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Gas-phase reactions of an iridium(I) complex with dioxygen – Comparison to solution-phase reactivity

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Abstract

The unique advantage of working in the gas phase, i.e., in the absence of solvent and counterions, is that the intrinsic reactivity of a catalyst can be determined. Although back translation to solution-phase reactivity is not necessarily straightforward, both the similarities and the differences between gas-phase and solution-phase chemistry hold information useful to the analysis of complex reaction pathways. Here we describe the oxidation of an iridium–ethene complex with molecular oxygen in the gas phase. Contrary to the solution-phase reactivity, in the gas phase only one single product is formed, namely a peroxo-ethene complex. Also in contrast to solution, full conversion of the ethene complex into the peroxo-ethene product is observed in the 24-pole ion guide under near-zero collision energy conditions and at relatively high collision gas pressures (up to 100 mTorr). These differences can be explained by the fact that the electron transfer pathway that plays a dominant role for product formation in condensed phase is shut off under these conditions.

Keywords: Electrospray ionization; Multipole ion guide; Dioxygen; Peroxo-complexes; Iridium

1. Introduction

Transition-metal complexes are often employed as catalysts in the synthesis of organic molecules under conditions in which reactant(s) and catalyst are mixed homogeneously. These catalysts usually work under milder conditions and provide higher selectivity than their heterogeneous counterparts. The polarity and coordinating properties of a solvent can influence the activity as well as deactivation/decomposition of a catalyst. The balance between these two factors can be very subtle. Also, a solvent can affect both binding preferences of ligands [1] and the final geometry of the complexes [2]. The importance of the solvent influence on molecular structure as well as inter- and intramolecular reactivities is reflected by the increasing number of reports on this topic [3–8]. When ionic complexes are used, counterions will invariably be present, and these too are known to affect reactions [9–11]. In the gas phase, where solvent and counterions are absent, it is possible to study the intrinsic reactivity of a catalyst. Although back translation to solution-phase chemistry is anything but straightforward, both the similarities and the differences between gas-phase and solution-phase chemistry hold information useful to the analysis of complex reaction pathways [12–15]. In the present article, gas-phase studies are compared to solution-phase chemistry in order to improve our general understanding of catalytic olefin oxygenation. For this we studied a relevant model reaction, namely the oxidation of a low-valent transition metal–olefin complex by molecular oxygen [16–21]. When using mass spectrometry for the investigation of ion–molecule reactions one has to bear in mind that reaction conditions may differ considerably for each type of mass spectrometer. A serious disadvantage of most triple quadrupole mass spectrometers, ion traps and FTICR instruments is that the collision gas pressures applied are relatively low. As a result, the number of collisions per second an ion undergoes in the gas phase will be orders of magnitude lower than in solution. As a consequence, molecules formed in

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exothermic reactions cannot readily dissipate their excess energy and will therefore enter reaction pathways that are normally not accessible in condensed phase. A device that can accommodate higher collision gas pressures for complete thermalization or for reaction without significant degradation of the ion current is a higher order radio frequency (rf) multipole. Such multipoles were first devised and built by Gerlich and co-workers [22–24]. In our mass-spectrometric setup, a 24-pole ion guide was used to replace the transfer octopole of the commercial instrument. The advantages of this modification with respect to thermalization and reduction of nonadiabatic effects have been described elsewhere, as have been the details of the construction and circuits [25,26].

