spectra of Dimethoxybenzene Complexes[a]

	9/Fe^+	9a/Fe^+	9b/Fe^+	10/Fe^+	10a/Fe^+	10b/Fe^+	11/Fe^+	11a/Fe^+	11b/Fe^+
H_2				55	55		2	2	
HD					35	40		1	1
$CH_3·$	95	50		3	2		25	12	
$CD_3·$		30	100		2	4		13	22
CH_2O		2		100	100		100	100	
C_2H_6	100[b]								
CD_2O		2	4		85	100		90	100
$C_2H_3D_3$		100							
C_2D_6			70						
Fe							7	12	10

[a] See footnote *a* to Table I. [b] Signal may contain minor contribution of isobaric CH_2O (<4%).

Unfortunately, the MI/CA spectra of all the $[FeC_6H_4O_2]^+$ ions, derived from the various ortho-compounds shown in Scheme IV, do not allow a distinction between these two valence isomers.

As indicated by the data given in Table IV, the reactions of the meta- and para-isomers **7**/Fe^+ and **8**/Fe^+ can be described in terms of a superposition of the reactions of **1**/Fe^+ and **2**/Fe^+. However, the processes typical for the phenol/Fe^+ complex (Table I) are of minor importance only. Instead, losses of molecular hydrogen and of formaldehyde prevail, whereas dehydration and decarbonylation are less prominent. These findings lend further support to our supposition that the energy demand for the activation of a methoxy group is lower as compared to that of a hydroxy functionality (vide supra). Similar to **2**/Fe^+, the MI/CA spectra of the $[M - CH_2O]^+$ ions from **7**/Fe^+ and **8**/Fe^+ (Table II) are in line with a completely reversible insertion of the metal cation in the aromatic CH bond, thus resulting in the formation of **1**/Fe^+. Quite unexpected is the HDO loss from **8b**/Fe^+ (Table IV); this points to an interaction of both ligands in the para-isomer. This functional-group interaction is also indicated by the relatively weak dehydrogenation of **8**/Fe^+, as compared to the MI spectra of **2**/Fe^+ and **7**/Fe^+. As reported previously for the ion/molecule reactions of bare Fe^+ with methoxyphenols, water loss is quite intense from the para-isomer **8** as compared to both the ortho- and meta-compounds.[2] Since activation of an aromatic hydroxy group is less facile than that of a methoxy moiety, the substantial water loss from **8**/Fe^+ may indicate that a particularly stable product structure favors the dehydration path. Alternatively, one can argue that (i) migration of the iron cation from one to another oxygen functionality of the arene is not facile and (ii) substituent interaction is negligible, with the consequence that the initial coordination of the metal ion determines its unimolecular reactivity.[25] However, the observed HDO loss from **8b**/Fe^+ renders the latter explanation unlikely. In addition, this reasoning would equally apply to the meta-complex **7**/Fe^+, whose behavior however, differs from that of **8**/Fe^+. Furthermore, in the MI/CA spectra of $[FeC_7H_6O]^+$ derived from **8**/Fe^+ decarbonylation is the prevailing degradation reaction (Table II); this points to a complex rearrangement process in which, most likely, benzaldehyde/Fe^+ is formed.[18]

Among the minor products reported in Table IV, charge transfer is of relevance for the para-isomer **8**/Fe^+ only.

Dimethoxybenzene Complexes. Similarly to the other ortho-compounds, deethanation of **9**/Fe^+ leads also to the formation of **22** (Scheme IV), and anew formaldehyde loss can hardly compete with this reaction (Table V). This is demonstrated by the prominent losses of $C_2H_3D_3$ and C_2D_6 from **9a**/Fe^+ and **9b**/Fe^+, respectively. In contrast, CH_2O and CD_2O are formed in small amounts only (2–4%). MI/MI experiments[26] provide no evidence for successive methyl radical losses from **9**/Fe^+; rather we suggest reductive elimination of a genuine ethane molecule from **26** (Scheme V). In addition, unimolecular loss of a methyl radical is observed from **9**/Fe^+.[27] The MI/CA spectrum (Table II) of $[9/Fe^+ - CH_3^•]$ is in keeping with the formation of the iron methoxyphenolate cation **27** (Scheme V).

