102. Benzene Oxidation by 'Bare' FeO^+ in the Gas Phase

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Bare FeO^+ reacts in the gas phase with benzene at collision rate ($k = 1.3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}), giving rise to the formation of $Fe(C_6H_4)^+/H_2O$ (5%), $Fe(C_5H_6)^+/CO$ (37%), $Fe(C_5H_5)^+/CO/H\cdot$ (2%), and Fe^+/C_6H_5OH (56%). Neither the reaction rate nor the product distribution are subject to a significant kinetic isotope effect, thus, ruling out several mechanistic variants described in the literature to be operative for 'analogous' arene oxidation processes in solution. A mechanism is suggested which is in keeping with the experimental findings, and which also accounts for some remarkable results obtained, when two $[Fe,C_6,H_6,O]^+$ isomers are generated and subjected to a neutralization-re-ionization experiment in the gas phase.

Introduction. – Studies on the transition-metal-mediated activation of C–H and C–C bonds of hydrocarbons have not ceased to attract the attention of chemists [1]. This is due not only to the great economic interest in the direct conversion of hydrocarbons to 'valuable' products, but also to the inherent scientific challenge, which still remains to be met as far as the mechanistic details of the various processes are concerned. For example, for the hydroxylation of benzene ($C_6H_6 \rightarrow C_6H_5OH$) which is attractive industrially [2], and which is one of the most important biological reactions of aromatic hydrocarbons (*i.e.* conversion of L-phenylalanine to L-tyrosine and the metabolism and detoxification of aromatic hydrocarbons by hydroxylases) numerous mechanistic schemes exist in the literature, and they encompass the entire spectrum of direct hydroxylation processes *via* O-atom insertion in a C–H bond [3], the initial formation of aryl radicals *via* H abstraction [4], or single-electron-transfer reaction to generate arene radical cations as the pivotal intermediates [5]. The arene-oxide path [6], followed by the classical NIH shift [7] has recently been questioned [8] as a dominant metabolic path for the hydroxylation of several arenes.

As an important mechanistic criterion, the study of kinetic isotope effects has been repeatedly employed. While the H-abstraction path, which is often suggested to be operative in the transition-metal-mediated oxygenation of arenes [4], is usually associated with large kinetic isotope effects, the k_H/k_D values are much smaller if not close to unity for the P-450 or related oxygenation processes of arenes [1d]. These results are in distinct contrast with the findings obtained for the hydroxylation of alkanes or benzylic C–H bonds by P-450 and its synthetic analogues for which large k_H/k_D values were reported [1d] [9].

In recent years, it was amply demonstrated that gas-phase studies are particularly well-suited for the elucidation of mechanistic aspects of ionic processes, since they are not hampered by the various disturbing factors that prevail in solution (*e.g.* association, counter-ion and solvent effects)[1]). With regard to the oxygenation of C–H bonds of alkanes by 'bare' FeO^+ a quite detailed picture was indeed obtained [11], and here we shall describe the reactions of benzene and two of its deuterated analogues with FeO^+ in the gas phase.

Experimental. – Most of the experiments were performed by using a *Spectrospin CMS 47X Fourier*-transform ion-cyclotron-resonance (FTICR) mass spectrometer which is equipped with an external ion source [12]; the instrument and further details of its operation have been described in [13]. Briefly, Fe^+ ions were generated by laser desorption/ionization [14] by focussing the beam of a *Nd:YAG* laser (*Spectron Systems*, 1064 nm) onto a high-purity rod of stainless steel, which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (*Balzers TPU 330* for source and cell and *Balzers TPU 50* in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (*Oxford Instruments*), which has a maximum field strength of 7.05 Tesla. The metal's most abundant isotope, $^{56}Fe^+$, is isolated by using FERETS [15] and allowed to react with pulsed-in N_2O ($p_{max} \approx 10^{-5}$ mbar) to give FeO^+. This reaction is strongly exothermic [16]; the excess energy and the kinetic energy remaining from the transfer of the Fe^+ was removed by collision with excessive N_2O and Ar; the latter was present as a buffer gas with a constant pressure of $(2–10) \times 10^{-8}$ mbar, as measured with an uncalibrated ionization gauge (*Balzers IMG 070*). Benzene and its isotopomers were introduced *via* a leak valve; the constant pressure amounts to $(2–10) \times 10^{-9}$ mbar. All functions of the instrument were controlled by a *Bruker Aspect 3000* minicomputer. The rate constant for the reaction of 'isolated' FeO^+ with benzene was determined by calibrating our reaction rate using the rates of well-known ion/molecule processes [17]. The error is estimated to ± 25%. Intermolecular kinetic isotope effects were obtained by studying the reactions of FeO^+ with a mixture of benzene, [1,3,5-D_3]benzene and (D_6)benzene, thus avoiding any possible errors due to calibration problems.