2. Experimental

2.1. Instrumentation

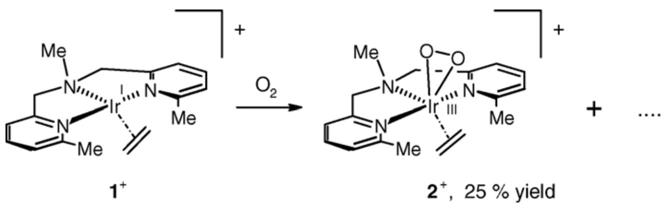
The gas-phase experiments were performed on modified Finnigan MAT TSQ 700 and TSQ 7000 spectrometers at the Zurich and Freiburg laboratories, respectively [25]. The major modification comprises the replacement of the first octopole by a rf 24-pole. All gaseous ions produced in the tube lens region enter the 24-pole region. The multipole basically separates ions from neutral molecules, which are removed by a turbo pump located underneath the 24-pole. The length of the 24-pole is 38 cm as compared to the 11.75 cm octopole in the commercial instrument; the inner diameter is 0.6 cm. The multipole is fitted with an open cylindrical PEEK sheath (18 cm long) around the lamellas into which a collision gas can be bled for thermalization or reaction at pressures up to at least 150 mTorr. The ions enter the 24-pole region at near-zero kinetic energy. The collision energy cannot be varied [27]. Although no longitudinal electric field is externally applied, the continuous ion current into the 24-pole creates – by way of space–charge effects – a slight longitudinal potential that drives the ions through. Once the ions have entered the 24-pole, they “diffuse” through the ion-guide region. Collision frequencies of 10^6 to 10^7 s^{-1} can be achieved in this region (corresponding to around 10^5 collisions as suggested by Monte Carlo simulations using Langevin theory) [27]. As a result, one important property of condensed media is retained: efficient thermalization and efficient transfer of energies built up in exothermic reactions. In short, *zero-collision-energy collisions at relatively high collision gas pressures* can be performed. The octopole region, the CID chamber, differs from the 24-pole region in two ways: (1) collision gas pressures of only up to 5 mTorr can be applied which decreases the number of collisions an ion can undergo by two orders of magnitude and (2) the kinetic energy of the ions can be varied up to about 150 eV (laboratory frame). In other words, in the octopole region *tunable low and high-energy collision experiments at low collision gas pressures* can be carried out. Pressures in the 24-pole and the octopole region were read from Pirani gauges directly attached to the housing of the multipoles. To calibrate the readings of these gauges a published calibration protocol was used [28].

2.2. Starting materials and measurements

The synthesis of $\mathbf{1}^+$ $PF_6{}^-$, $[(\kappa^3\text{-}Me_2\text{-bpa-Me})Ir(C_2H_4)_2]$ PF_6 (Me_2-bpa-Me=*N*-methyl-*N*,*N*-di[(6-methyl-2-pyridyl)methyl]amine), was described previously [29]. Solvents (Aldrich, p.a.) were distilled under nitrogen atmosphere to remove last traces of water and dioxygen. Acetonitrile was distilled over potassium, THF over CaH_2. Dioxygen (PanGas 4.5, 99.995%) or argon (PanGas 4.8, 99.998%) were used as collision gas. Electrospray ionization (ESI) was used to transfer the ionic complexes to the gas phase. 10^{-4} to 10^{-5} M solutions of the iridium compound in 0.02% MeCN in THF were prepared under a nitrogen atmosphere using standard Schlenck techniques. These solutions were then electrosprayed at a flow-rate of 3–15 μl/min, at 3–5 kV and a capillary temperature of 150 °C. The tube lens potential was set in such a way that the intensity of the iridium mono-ethene complex was maximized. Reactions in the 24-pole region were performed at five different dioxygen pressures. For the calculation of product yields only those species whose intensities changed upon increase in dioxygen pressure were taken into account for calculation of the total ion intensity (TIC). The intensities of other “spectator” complexes (e.g., $[(Me_2\text{-bpa-Me})Ir(C_2H_4)_2]^+$) remained constant and were thus omitted in this calculation. The structures of the reaction products were confirmed by subsequent fragmentation of the product ion *m*/*z* by collision with argon in the CID chamber. Collision reactions in the octopole region were monitored in the daughter-ion scan mode. CID was performed at varying collision energies (0–1.2 eV in the center-of-mass frame) and at dioxygen pressures of 0.8 and 1.0 mTorr. Intensities of species are calculated as percentage of the total ion intensity in which the intensity of the parent ion is included.

3. Results and discussion

The solution-phase reaction of the iridium(I) complex cation $[(\kappa^3\text{-}Me_2\text{-bpa-Me})Ir^I(C_2H_4)]^+$, $\mathbf{1}^+$, towards dioxygen has been reported previously [29]. In a non-selective reaction, $\mathbf{1}^+$ is converted by O_2 to only 25% of the iridium(III) peroxo-ethene complex $\mathbf{2}^+$ in dichloromethane at room temperature (Scheme 1). The major part, however, is converted to some unidentified species which display very broad ^1H NMR signals. These species are likely paramagnetic, but their nature remains unclear. No EPR signals (X-band) could be detected, neither could NMR spectroscopy be used for their characterization. (Perhaps these species are triplet binuclear in nature, which would at least explain the absence of EPR signals. Two possible ways of obtain-



