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Oxidation of Benzene Mediated by First-Row Transition-Metal Oxide Cations: The Reactivity of ScO^+ Through NiO^+ in Comparison[†]

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Abstract: Fourier-transform ion cyclotron resonance mass spectrometry has been used to study the gas-phase oxidation of benzene mediated by "bare" MO^+ cations (M = Sc, Ti, V, Cr, Mn, Co, and Ni). Oxidation reactions by the oxides of Sc, Ti, and V were not observed, consistent with the stability of the MO^+ bond for the early-transition-metal oxides, and only condensation products, i.e., $MO(C_6H_6)^+$, were formed. For Cr through Ni oxide cations, the most abundant process corresponds to the exothermic conversion of benzene to phenol. All oxidation reactions are kinetically efficient; i.e., $k_f/k_C \approx 1$. The reactivity of each metal oxide cation is examined, and mechanistic details for various processes have been uncovered based on mass spectrometric evidence and labeling studies by using $[D_6]$benzene and $[1,3,5\text{-}D_3]$benzene. The operation of an intramolecular isotope effect of $k_H/k_D = 3.7$ for MnO^+ was evaluated from the relative product intensities of $MnOH^+$ and $MnOD^+$ generated from the reaction with $[1,3,5\text{-}D_3]$benzene. BDE($Mn^+\text{–}OH$) = 82 ± 7 kcal/mol has been derived from H-atom-transfer reactions.

Introduction

Gas-phase experiments of metal–organic systems provide insightful details with regard to fundamentally relevant chemical transformations. The application of mass spectrometry, guided ion beam techniques, and theoretical studies have been important in clarifying mechanistic aspects, developing metal–ligand bond energy data, and comprehensively exploring the intrinsic properties of transition-metal chemistry.[1] Of recent interest has been the investigation of oxidation processes mediated by transition-metal oxide cations.[2–7] These reactions serve to elucidate key steps in industrially and biologically significant oxidation and O-atom-transfer processes.

Transition-metal oxides have proved to mediate the oxidation of hydrocarbons in the gas phase.[2–5] Iron cation, for example, functions as a gas-phase catalyst in the oxidation of ethane after being oxidized by N_2O.[2] The oxides of Cr^+, Mn^+, Co^+, and Ni^+ have also been observed to induce C–H bond activation.[3–5] Perhaps not surprisingly, the overall reactivity of the metal oxide cations differs. For example, MnO^+ primarily undergoes metathesis with ethylene to produce CH_2O,[3] while FeO^+ and CoO^+ preferentially eliminate C_2H_4O regenerating M^+.[2b,4b] In another example, stoichiometric activation of methane occurs for FeO^+ and MnO^+,[2b,8] is inefficient for CoO^+ and NiO^+,[4,8] and is unobserved for VO^+ [9] and CrO^+.[5]

A comparative study of the reactivity of the first-row transition-metal oxides is interesting because the reactivity of each MO^+ species is expected to be distinct due to differences in the estimated reaction thermochemistry and the diversity of electronic configurations.[7] We report herein the reactions of the first-row transition-metal oxide cations with benzene in an effort to assess general trends. The oxidation of benzene is fundamentally important for the industrial production of phenol.[10] Additionally, enzymatic conversions of aromatic compounds to their hydrogenated congeners are key biological processes for the detoxification of deleterious aromatic species.[11] In gas-phase experiments with benzene, various reaction channels with MO^+ species are expected to exist as confirmed by earlier reports[12–14] concerning FeO^+, and strategic isotopic labeling studies can be effectively applied

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[†] Dedicated to Professor Giorgio Modena, Padova, Italy, in recognition of his fundamental contribution to physical organic chemistry.

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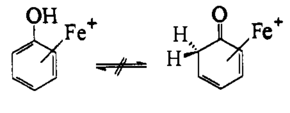
Table 1. Branching Ratios and Estimated Enthalpy of Reaction Data, $-\Delta H_r^\circ$ at 300 K, for Selected Processes of MO^+ with Benzene

MO^+	reagent	neutral eliminated	product ion	(%)	$-\Delta H_r^\circ$ (kcal/mol)[a]
ScO^+	C_6H_6	*b*	$ScO(C_6H_6)^+$		49
TiO^+	C_6H_6	*b*	$TiO(C_6H_6)^+$		49
VO^+	C_6H_6	*b*	$VO(C_6H_6)^+$		42
$CrO^{+\,c}$	C_6H_6	C_6H_5OH	Cr^+	(100)	16
MnO^+	C_6H_6	C_6H_5OH	Mn^+	(67)	33
		$C_6H_5^\bullet$	$MnOH^+$	(15)	
		H_2O	$Mn(C_6H_4)^+$	(18)	
MnO^+	$C_6H_3D_3$	$C_6H_2D_3OH$/ $C_6H_3D_2OD$	Mn^+	(76)	
		$C_6H_2D_3^\bullet$	$MnOH^+$	(11)	
		$C_6H_3D_2^\bullet$	$MnOD^+$	(3)	
		HDO	$Mn(C_6H_2D_2)^+$	(10)	
MnO^+	C_6D_6	C_6D_5OD	Mn^+	(80)	
		$C_6D_5^\bullet$	$MnOD^+$	(10)	
		D_2O	$Mn(C_6D_4)^+$	(10)	
CoO^+	C_6H_6	C_6H_5OH	Co^+	(70)	25
		CO	$CoC_5H_6^+$	(30)	<52[d]
CoO^+	C_6D_6	C_6D_5OD	Co^+	(70)	
		CO	$CoC_5D_6^+$	(30)	
NiO^+	C_6H_6	C_6H_5OH	Ni^+	(100)	45