Some preliminary experiments were performed by generating FeO^+/benzene and Fe^+/phenol complexes in the chemical ionization source of our four-sector BEBE-mass spectrometer (*B* stands for magnetic and *E* for electric sector)[2]) by bombarding mixtures of either $Fe(CO)_5/N_2O$/benzene or $Fe(CO)_5$/phenol with electrons. Subsequently, an 8-keV beam of $B(1)E(1)$ mass-selected ions of the elemental composition $[Fe,C_6,H_6,O]^+$ was subjected to a neutralization-re-ionization (NR) experiment [19] using c-C_3H_6/O_2 as collision gases (80% transmission for each collision). Recent studies [20] indicated that NRMS might be valuable in probing the bonding properties of organometallic systems in the gas phase.

Results and Discussion. – The products generated in the reaction of FeO^+ with benzene are given in *Scheme 1*. From the measured rate constant of the process $k_r = 1.3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, and its comparison with the rate constant calculated for a *Langevin* collision process [21] ($k_L = 1.3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}), it follows that the reaction occurs with 100% efficiency.

H_2O loss (*Reaction a*) from the collision complex FeO^+/C_6H_6 most likely results in the formation of Fe(benzyne)$^+$[3]). This is supported by the thermochemistry of the reaction as well as the exclusive loss of HDO (1,2 elimination) from the FeO^+/[1,3,5-D_3]benzene system (*Table*).

Loss of CO from the FeO^+/C_6H_6 system (*Reaction b*) gives rise to the well-known and characterized Fe^+(cyclopentadiene) complex [24b] [25]. The species $Fe(C_5H_6)^+$ is characterized by its typical ion/molecule reactions with benzene, in the course of which $FeC_{11}H_{11}^+$ and H· are generated. For the formation of $Fe(C_5H_5)^+$ (presumably as the

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[1]) For a recent review, entitled 'Organometallic Chemistry in Gas Phase', which includes more than 700 references and covers literature up to early 1991, see [10].

[2]) For a description of the machine and its operation, see [18].

[3]) For other studies on Fe(benzyne)$^+$ in the gas phase, see [23] [24].

Scheme 1

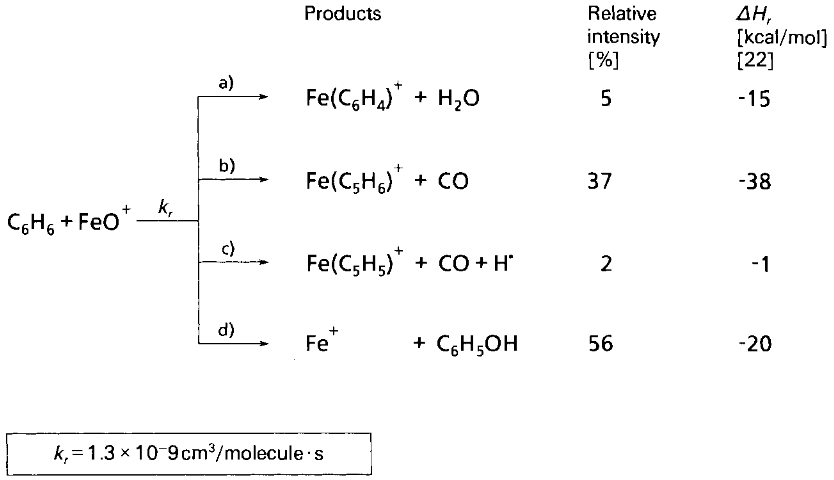

Table. *Products Generated in the Reaction of* FeO^+ *with Benzene and Its Isotopomers*

Precursor	H_2O	HDO	D_2O	CO	CO/H·	CO/D·	Phenol
C_6H_6	5			37	2		56
[1,3,5-D_3]Benzene[a])		3		38	2	< 1	57
C_6D_6[b])			2	37		2	59

[a]) 99.4% D_3. [b]) 99.6% D_6.

iron-cyclopentadienyl complex), there exist two options as far as the co-generated neutrals are concerned: *i*) CO and H· are consecutively eliminated; this possibility is supported by the fact that $Fe(C_5H_6)^+$ is known to undergo H· loss. *ii*) Alternatively, the metal ion in the $[FeO(C_6H_6)]^+$ complex serves as a template to couple H· and CO to HCO·, and the latter is reductively eliminated. A clear-cut distinction is not possible.