Scheme 1. Reaction of $[(\kappa^3\text{-}Me_2\text{-bpa-Me})Ir^I(C_2H_4)]^+$ with dioxygen in CH_2Cl_2 at rt.

ing such a triplet: (1) by having two unpaired electrons on iridium or a (weak) ferromagnetic coupling between a superoxide fragment and an iridium(II) radical, or (2) by having a species that has a diamagnetic ground state (i.e., no EPR signal at 20 K), but that thermal occupation of a triplet state (as described above) is possible (as a consequence no or very broad NMR signals at rt).) These (paramagnetic) species might be the result of electron transfer (ET) reactions to dioxygen.

We now monitored the reaction of **1**$^+$ with dioxygen by mass spectrometry, and observed a much cleaner reaction compared to the reaction in solution. Gas-phase kinetics (vide infra) are clearly consistent with a bimolecular reaction, first order in both **1**$^+$ and O_2.

In the octopole region, hardly any reaction products were detected upon collision of the Me_2-bpa-Me iridium mono-ethene complex **1**$^+$ with dioxygen. Only up to 0.4% (of the TIC) of complex **2**$^+$ was obtained at near-zero collision energies (Fig. 1a). The yield of **2**$^+$ depends on the dioxygen pressure. An explanation for this can be that the formation of the encounter complex between the iridium–ethene complex and O_2 is the rate-determining step, which would be expected for an associative reaction mechanism. At higher collision energies, fragmentation of **1**$^+$ sets in (Fig. 1b).

CID experiments, in which **2**$^+$ was collided with argon (Fig. 2), show that this complex preferably loses ethene. And from additional CID experiments (argon) with both the peroxo-complex and the mono-ethene complex it is clear that both $\{[(N_3)Ir(O_2)]\text{-}H_2O\}^+$ and $\{[(N_3)Ir]\text{-}CH_4\}^+$ are daughters of the peroxo (and thus also the peroxo-ethene) complex, not of the mono-ethene complex **1**$^+$.

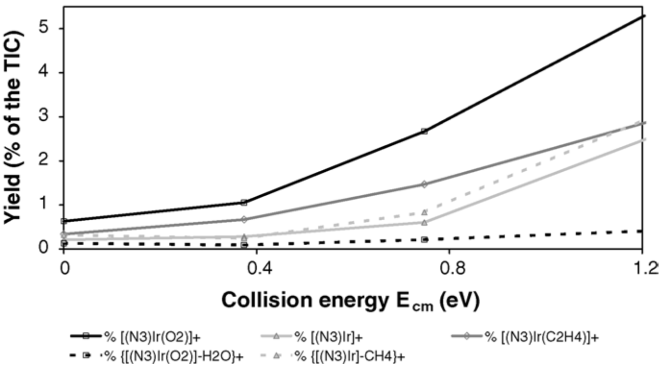


Fig. 2. Yields of ions formed upon collision of **2**$^+$ with 0.2 mTorr argon in the octopole.