[a] Enthalpy of reaction values were derived by using data from ref 15 unless indicated otherwise in the text. Thermodynamic data for metal oxide cations were taken from ref 6c with uncertainties of ±7 kcal/mol. [b] Adduct formation is observed for ScO^+, TiO^+, and VO^+. [c] Reaction observed for CrO^{+*} (see text). [d] Value was estimated by assuming $D^\circ(Co^+\text{–}C_5H_6) > 51$ kcal/mol, taken from ref 29.

to elucidate possible reaction pathways. Furthermore, benzene represents the most fundamental aromatic substrate, and it is hoped that the information obtained from this report will further understanding of oxidation processes involving other aromatic systems as well.

The benzene oxidation mediated by FeO^+ proceeds through several reaction channels including the elimination of CO and "HCO"; however, the major reaction pathway corresponds to the formation of phenol.[12] Not surprisingly, the reaction efficiency was measured to be essentially unity; i.e., the reaction products are formed upon every FeO^+/C_6H_6 collision. Although an *intermolecular* isotope effect was not observed,[12] which is not unexpected for a collisionally controlled process, an *intramolecular* isotope effect was not observed for the FeO^+/C_6H_6 system either. Another significant finding was that the reaction of FeO^+ with [1,3,5-D_3]benzene generated the $Fe(C_6H_2D_2)^+$ benzyne complex with HDO elimination.[12a] As H_2O or D_2O loss was not observed, the keto/enol tautomerism process shown below was concluded to be slow on the time scale of the ICR experiment. However, in the presence of *one* water molecule, irreversible conversion of **2** to **1** takes place.[12b]



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Results and Discussion

Branching ratios and ΔH_r° values for selected reaction processes of MO^+ with benzene are given in Table 1. In several cases, neutral structures are assigned based on the reaction thermochemistry. For example, regeneration of the bare metal cation during the course of the reaction is assumed to be accompanied by phenol elimination. Although other C_6H_6O isomers are conceivable thermodynamically, phenol is the most reasonable species to be eliminated.[15] Thermodynamic values reported in this work include uncertainties resulting from the mixing of energy and enthalpy terms in addition to the uncertainties of the literature values.[15] Rate constant data for some reactions of MO^+ with benzene and its isotopomers are given in Table 2. Values for k_f are reported with ±30% error unless noted otherwise.

Table 2. Rate Constant Data for the Reactions of Some Metal Oxide Cations with C_6H_6 and C_6D_6

M^+	$k_f(C_6H_6)$[a]	$k_f(C_6D_6)$[a]	$k_f(C_6H_6)/k_C(C_6H_6)$[b]
ScO^+		2	0.15[c]
TiO^+	4.0	3.9	0.31
VO^+	12.2	11.8	0.95
CrO^+	14	13	1.08
MnO^+	13.9	12.9	1.10
CoO^+	12.9	12.1	1.07
NiO^+	12.4	1.14	1.01

[a] Rate constants are reported in units of 10^{-10} cm^3 molecule^{-1} s^{-1} with ±30% uncertainties except for reactions involving Sc and Ti, in which uncertainties are ±50%. [b] The collision rate constant k_C reported by Su and Chesanvich (Su, T.; Chesanvich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183) was used to derive reaction efficiencies. [c] The reaction for C_6D_6 was used to estimate the efficiency, and k_C was adjusted to account for the mass difference.

The formation and thermalization of metal oxide cations is first addressed as several approaches were required to generate the MO^+ ions. The oxidation of benzene mediated by the first-row transition-metal oxides is grouped into three sections. The chemistry of benzene with ScO^+, TiO^+, and VO^+ will be discussed first, followed by CrO^+ and MnO^+, and finally the chemistry of CoO^+ and NiO^+ will be presented together with a discussion of the previously studied benzene/FeO^+ system.[12]

Production and Thermalization of Metal Oxide Cations. Scandium, titanium, and vanadium form extremely strong M^+–O bonds.[6] The reaction of the M^+ with N_2O is highly exothermic (eqs 1–3) and essentially results in complete conversion to the corresponding metal oxide cation.

$$Sc^+ + N_2O \rightarrow ScO^+ + N_2 + 120\ \text{kcal/mol} \tag{1}$$

$$Ti^+ + N_2O \rightarrow TiO^+ + N_2 + 122\ \text{kcal/mol} \tag{2}$$

$$V^+ + N_2O \rightarrow VO^+ + N_2 + 99\ \text{kcal/mol} \tag{3}$$

Although the reactions of Cr^+, Mn^+, Co^+, and Ni^+ with N_2O to form the respective oxides are also exothermic,[6] spin state requirements for these metal cations include that the processes must proceed via curve-crossing.[6b,16] Therefore, MO^+ (M = Cr, Mn, Co, and Ni) were generated from N_2O and excited M^{+*}, produced from laser desorption and translational excitation, as previously described.[4b] Note that the first excited state of Cr^+ is 1.52 eV higher than the ground state;[17] thus the yields of CrO^+ are primarily dependent upon translationally excited Cr^+ through rf acceleration rather than the negligible population of electronically excited Cr^{+*} states. As described often in the literature, translational excitation is limited because, at higher kinetic energies, ion activation in an ICR experiment becomes an ion ejection process. Therefore, the absolute yields of MO^+ will decrease although the ion yields relative to M^+ increase. Since these ion activation processes, i.e., excitation, ejection, and quenching of excited reactant ions, are in competition with each other, the optimal yield of the metal oxide cations is ca. 20%. Effective thermalization of the MO^{+*} cations prior to their reactions with benzene was confirmed by the measurement of reproducible pseudo-first-order kinetics and product branching ratios. Additionally, the formation of $C_6H_6^{\bullet+}$, resulting from