The major product in the reaction of FeO^+ with benzene is due to the generation of Fe^+ (*Reaction d*). Although the co-generated neutral cannot directly be characterized in the ICR experiment, on thermochemical grounds, the only possible product corresponds to the formation of phenol. Conceivable isomers like benzene oxide or oxepin, not to mention acyclic C_6H_6O products, are much too high in energy [22] [26] in order to be formed at thermal energies with collision rate from FeO^+ and C_6H_6.

To obtain information as to whether the cleavage of a C–H bond is associated with the rate-determing step in the reactions of FeO^+ with benzene, a competition experiment was conducted such that a *ca.* 1:1:1 mixture[4]) of C_6H_6, [1,3,5-D_3]benzene, and C_6D_6 were simultaneously reacted with FeO^+. For the rates of the two isotopomers, we obtain an intermolecular kinetic isotope effect of 1.00 ± 0.03. Similarly, the data in the *Table*

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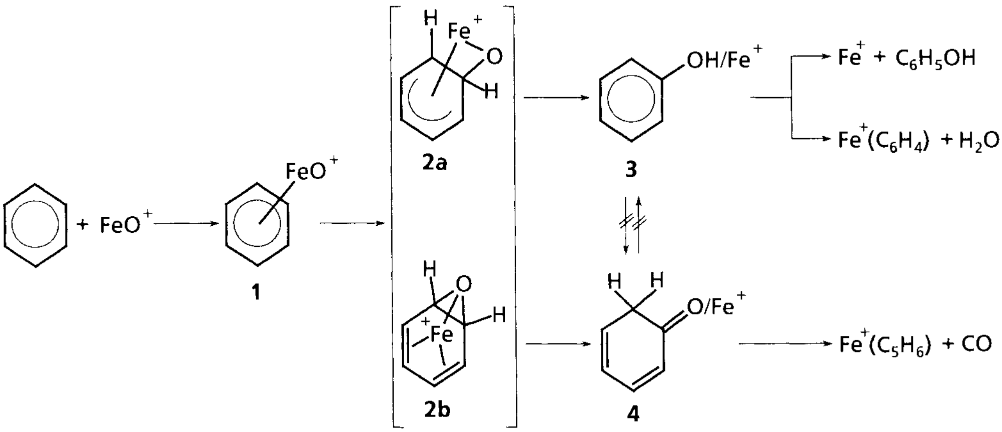
[4]) The composition of the mixture was determined by internal electron-impact ionization (15 eV) in the FTICR cell.

demonstrate that the product distribution is not greatly affected by the presence of D in the benzene precursor. Consequently, it is not likely that cleavage of a C–H(D) bond is associated with the rate-determining step[5]).

A mechanism, which is in keeping with the absence of kinetic isotope effects for both the reaction rate and the product distribution, is suggested in *Scheme 2*. In the initial stage, FeO^+ approaches the benzene ring to form the π complex **1**. While the detailed structure of **1** is not yet known, the ionization energies of FeO (*I.E.* = 8.6 eV) [16] and of C_6H_6 (*I.E.* = 9.25 eV) [27] rule out a complete charge transfer from the iron oxide to the benzene ring to result in a benzene-cation radical. This is further substantiated by the finding that *all ionic* fragments generated from $FeO(C_6H_6)^+$ contain the Fe-atom (*Scheme 1*). The energy gained in generating **1** is also not known[6]); however, it must be large enough in order to account for the 100% efficiency in the product formation. As often in ICR studies, the intermediates are difficult if not impossible to structurally characterize [11g] [28], and we are facing a related situation in the present case in that we do not know which species are formed en route to the Fe^+-complexed phenol **3** and cyclohexadienone **4**. Chemically feasible intermediates might be the σ complex **2a** or the arene-oxide complex **2b** which upon 1,2-hydrogen migrations rearranges to **3** and/or **4**. From **3**, the two pairs of dissociation products $Fe(C_6H_4)^+/H_2O$ and Fe^+/C_6H_5OH originate, while **4** serves as a source for decarbonylation to generate $Fe(C_5H_6)^+$ and $Fe(C_5H_5)^+$. The keto/enol tautomerization **3** ⇆ **4** must be too slow on the time scale of the experiment to take place as indicated by the absence of loss of H_2O/D_2O in the reaction of FeO^+ with

Scheme 2



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[5] Strictly speaking, this conclusion does not hold true, since the overall reaction is collision-controlled. However, if C–H(D) bond cleavage were associated with the rate-limiting step, one would expect a more dramatic effect on the product distribution. This is not observed experimentally.

[6] The bond-dissociation energy for the $Fe(C_6H_6)^+$ system has been determined as 55 kcal·mol^{-1} [27], and it is not unreasonable to expect a comparable value for the π complex between FeO^+ and benzene.

[1,3,5-D_3]benzene (*Table*). In contrast, the H migrations preceding the formations of **3** and **4** have to be facile in order to account for absence of kinetic isotope effects.