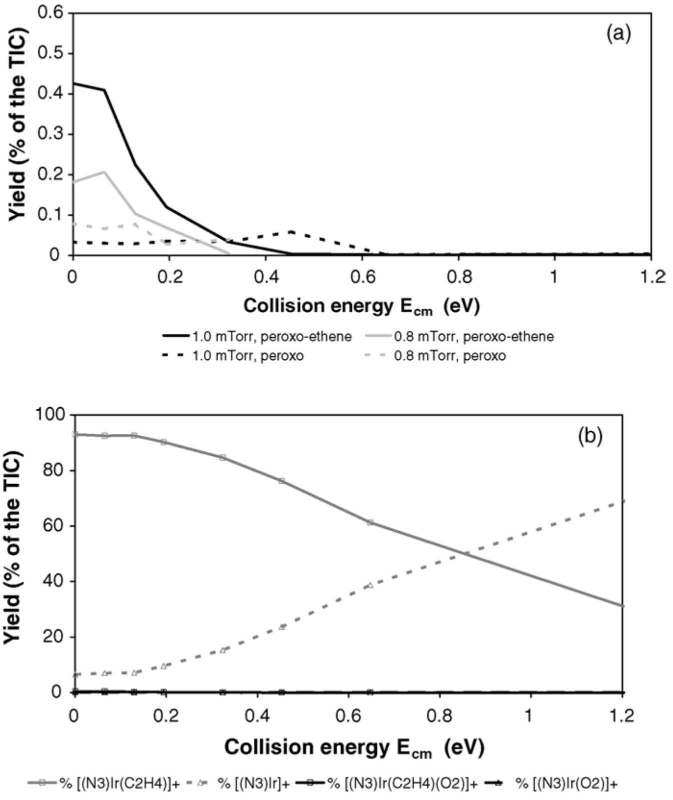


Fig. 1. (a) Yield of peroxo-ethene complex **2**$^+$ and of the peroxo-complex (fragment of **2**$^+$) upon collision of **1**$^+$ with dioxygen in the octopole region at two different dioxygen pressures. (b) Yield at 1.0 mTorr dioxygen pressure of all reaction products upon collision of **1**$^+$ with dioxygen in the octopole region (yield of **2**$^+$ and the peroxo negligible).

In other words, on the basis of the known fragmentation behavior of **1**$^+$ and **2**$^+$ we can conclude that at higher collision energies no associative reaction (to form **2**$^+$) takes place anymore in the octopole region; instead dissociative reactions (to form only $[(Me_2\text{-bpa-Me})Ir]^+$) have taken over.

When this same reaction with dioxygen was performed in the 24-pole region, the yields of peroxo-ethene complex **2**$^+$ were substantially higher. The amount of peroxo-ethene complex formed increases with higher dioxygen pressures (Fig. 3). **1**$^+$ is practically fully converted to **2**$^+$ at 150 mTorr. A very small amount (up to ca. 0.05% of the TIC) of peroxo-complex, most likely a daughter of **2**$^+$, was visible in the spectra as well.

Previous gas-phase studies of the oxidation of $[M(bipy)_2]^{2+}$ (M = Cr, Ru) and $[M(bipy)_2]^+$ (M = Co, Ni) with molecular oxygen by McKenzie and co-workers [30] also showed formation of the respective peroxo-species, in agreement with the solution and solid-state chemistry. The yield in these experiments was limited by the dioxygen pressure (ca. 3 mTorr). Uggerud and co-workers determined rate coefficients for the formation of adduct ions in ion–molecule reactions between $[M(bipy)_2]^{2+}$ (M = Cr, Ru, Os; bipy = bipyridine) and molecular oxygen [31]. Dioxygen leads to the formation of adducts of the general formula $[M(bipy)_2(O_2)]^{2+}$. Experiments showed that the adduct

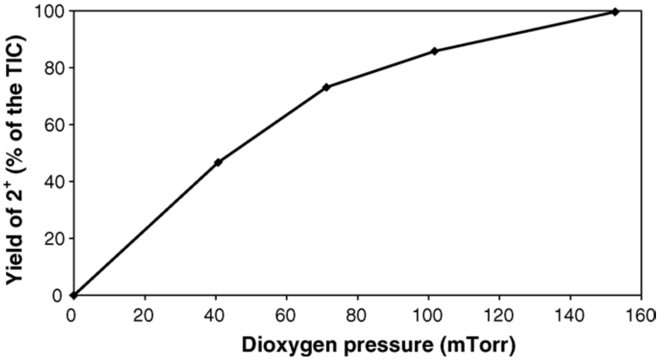


Fig. 3. Dependence of the yield of **2**$^+$ on the dioxygen pressure in the 24-pole region.

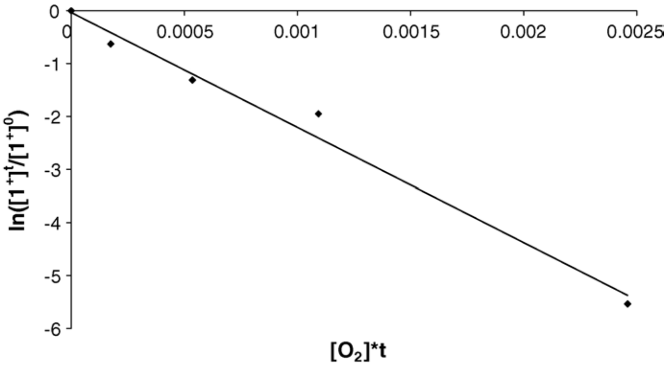


Fig. 4. Plot of $\ln [\mathbf{1}^+]^t/[\mathbf{1}^+]^0$ vs. the $[O_2] \times t$ in the conversion of $\mathbf{1}^+$ to $\mathbf{2}^+$ showing first order kinetics in both $\mathbf{1}^+$ and O_2.

yield does not increase with substrate pressure. These workers observed only a low efficiency for O_2-adduct formation compared to reactions with olefins or alkanes, which is indicative of a weak binding between these doubly charged metal complexes and dioxygen. However, these results were obtained with the very low collision gas pressures (around 10^{-7} mbar) within the FTICR setup.