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charge transfer from excited MO^{+*} ions to benzene, was used as a "thermometer" to assess the presence of nonthermal ions. Since the ionization energy of benzene (9.25 eV)[15] is greater than that of the metal oxides,[6c] the charge-transfer process to form $C_6H_6^{\bullet+}$ most likely involves MO^{+*} cations. This presumption is supported by the observation that relatively low reagent pressures, as compared to buffer gas pressures, ensured that MO^{+*} ions were effectively quenched and $C_6H_6^{\bullet+}$ was not observed. In the case of CrO^+, charge-transfer bracketing experiments were used to probe the presence of excited cations, as will be discussed later.

Reactions of Benzene with Scandium, Titanium, and Vanadium Oxide Cations. The reactions of the early-transition-metal oxides with benzene with explored in order to fully assess periodic trends. The absence of any oxidation products is consistent with the significant endothermicity due to the high stability of the M^+–O bond.[6] Estimates for $\Delta H_r°$ values,[6,15] all endothermic, for eq 4 are 51, 59, and 36 kcal/mol for M = Sc, Ti, and V, respectively. Recently, Armentrout and co-workers noted that translationally excited early-transition-metal oxides slowly react endothermically with D_2 to form water.[18] Although a lack of spin conservation was implicated to impede the reactivity, the thermochemistry also clearly indicates why D_2 oxidation is not observed for these ground-state metal oxides.

$$MO^+ + C_6H_6 \not\rightarrow M^+ + C_6H_5OH \tag{4}$$

$$(M = Sc, Ti, V)$$

Condensation products are only observed in the reaction of benzene with the early-transition-metal oxide cations forming the adduct complex $MO(C_6H_6)^+$, eq 5, where M = Sc, Ti, or V. The excess energy resulting from the BDE(OM^+–C_6H_6) is removed either by collisional relaxation due to the presence of the buffer gas or by radiative cooling.[19] The secondary products $MO(C_6H_6)_2^+$ can be observed at long reaction times. This observation is a further example of the notion that early transition metals prefer large coordination numbers to satisfy an electron-deficient valence shell.[20] Estimates for $\Delta H_r°$ values for eq 5,

$$MO^+ + C_6H_6 \rightarrow MO(C_6H_6)^+ \tag{5}$$

which were derived by assuming BDE(OM^+–C_6H_6) ≈ BDE(M^+–C_6H_6),[14] are given in Table 1. The rate constant evaluations for ScO^+ and TiO^+ were complicated by the reaction of these ions with background contaminents ($p_{Background} \approx 2 \times 10^{-9}$ mbar) and the propensity of these cations to form adducts;[21] thus, an uncertainty of ±50% is assigned.

For the $MO(C_6H_6)^+$ species (M = Sc, Ti, V) the observation of a degenerate ligand exchange reaction, i.e., exchanging C_6H_6 for C_6D_6 without H/D scrambling, indicates that benzene and oxygen are coordinated as separate, intact ligands and not as metallacycle or oxometallacycle. These ligand exchange reactions were quite inefficient, similar to the slow formation of the $MO(C_6H_6)_2^+$ complexes. Presumably, the coordination sphere of the early-transition-row MO^+ species becomes too bulky for facile coordination of a second arene ligand. Low-energy collision-induced dissociation (CID) experiments ($E_{lab} < 30$ eV) on $MO(C_6H_6)^+$ ions yield MO^+ as the sole fragment ion, in keeping with BDE(M^+–O) > BDE(M^+–C_6H_6).[6,13,14,22] Neither the bare metal ion nor the metal–benzyne cation, from dehydration of $MO(C_6H_6)^+$, was formed upon collisional activation in the energy regime applied.

Benzene Oxidation Mediated by CrO^+ and MnO^+. The reaction of CrO^+ with benzene produces Cr^+ as the only product ion with concomitant elimination of phenol, eq 6. The pseudo-first-order rate constant is estimated to be collisional ($k_f/k_C = 1.1$).[23] A measurable intermolecular isotope effect was not observed by using C_6D_6.

$$CrO^+ + C_6H_6 \rightarrow Cr^+ + C_6H_5OH + 16\ \text{kcal/mol} \tag{6}$$

The formation of phenol under ICR conditions is in contrast to the ion-beam results of Kang and Beauchamp, who reported[5a] that benzene does not react with CrO^+. As CrO^+ is completely isolated prior to reaction (see Experimental Section), the Cr^+ product ion undoubtedly results from the oxidation of benzene to phenol. Other channels such as combined C_6H_6/O elimination are expected to be endothermic.[15] However, it is possible that excited CrO^{+*} accounts for the reactivity in eq 6. Therefore, the following facts should be considered for further assessment of this problem. (i) Formation of $CrCH_2^+$ from the reaction of CrO^+ with ethylene occurs at kinetic energies above 1 eV.[5] (ii) There have been controversial discussions[6c,7] on the first excited state of CrO^+ (which is either $^4\Pi$ or $^4\Sigma^-$); in addition, the respective energy separation between the ground state and the first excited state ranges from 0.12 to 0.65 eV.[7] (iii) The experimentally determined IE(CrO) has been reported to be 7.85 ± 0.02 eV by Dyke et al.[7a] and 7.56 ± 0.19 eV by Fisher et al.[6c]