The reactions of the meta- and para-isomers **10**/Fe^+ and **11**/Fe^+ are similar to those of the monomethoxy derivatives **7**/Fe^+ and **8**/Fe^+. As in the case of the monoethers, hardly any molecular hydrogen is formed from the para-complex **11**/Fe^+ (2%). The products due to elimination of CH_2O from **10** and **11**, i.e. $[10/Fe^+ - CH_2O]$ and $[11/Fe^+ - CH_2O]$,

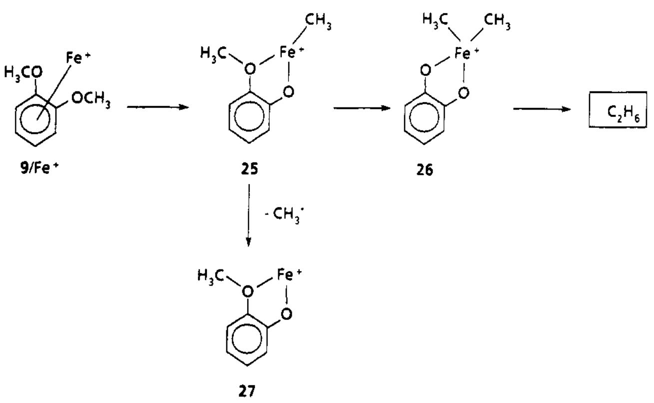
---

(25) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396. (b) Hankinson, D. J.; Miller, C. B.; Allison, J. *J. Phys. Chem.* **1989**, *93*, 3624.

(26) The MI/MI spectrm of $[9/Fe^+ - CH_3^•]$ does not contain an intense signal due to unimolecular $CH_3^•$ loss; hence, a facile consecutive reaction of two methyl groups is rather unlikely. For examples of consecutive decays of metastable ions and further leading references, see: (a) Scheier, P.; Märk, T. D. *Chem. Phys. Lett.* **1988**, *148*, 393. (b) Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 5947.

(27) For other examples of methyl losses from cationic iron complexes, see: (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (b) Fisher, E. R.; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 7382. (c) T. Prüsse, Ph.D. Thesis, TU Berlin, D 83, 1991. (d) Schröder, D.; Schwarz, H. *Organometallics* **1992**, *11*, 2296. (e) Reference 16.

Scheme V



are identical to those of authentic **2**/Fe$^+$; thus, hydrogen transfer between the metal atom and the aromatic ring must be facile on the μs time scale of the experiment. Again, charge transfer is of relevance for the para-compound **11**/Fe$^+$ only. Although we cannot stricly exclude charge transfer to be also operative in the other unimolecular reactions of **11**/Fe$^+$, typical metal ion chemistry still dominates; i.e., although the metastable radical cation **11**$^{\bullet+}$ looses a methyl radical too, the secondary kinetic isotope effects associated with the formation of a methyl radical are different for the metal-free and metal-containing substrates. For **11**$^{\bullet+}$ this reaction is associated with a ratio of $k_{CH_3}/k_{CD_3} = 1.30$, and for **11a**/Fe$^+$ this figure amounts to 0.98. Further, neither in the unimolecular dissociation of **11**$^{\bullet+}$ nor upon collisional activation formaldehyde loss occurs.

As far as kinetic isotope effects are concerned, we can state the following: (i) Dehydrogenation of **10a**/Fe$^+$ is associated with a primary kinetic isotope effect of $k_H/k_D = 1.57$. This value is relatively small as compared to typical data obtained for CH activation by transition metals in the gas as well as in the condensed phase.[28] Our result suggests that activation of the aromatic CH bond may be involved in the rate-determining step of this reaction too; however, as no corresponding deuterium-labeling experiments have been performed, this point cannot be pursued further. (ii) The intramolecular deuterium isotope effects for the formaldehyde losses from **10a**/Fe$^+$ and **11a**/Fe$^+$ are also relatively small ($k_H/k_D = 1.17$ and 1.11, respectively); thus, CH-bond activation of the methoxy moiety is not likely to be rate-determining for this reaction pathway (vide infra).