A further clue to the understanding of the rather complicated reaction sequence operative in the $FeO(C_6H_6)^+$ system is provided by a neutralization-re-ionization (NR) experiment. If the phenol–Fe^+ complex **3**, generated directly by bombarding $Fe(CO)_5$ with 100-eV electrons in the presence of phenol, is subjected to a NR experiment, in line with previous findings [20], we do not observe a 'recovery signal'. Rather, the NR mass spectrum (*Fig., a*) exhibits intensive signals for $C_6H_6O^{+\cdot}$ and Fe^+ and of secondary fragment ions generated from the former. This is exactly what one would expect from a weakly-bound organometallic *neutral* complex, like C_6H_5OH–Fe; dissociation in its building blocks C_6H_5OH and Fe precedes re-ionization. Consequently, the NR spectrum does not contain a recovery signal for the intact $Fe(C_6H_5OH)^+$ system. We also note the absence of a $C_6H_6^{+\cdot}$ signal, thus indicating that the reaction **3** → **1** does not take place. The

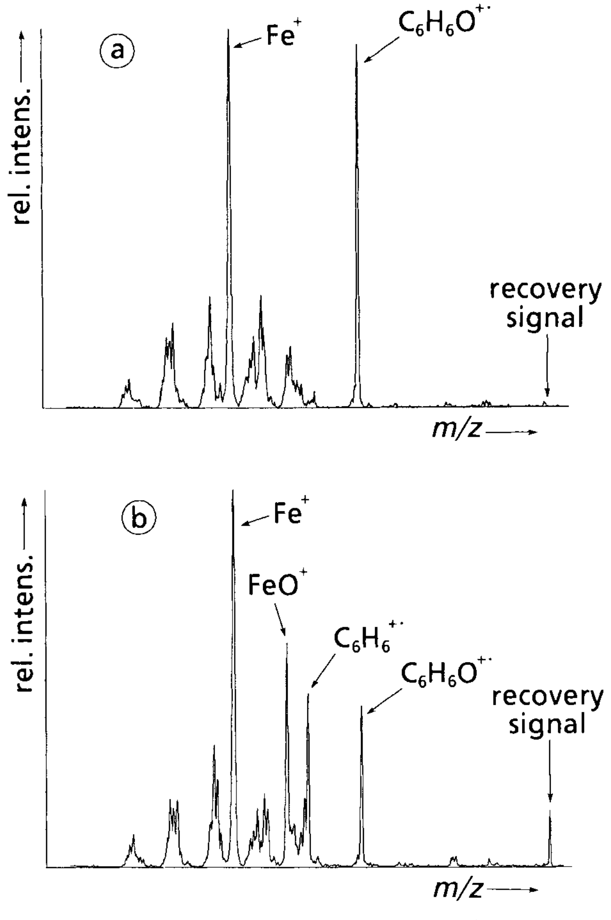

Figure. *Neutralization-reionization (NR) mass spectrum of [Fe,C_6,H_6,)]$^+$ isomers (m/z 150) generated from electron-impact ionization of mixtures of* a) *Fe(CO)$_5$/phenol and* b) *Fe(CO)$_5$/benzene/N_2O*

NR mass spectrum of the second isomeric $[Fe,C_6,H_6,O]^+$ system, generated by electron bombardment of a 1:20 mixture of $Fe(CO)_5/C_6H_6/N_2O$, is distinctly different (*Fig.*, *b*). We note in particular the presence of a recovery signal and of signals due to $C_6H_6O^{+\cdot}$, Fe^+, $C_6H_6^{+\cdot}$, and FeO^+. Although we do not have detailed information on the kind of ion/molecule reactions occurring in the $Fe(CO)_5/C_6H_6/N_2O$ system, it is chemically feasible that FeO^+ is formed from which in a secondary reaction with benzene the π complex **1** is generated. However, if only **1** was formed, the NR mass spectrum is not expected to contain a recovery signal in view of the expected small binding energy between C_6H_6 and *neutral* FeO. Rather, the spectrum should contain only signals due to re-ionized C_6H_6 and FeO. While these signatures do indeed show up in the *Figure* (*b*) the intensive signal for Fe^+ indicates that O transfer has taken place, prior to neutralization, and the $C_6H_6O^{+\cdot}$ signal cleary reveals that it is the C_6H_6 ligand to which the O-atom has been transferred. In addition, the presence of the recovery signal for the $[Fe,C_6,H_6,O]$ species in this system requests the intermediacy of a strongly-bound, *neutral organometallic* fragment. It remains to be established, if the neutral analogue corresponds to **2a**, or if an insertion product, like $C_6H_5{-}Fe{-}OH$, accounts for these findings.

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