With regard to the above points, we now address the following observations: The CrO^+ cation formed according to *our* method does not react with C_2H_4 to yield $CrCH_2^+$; this indicates that the translational energy of CrO^+ is at least below the 1 eV threshold for this process. Charge-transfer reactions have been used to bracket the ionization energy of CrO, formed under our experimental conditions, between 8.44 and 8.58 eV with *p*-xylene and *o*-bromotoluene being used as reference compounds.[15a] We estimate that we are dealing with a mixture of ground- and excited-state CrO^+ that consists of at least 60% excited CrO^+. The excess energy amounts to approximately 0.7 eV relative to the ground state as determined from the photoelectron spectrum measured by Dyke and co-workers.[7a] Therefore, it is likely that the ground state of CrO^+ does not react (or reacts significantly slower than the diffusion limit) with benzene at thermal energies. Note that if the reaction depicted in eq 6 is very inefficient (i.e., $k_f/k_C < 10^{-4}$), it is possible that the ion beam experiments may be unable to clearly detect a reaction due to kinetic energy shifts in the spectrometer or the diminished sensitivity for reactions with small cross sections. According to Harrison,[7c] the BDE value for the first excited state of CrO^+ is 6 kcal/mol weaker than the corresponding ground-state value. This energy difference may be sufficient to overcome any threshold associated with eq 6. It remains unclear why collisional cooling of CrO^+ (ca. 100 thermalizing collisions with pulsed-in argon buffer gas) is so inefficient.

The oxidation of benzene mediated by MnO^+ proceeds at the collisional limit, and consistently, an intermolecular isotope effect could not be discerned considering the uncertainty of the k_f data (Table 2). In agreement with the estimated thermochemistry, phenol is the most abundant neutral eliminated as inferred from the relative intensity of Mn^+ (Table 1). Formation of $Mn(C_6H_4)^+$ with concomitant H_2O elimination is also observed; therefore, an estimate of a lower limit for BDE(Mn^+–C_6H_4) > 37 kcal/mol is established.[24] An upper limit for BDE(Mn^+–C_6H_4) of 67 kcal/mol can be obtained from data reported by Bjarnason.[13e] For comparison, BDE(Fe^+–C_6H_4) = 76 kcal/mol.[25]

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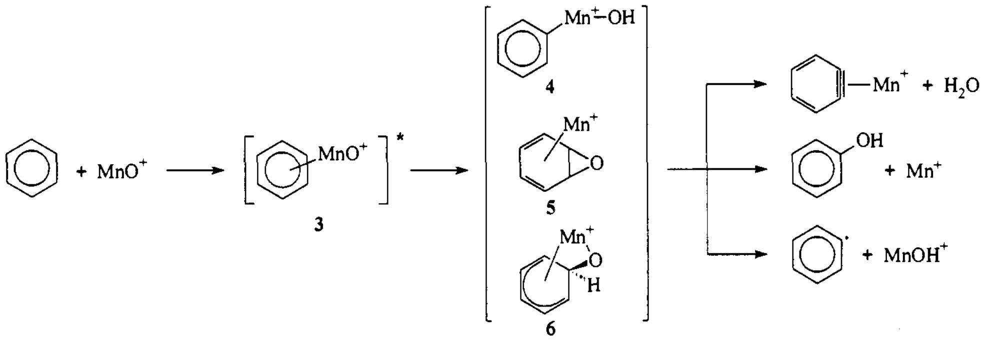
(24) (a) This estimate is based on the assumptions that (i) $\Delta H_f°$ for $Mn(C_6H_4)^+$ formation is at least thermoneutral and (ii) there is no barrier associated with the H-atom abstraction from water. Thermochemical data are taken from ref 14. Data for $\Delta H_f°(C_6H_4)$ are taken from the following: (b) Riveros, J. M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1991**, *113*, 1053. (c) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414.

Scheme 1



The $MnOH^+$ cation is presumed to result from direct hydrogen abstraction. From the formation of $MnOH^+$ in the reaction of MnO^+ with benzene and the absence of a H-atom transfer from water, an estimate of BDE(Mn^+–OH) = 82 ± 7 kcal/mol is derived.[26] This value is larger than the MnO^+ bond energy, BDE(Mn^+–O) = 68 ± 3 kcal/mol.[6c] Formation of the $MnOH^+$ cation in the reaction with benzene is expected to pair an electron from a π^* or a σ_n orbital of the metal oxide cation with the corresponding change in the electronic configuration.[6c,7h] Thus, the differences in the Mn^+–O and Mn^+–OH bond strengths primarily results from a decrease of the antibonding character to form a more stable Mn^+–O "single" bond.