Surprisingly, the secondary deuterium isotope effect for the methyl radical loss from **9a**/Fe$^+$ seems to be larger than that expected for such a process ($k_{CH_3}/k_{CD_3} = 1.69$). For the analogous reactions from **10a**/Fe$^+$ and **11**/Fe$^+$, this ratio is close to unity (1.05 and 0.98, respectively). It should be recalled, however, that the relative abundances of $CH_3^\bullet$ and $CD_3^\bullet$ losses from **9a**/Fe$^+$ have to be treated as a superposition of the isotope effects associated with both the methyl and the ethane losses; i.e. after activation of the O–CH$_3$ bond in **9a**/Fe$^+$, which is presumably favored with respect to that of the OCD$_3$ group, a secondary isotope effect hampers the activation of the OCD$_3$ group to yield CH_3CD_3. In contrast, upon O–CD$_3$ activation, a CH$_3$ group has to be transferred prior to ethane elimination. Both isotope effects are coupled with each other such that the formation of [**9a**/Fe$^+$ − $CD_3^\bullet$] is doubly disfavored.[29]

Interestingly, the loss of a methyl radical is negligible for the meta-compound **10**/Fe$^+$ (3%). This finding may point to an additional stabilization of the product ions generated from the ortho- and the para-isomers by quinoide resonance structures, thus making the radical abstraction from these isomers more favorable in comparison with the meta-complex.

Trends in Reactivity. As shown by Bjarnason et al.,[2] the use of bare metal ions is a valuable tool to distinguish and identify various isomeric dioxygenated benzenes; i.e., whereas the ortho-derivatives exhibit a characteristic ortho-effect,[3] charge transfer allows a unambigous distinction of the meta- and para-isomers.

For phenol complexes, both dehydration and decarbonylation by bare Fe$^+$ occur to a comparable extent; in contrast, the complexes of methoxy ethers predominantly lose molecular hydrogen and formaldehyde. The unimolecular reactions of methoxyphenols reveal that, in the intramolecular competition between the OH and the OCH$_3$ group, the activation of a methoxy moiety is more facile than that of an aromatic hydroxy group. From the ortho-derivatives **3**/Fe$^+$, **6**/Fe$^+$, and **9**/Fe$^+$ the iron catecholate **22** is formed in great abundance, reflecting the strong interaction of both oxygen functionalities in the ortho-compounds. In a sense, this observation parallels the well-known ortho-effect in the electron impact mass spectra of substituted arenes.[3b] Synergistic effects of both functionalities are much less pronounced in the reactions of the meta-compounds, which do react similarly to the parent singly-substituted benzene complexes. The para-derivatives also resemble the chemistry of the parent compound; however, minor reaction channels point to an interaction of both functionalities, most probably via quinoid resonance structures. In particular, the dehydrogenation of methoxyarenes is almost absent in the case of the para-isomers. In conclusion, the interaction of both functionalities in Fe$^+$ complexes of disubstituted benzenes is not determined by the spatial distance of the substituents, but by specific effects operative in the ortho- and para-derivatives.

Mechanism of Formaldehyde Loss from Methoxyarene/Fe$^+$. As far as the reaction mechanism depicted in Scheme II for the formaldehyde loss from a methoxy moiety is concerned, two interesting conclusions can be drawn from the present experimental findings: (i) After correction for the number of hydrogen/deuterium atoms in **2a**, the intramolecular kinetic isotope effects of **2a**/Fe$^+$ amount to $k_H/k_D = 2.17$ for the dehydrogenation and to $k_H/k_D = 1.54$ for the β-H transfer preceding the formaldehyde loss, respectively. (ii) The kinetic isotope effects for the analogous reactions as being derived from the intramolecular competition in the *m*-dimethoxybenzene complex **10a**/Fe$^+$ amount to $k_H/k_D = 1.57$ for dehydrogenation and $k_H/k_D = 1.17$ for formaldehyde loss. Similarly small intramolecular isotope effects are observed for the formaldehyde losses from **9a**/Fe$^+$ and **11a**/Fe$^+$ (1.1 and 1.09, respectively[30]). These differences imply that

---

(28) Sorokin, A. B.; Khenkin, A. M. *J. Chem. Soc. Chem. Commun.* **1990**, 45.

(29) For a discussion of the relationship between measured product ratios and kinetic isotope effects in parallel and consecutive reactions, see: Thibblin, A.; Ahlberg, P. *Chem. Soc. Rev.* **1989**, *18*, 209.

(30) The determination of the kinetic isotope effects associated with the small formaldehyde losses from **9a**/Fe$^+$ is hampered by the intense $C_2H_3D_3$ loss from this ion. The "foot" of this signal interferes with the CD_2O loss; thus the experimental error of the KIE is ±/−20%.