The fact that in our case a peroxo-ethene complex is obtained in such high yields in our experiments indicates that in the 24-pole, where mild collision conditions prevail, reactions take place via associative pathways, usually accompanied with low reaction barriers. A dissociative pathway, associated with higher activation energies, is suppressed at near-zero collision conditions, as can be seen from the negligible amounts of “naked” peroxo-complex formed.

Assuming a bimolecular reaction mechanism, the reaction should follow the rate law

$$\ln\left(\frac{[\mathbf{1}^+]^t}{[\mathbf{1}^+]^0}\right) = -k_{\mathrm{add}}[\mathrm{O}_2]t$$

where k_{add} is the rate constant for adduct formation between $\mathbf{1}^+$ and an O_2 molecule, t the time in s and $[O_2] = P/RT$ (in mmol/l).

When a linear regression is applied to $\ln([\mathbf{1}^+]^t/[\mathbf{1}^+]^0)$ versus $[O_2] \times t$, a straight line results with a standard deviation of 0.98, as can be seen from Fig. 4. This is consistent with a bimolecular reaction path in the gas phase that is first order in both $\mathbf{1}^+$ and O_2. Based on Monte Carlo simulations using Langevin theory for the calculation of the number of collisions an ion undergoes we arrive at retention times in the 24-pole in the range of 0.1–0.3 s (40–150 mTorr). From this estimate, a pseudo-first order rate constant (steady-state approximation for $[O_2]$) of 2.2×10^6 cm^3 mol^{-1} s^{-1} follows for the reaction of $\mathbf{1}^+$ with O_2 in the gas phase.

Although the reaction conditions in the 24-pole region with a collision frequency of up to 10^7 s^{-1} resemble solution-phase conditions (collision frequency 10^9 s^{-1}) very closely, at least as far as “normal” gas-phase ion–molecule reactions are concerned, the gas-phase reactivity of $\mathbf{1}^+$ towards O_2 is much more selective compared to the reported solution-phase reaction [29]. In solution it was not possible to isolate more than 25% peroxo-species. The poor selectivity in solution could well be related to formation of (albeit unidentified) paramagnetic species formed by ET reactions between Ir^{I} and O_2 to give highly reactive $\mathrm{Ir}^{\mathrm{II}}$ and superoxide/peroxide species. In solution, such charge separation reactions are relatively easy to accomplish because the resulting charged species are readily stabilized by solvent interactions. In the gas phase, however, such ET reactions are much less likely to occur.

Formation of an iridium(II)–ethene/O_2^- ion pair is rather unlikely because charge separation is a kind of worst-case scenario in the gas phase. Even if electron transfer and formation of the +2/−1 ion pair were to occur, the ions are not going to separate spontaneously in the gas phase under these conditions, and thus the dicationic iridium(II) species will never be detected by MS. ET could still play a role as the first step of a series of reactions occurring *within* the ion/molecule pair, but this cannot be distinguished from any other direct O_2 binding. We think that the elimination of any charge separation steps from the possible reaction sequences in the reaction of $\mathbf{1}^+$ with O_2 gives a plausible explanation for the improved selectivity in the gas phase compared to solution.

Interestingly, in the octopole region $\mathbf{2}^+$ can only be detected at near-zero collision energies (the same energetic conditions as in the 24-pole). At higher collision energies no associative reaction takes place; instead dissociative reactions begin to occur. The lower yield of $\mathbf{2}^+$ upon collision with dioxygen at near-zero collision energy in the octopole region compared to that the 24-pole region can be explained by the lower collision frequency. This reduces both the amount of reactive collisions and the possibility of dissipation of excess energy of the product ions, resulting in excessive product fragmentation.

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