A possible mechanism for the activation of benzene by MnO^+ is shown in Scheme 1. Following the formation of the C_6H_6–MnO^+ collision complex **3**, a likely first step in the reaction sequence is the insertion into a C–H bond[12] to generate intermediate **4** although, as indicated from previous work,[12b] **5** and **6** cannot be ruled out. As a phenyl radical is eliminated, which is unobserved in the oxidation of benzene by FeO^+,[12] intermediate **4** is plausible in the MnO^+/C_6H_6 system. Water elimination requires a second hydrogen transfer, and similar to the reactivity of FeO^+ with [1,3,5-D_3]benzene,[12] H_2O or D_2O elimination is also not observed from the reaction of MnO^+ with [1,3,5-D_3]benzene. This implies that β-hydrogen transfer from **4** to yield the (C_6H_4)–Mn^+–OH_2 intermediate is irreversible on the time scale of the experiment. The second hydrogen transfer arises specifically from an *ortho* position, which explains why HDO elimination is exclusively observed from the reaction with [1,3,5-D_3]benzene. An additional contribution to the C–H bond activation step required for water loss is supported by studying the reactions of C_6D_6 and $C_6H_3D_3$ in which the yields of phenol increase relative to that obtained in the reaction with C_6H_6. Since the second C–H bond activation step is envisioned to have an activation barrier,[12b] an isotope effect, as inferred from the variance of the respective branching ratios in Table 1, is expected.

An intramolecular kinetic isotope effect (KIE)[27,28] of 3.7 for $MnOH^+/MnOD^+$ formation was determined from the reaction with [1,3,5-D_3]benzene. Similar intramolecular isotope effects for the reactions of other metal oxide cations with benzene have not been reported. However, the intramolecular KIE for the H-atom abstraction reaction of MnO^+ with CH_2D_2 is k_H/k_D = 2.0. An intramolecular KIE of 3.7 for the $MnO^+/C_6H_3D_3$ couple as compared to the value for the MnO^+/CH_2D_2 system is in keeping with the differences in the C–H bond dissociation energies for C_6H_5–H (110 kcal/mol) and H_3C–H (105 kcal/mol).[15a] Since an independent value for the Mn^+–OH bond strength is unavailable, assessment on the reaction thermochemistry for hydroxide formation is based on the presently bracketed value of BDE(Mn^+–OH) = 82 ± 7 kcal/mol.[26b] An unambiguous differentiation between a C–H bond insertion process via **4** and direct H abstraction cannot be resolved.

Qualitatively, an increase in electronic multiplicity of the MO^+ cations coincides with an increase in the richness and variety of the products formed in the reaction with benzene. The FeO^+ ($^6\Sigma^+$) cation, in which the electronic multiplicity is maximized for the first-row transition-metal oxide cations, undergoes C–H and C–C bond activation, including expulsion of radicals, e.g., $HCO^•$ or $H^•/CO$.[12] For the MnO^+ ($^5\Sigma^-$) case, C–H bond activation, associated with phenyl radical elimination, occurs but not C–C bond activation. Further, quartet CrO^+ is not observed to react with benzene,[5] while CrO^{+*} generates phenol in its reaction with benzene. Thus, a decrease in the multiplicity of the oxide cation apparently corresponds to a decrease in the diversity of products. In addition, low-spin species were found to insert into C–H bonds more easily than high-spin species, if the latter react in this manner at all.[7h]

Benzene Oxidation Mediated by CoO^+ and NiO^+. Cobalt oxide cation readily reacts with benzene to eliminate neutral phenol and CO (Table 1). The $\Delta H_r°$ estimate for CO elimination is based on a lower limit for the BDE(Co–$C_5H_6^+$) > 51 kcal/mol reported by Jacobson and Freiser.[29] Similar to the reactions of FeO^+ with benzene and its isotopologs,[12] the branching ratio for the reaction of the CoO^+/C_6D_6 couple is identical with that of the CoO^+/C_6H_6 couple.

Although $Co(C_5H_5)^+$ formation is anticipated to be exothermic for $H^•/CO$ elimination,[15,30] this process is not observed; for FeO^+, the $Fe(C_5H_5)^+$ ion was formed in only 2% yield.[12] If excited CoO^{+*} ions are allowed to react with benzene, in addition to $C_6H_6^{•+}$, $Co(C_5H_5)^+$ is also observed. However, thermalization of CoO^{+*} results in the suppression of both $C_6H_6^{•+}$ and $Co(C_5H_5)^+$. Secondary products, i.e., $Co(C_6H_6)^+$ and $Co(C_6H_6)_2^+$, were observed at long reaction times. Double-resonance experiments confirmed the reaction sequence depicted in eq 7. The $Co(C_6H_6)^+$ ion is not the result of a ligand exchange reaction with CoO^+, which is ca. 18 kcal/mol endothermic.

$$CoO^+ + C_6H_6 \rightarrow Co^+ + C_6H_5OH \tag{7a}$$

$$Co^+ + C_6H_6 \rightarrow Co(C_6H_6)^+ \tag{7b}$$

$$Co(C_6H_6)^+ + C_6H_6 \rightarrow Co(C_6H_6)_2^+ \tag{7c}$$

The decrease in electronic multiplicity for CoO^+ ($^5\Delta$) relative to FeO^+ ($^6\Sigma^+$) is consistent with the decrease in the richness of

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(26) The estimate for BDE(Mn^+–OH) is derived by using the following thermochemical data: $\Delta H_f°(MnO^+)$ = 229 kcal/mol (ref 6), $\Delta H_f°(C_6H_6)$ = 20 kcal/mol, $\Delta H_f°(H_2O)$ = −58 kcal/mol (ref 15a), $\Delta H_f°(C_6H_4)$ = 105 kcal/mol (ref 24b,c). Other data are from ref 15. In good agreement with the present value, there is a previous value for BDE(Mn^+–OH) = 82 kcal/mol: Clemmer, D. E.; Armentrout, P. B. In Martinho Simões, J. A., Ed. *NATO ASI Proceedings Series C, Vol. 367: Energetics of Organometallic Species*; Kluwer: Dordrecht, 1992; p 321.