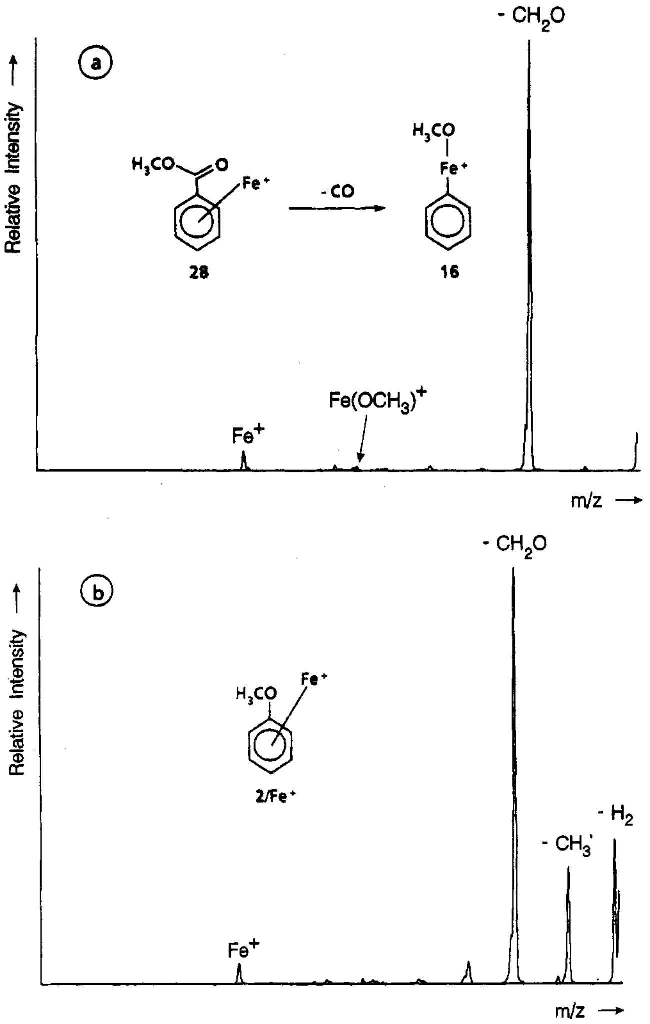


Figure 1. (a) MI/CA spectrum of **16** as generated by decarbonylation of **28** in the field-free region preceding E(1). (b) CA mass spectrum of **2**/Fe^+ having the same kinetic energy as **16** in Figure 1a.[31]

dehydrogenation and formaldehyde loss do not proceed via a common intermediate. A possible explanation is that dehydrogenation involves initially activation of the CH bond of the methoxy group (leaving the O–C bond intact), whereas insertion in the aromatic C–O bond is rate determining for formaldehyde loss.

In order to support this presumption, the intermediate phenyliron(III) methoxide cation **16** (Scheme II) has been generated by Fe^+-mediated decarbonylation of methyl benzoate.[5c] Indeed, the MI/CA spectrum of this product ion establishes the formation of **16** (Figure 1a); i.e., dehydrogenation as well as methyl loss, both being characteristic for **2**/Fe^+ (Figure 1b), are hardly observed; in contrast, formaldehyde loss corresponds to the base peak in the spectrum. In addition, the weak (though nevertheless structure-indicative signal) at m/z = 87, corresponding to the loss of a phenyl group, evidences the formation of **16**. This contrasts with the behavior of **2**/Fe^+, which upon collisional activation in addition to formaldehyde loss, exhibits the characteristic features of the elimination of molecular hydrogen and of a methyl radical (Figure 1b).[31] These observations strongly support the conjecture that aromatic C–O insertion is rate determining for the formation of formaldehyde from Fe^+ complexes of methoxyarenes.

Thus, the intramolecular isotope effects associated with the CH_2O versus CD_2O losses from the dimethoxybenzene complexes reflect the small secondary deuterium isotope effect associated with the C–O insertion (**2**/Fe^+ → **16**). In contrast, the ratio of CHDO and CD_2O losses from **2b**/Fe^+ resembles the intrinsic isotope effect for the β-hydrogen transfer (**16** → **17**) after the rate-determining C–O insertion. The relatively small value (k_H/k_D = 1.54) agrees well with isotope effects reported previously for hydride-transfer reactions of isotopomeric iron methoxide cations $Fe(OCX_3)^+$ (X = H, D).[32]

Acknowledgment. The continuous financial support by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Volkswagen-Stiftung is acknowledged.

OM9207121

---

(31) The CA spectrum of **2**/Fe^+ was recorded at a reduced acceleration voltage of 6828 V, in order to ensure that this ion has the same kinetic energy as the one produced unimolecularly from **28** by loss of CO.

(32) Schröder, D.; Schwarz, H. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 910.