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the reactivity of CoO^+ with benzene. Whereas MnO^+ ($^5\Sigma^-$) was observed to activate C–H bonds with concomitant H_2O, C_6H_6-OH, and $C_6H_5^{\bullet}$ eliminations, CoO^+ activates C–H and C–C bonds of benzene *without* radical expulsion.

The $Co(C_6H_4)^+$ cation is not formed, although MnO^+ and FeO^+ both generate cationic metal–benzyne complexes. This product was searched for by focusing on the expected m/z of $Co(C_6H_4)^+$, i.e., $m/z = 134.9645$ under high-resolution narrow-band conditions. However, no definite ion signal indicative of the $Co(C_6H_4)^+$ product was observed. Bjarnason has bracketed BDE(Co^+–C_6H_4) = 71 kcal/mol;[13e] thus, $Co(C_6H_4)^+$ is thermochemically accessible from the CoO^+/C_6H_6 reaction couple,[24b,c] and the nonoccurrence of the reaction may point to a kinetic barrier or may indicate that the reaction rate constant for $Co(C_6H_4)^+$ formation is $<10^{-14}$ cm³/molecule·s. The nonoccurrence of $Co(C_6H_4)^+$ formation and the elimination of CO indicate that an intermediate similar to **2** may be operative in the CoO^+/C_6H_6 system.

The oxidation of benzene to phenol is the most exothermic for NiO^+ and is the sole observed product. The low Ni^+–O bond strength[6] opens the possibility for numerous reaction channels, yet only O transfer is observed. An explanation for the overall reactivity of NiO^+ can be assessed by examining the thermochemistry for eq 8. In the absence of three-body collisions, facile reductive elimination of neutral products occurs. The Ni^+–(C_6H_6) bond dissociation energy has been determined to be 68 kcal/mol,[14,15b] and this energy is reasonably the approximate energy gained upon coordination of benzene to NiO^+. Rather than a situation in which a large thermodynamic driving force limits specific reaction channels, a small thermodynamic driving force may be implicated for CrO^+. Also note that both nickel oxide and chromium oxide cations are quartets as compared to the more reactive CoO^+ and MnO^+ ions, which are quintets.

$$NiO^+ + C_6H_6 \rightarrow [C_6H_5\text{–}Ni^+\text{–}OH] \rightarrow Ni^+ + C_6H_5OH \quad (8)$$

Gas-Phase Catalytic Oxidation of Benzene. Considering the method employed for generating metal oxide cations, catalytic oxidation of benzene fails by using M^+ (M = Cr, Mn, Co, Ni) and N_2O as a terminal oxidant (*vide supra* and Figure 1A).[6b,15] Because of the endothermicity of the reaction shown in eq 4, not even stoichiometric oxidation mediated by the early-transition-metal cations is possible in the gas phase at thermal energies. The implications of using Fe^+ as a gas-phase catalyst for oxidizing benzene, as demonstrated in Figure 1B, can be determined from previous reports[12a] with a turnover number of ca. 1.2, assuming the conditions given in Figure 2.

An alternative approach to gas-phase catalytic oxidations is presented in Figure 1C. The ligand association of benzene to Co^+ is both exothermic and efficient at higher pressures (at $p(Ar) = 7 \times 10^{-7}$ mbar, $k_f = 14 \times 10^{-10}$ cm³/molecule·s, $k_f/k_C = 1.1$). In order to design a catalytic process, it is necessary to "recover" the consumed Co^+ for further cycles. Reaction of isolated thermal $Co(C_6H_6)^+$ with N_2O yields Co^+ as the only product (eq 9), with a rate constant of $k_f = 12 \times 10^{-10}$ cm³/molecule·s ($k_f/k_C = 1.1$). With respect to thermochemistry,[15] the eliminated C_6H_5OH is most probably phenol although there is no way to analyze neutrals by using FTICR. The efficient formation of Co^+ implicates the process to be at least thermoneutral within experimental uncertainties demanding a slight correction for the Co^+–(C_6H_6) bond dissociation energy.

$$Co(C_6H_6)^+ + N_2O \rightarrow Co^+ + C_6H_5OH + N_2 \quad (9)$$

The literature-reported value of BDE(Ni^+–C_6H_6) = 68 ± 5 kcal/mol is equal to that of Co^+–(C_6H_6); however, the oxidation of $Ni(C_6H_6)^+$ with N_2O was not observed. On the basis of the observed reactivity of $Co(C_6H_6)^+$ and $Ni(C_6H_6)^+$, and BDE(Co^+–C_6H_6) value has to be smaller than 62 kcal/mol. According to the analytical solutions of the respective kinetic equations derived from Figure 1C, at pressures of $p(C_6H_6) = 0.4 \times 10^{-8}$ mbar, $p(N_2O) = 9.4 \times 10^{-8}$ mbar, and $p(Ar) = 30 \times 10^{-8}$ mbar, a turnover number of ca. 18 is expected for Co^+. Comparison with the experimental results (data points in Figure 2) evidences these predictions. The sink in the catalytic cycle results from the formation of $Co(C_6H_6)_2^+$. Concerning the effectivness of our system, the pressure of benzene must be kept as low as possible in order to suppress the consecutive ligand association which forms the $Co(C_6H_6)_2^+$ sandwich complex, and $p(N_2O)$ should be maximized to optimize conversion of $Co(C_6H_6)^+$. At higher overall pressures, the ligand association reaction to generate $Co(C_6H_6)_2^+$ is expected to compete with eq 9; further, other

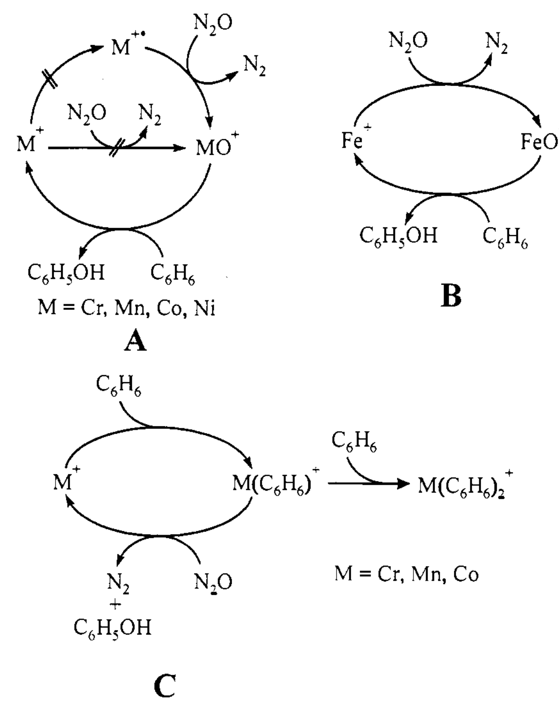

Figure 1. Schematic representations of stoichiometric (A) and catalytic (B and C) oxidations of benzene. Case A involves generation of an activated bare-metal ion prior to reaction with N_2O. Regeneration of the metal oxide with concomitant phenol elimination would require reactivation to form the metal oxide cation. Case B represents the catalytic conversion using Fe^+. In case C, $M(C_6H_6)^+$ adduct is directly formed, and in its reaction with N_2O, phenol is eliminated. Regeneration of the $M(C_6H_6)^+$ adduct does not require reactivation of the bare-metal cation.

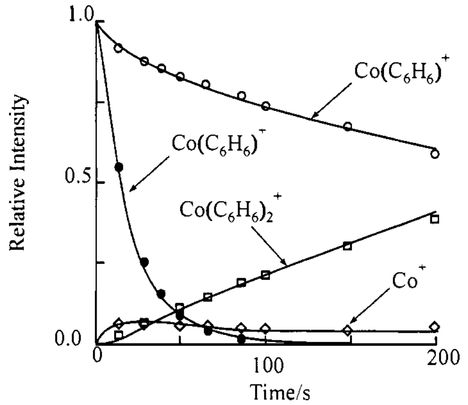

Figure 2. Temporal evolution for the various species involved in the Co^+-catalyzed oxidation of benzene. The open symbols indicate the time evolution of the ion abundances for Co^+, $Co(C_6H_6)^+$, and $Co(C_6H_6)_2^+$ in the catalytic cycle based on experimental data. The solid lines result from the analytical solutions of the respective differential equations by using the k_f values given in the text. Conditions: $p(N_2O) = 9.4 \times 10^{-8}$ mbar, $p(C_6H_6) = 0.4 \times 10^{-8}$ mbar, and $p(Ar) = 30 \times 10^{-8}$ mbar. The filled dots, indicating the disappearance of $Co(C_6H_6)^+$ in the stoichiometric reaction with N_2O when benzene is not present, are included for comparison.

condensation reactions may also interfere. The low turnover number of ca. 2 for Cr^+ or Mn^+ [31] is attributed to the slow ligand association reactions to form the $M(C_6H_6)^+$ complex ($k_f/k_C \approx 0.03$).

For the $M(C_6H_6)^+$ complexes of chromium and manganese, electrons occupying $d\epsilon_1$ and $d\alpha_1$ orbitals (and also 4s orbital in the case of Mn^+) increase the metal–benzene repulsions.[14a] The orbital repulsions result in an increase in the metal–benzene distance and, thus, a decrease in the ion-induced dipole interactions primarily responsible for bonding.[14a] This may explain the inefficiency of the ligand association reactions for Cr^+ and Mn^+ with benzene. Conversely, in the case of Co^+ and Ni^+, in which the ligand association reactions are collisionally controlled, π^* donations from the $d\epsilon_2$ orbitals result in a more stable $M(C_6H_6)^+$ complex.[14a]

Catalytic oxidations as indicated in Figure 1B,C are not possible with the early metal oxide cations due to the strength of the M^+–O bond for Sc, Ti, and V. Oxidation of $Fe(C_6H_6)^+$ with N_2O does not result in the formation of Fe^+ and phenol; however, other oxidation products such as $Fe(C_5H_6)^+$ and $FeO(C_6H_6)^+$ were observed.

Conclusions. In this study, the chemistry of the first-row transition-metal oxides with benzene has been extensively explored. The early metal oxide cations, ScO^+, TiO^+, and VO^+ are not capable of oxidizing benzene; rather, condensation products up to $MO(C_6H_6)_2{}^+$ are formed. Slow coordination of the second ligand observed from ligand exchange reactions is likely a result of saturation of the coordination sphere at the metal center. CID experiments confirm that the benzene ligands are intact units.

Manganese oxide demonstrates interesting reactivity with benzene in that, in relation to phenol formation, water elimination and H-atom abstraction are both observed. Cobalt oxide eliminates CO, which requires activation of the benzene skeleton. The nickel oxide cation eliminates neutral phenol as the sole product. As a general trend, the oxidation reactions of benzene mediated by metal oxide cations MO^+ (M^+ = Cr, Mn, Fe, Co, and Ni) are paralleled by an increase in spin multiplicity of the MO^+ cations. This is manifested in the number and type of reaction channels for FeO^+ ($^6\Sigma^+$) compared to MnO^+ ($^5\Sigma$), CoO^+ ($^5\Delta$), and CrO^+ ($^4\Pi$ or $^4\Sigma$) and NiO^+ ($^4\Sigma$). Note that FeO^+ eliminates water, CO, "HCO", and phenol in a complicated reaction sequence.[12] The stability of the M^+–O bond accounts for the lack of reactivity of the early transition-metal oxide cations.

An alternative route to benzene oxidation by using the bare metal ions of Cr, Mn, and Co as catalysts has been presented. Since formation of MO^+ by using N_2O is inhibited at thermal energies, benzene oxidation according to the method indicated in Figure 1C is only limited by the pressure of the oxidant and the formation of the metal–benzene cation.

Although the oxidation processes mediated by the metal oxide cation studied here are not really catalytic, insight into the mechanistic details has been revealed. Further, we are now beginning to acquire a clearer picture of the diverse activity of the first-row transition-metal oxide cations. We are presently orchestrating combined mass spectrometric and theoretical studies designed to outline the necessary underpinnings for comprehensive and lucid interpretations of the periodic trends and chemical reactivity for a broad series of MO^+ species and their reactions with organic reagents.

Experimental Section

Gas-phase experiments were performed by using a Spectrospin CMS 47X Fourier-transform ion cyclotron resonance mass spectrometer,[32] which is equipped with an external ion source[33] as previously described.[34] Metal ions were generated from laser desorption/ionization by focusing the beam of a Nd:YAG laser (Spectron systems; λ = 1064 nm) at a metal target which was mounted in the external ion source. The M^+ ions were transferred from the external ion source to the analyzer cell by a system of electrostatic potentials and ion lenses. The external ion source, the ion transfer system, and the main vacuum chamber of the spectrometer were differentially pumped by three turbo molecular pumps. After deceleration, the M^+ ions were trapped in the field of a 7 T superconducting magnet (Oxford Instruments). Ions of interest were isolated by using FERETS,[35] a computer-controlled ion ejection protocol which combines single-frequency ion ejection pulses with frequency sweeps to optimize ion isolation. All functions of the instrument including all pulse sequence steps were controlled by a Bruker Aspect-3000 minicomputer.

Several metal oxide cations were generated from the reaction of N_2O with M^{+*}. Because of the low MO^+ ion yields, Cr^+, Mn^+, Co^+, and Ni^+ were allowed to react with pulsed-in N_2O prior to collisional thermalization. Additionally, M^+ ions except for Sc^+, Ti^+, and V^+ were translationally excited to enhance the production of MO^+. Exact ion masses were evaluated from high-resolution narrow-band 1 K spectra (filled to 4K) for all ion excitation pulses. Prior to isolation of MO^+ cations, argon buffer gas was pulsed in several times. For several experiments, argon was present at a static pressure of 3–5 × 10^{-7} mbar. Pressures were measured with an uncalibrated ion gauge (Lambert) and corrected by using the method previously described by Bartmess and co-workers and others.[36,37] Pseudo-first-order rate constants reported in this study were determined from the logarithmic decay of reactant intensity over time and are reported with ±30% error unless stated otherwise.[37] Branching ratios were determined from the temporal ion distributions acquired during kinetic analysis and are reported with ±10% uncertainty.

Double-resonance experiments[38] performed on presumed reaction intermediates, i.e., $[Co,C_6,H_6]^+$ for the secondary reaction of $Co(C_6H_6)^+$ with benzene, were conducted by first obtaining a high-resolution spectrum (3–5 kHz; 1K data points filled to 4K). Then the broad-band spectrum, with rf irradiation focused at the measured cyclotron frequency of the ion of interest obtained under high-resolution conditions, was observed. Similar procedures were performed for all ion activation processes.[39]

Benzene was distilled from sodium and stored over molecular sieves. $[D_6]$Benzene (98% pure; Aldrich), and $[1,3,5\text{-}D_3]$benzene (98% pure; Aldrich) were used as supplied; and their purity was confirmed by mass spectrometry. Other reagents were obtained from commercial sources and used without further purification. Liquid samples were degassed by several freeze–pump–thaw cycles prior to mass spectral analysis.

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(31) Experimental conditions for the catalytic oxidation of benzene by Cr^+ and Mn^+ cations as depicted in Figure 1C are p(benzene) = 0.6 × 10^{-8} mbar, $p(N_2O)$ = 9.4 × 10^{-8} mbar, and p(Ar) = 30 × 10^{-8} mbar. The reactions of the bare metal cations of Cr and Mn with cyclohexene to generate $M(C_6H_6)^+$ complexes with concomitant $2H_2$ loss were also explored. These reactions gave higher turnover numbers due to the faster oxidation reaction ($k_f/k_C \approx 0.3$) relative to the ligand association reaction with benzene; however, strictly speaking, these processes do not correspond to a catalytic oxidation of benzene.

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