The Activation of O_2 at Ruthenium Complexes: Catalytic Chlorination of Unsaturated Organic Substrates within the System O_2/HCl/H_2O

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Abstract: A solution of $RuCl_3$ in concentrated hydrochloric acid is capable of chlorinating aromatic compounds catalytically, if O_2 is present as the oxidizing agent (brominations can be achieved in hydrobromic acid). When olefins are chosen as substrates, two Cl atoms are added to the double bond in an *anti* fashion, while hydrochlorination products are formed simultaneously. According to the products observed in both types of reactions for various substrates in this 3-phase system, the halogenations proceed via electrophilic pathways.

Keywords: acids; catalysis; halogenations; oxygen; ruthenium

In 1966 Halpern et al. showed that ruthenium(III) chloride dissolved in concentrated hydrochloric acid catalyses homogeneously the isotopic exchange between D_2 and H_2O.[1] This finding prompted us to investigate, whether the same is possible when employing C_6D_6 instead of D_2 as the substrate, i.e., whether ruthenium chloride is also capable of activating C-H/C-D bonds. We found, that D/H exchange is negligible under the conditions employed by Halpern. However, on raising the temperature to 145 °C in the presence of air an interesting observation was made: a small fraction of the benzene was oxidized to give *chlorobenzene*. As selective transformations of C-H bonds into more reactive, functionalized moieties are naturally of interest,[2] this result stimulated a more detailed exploration of this system.[3]

It is known that chlorobenzene can be obtained in technical amounts by streaming benzene, HCl, and air over a copper contact (this so-called "oxychlorination" process is in fact limited to the substrate benzene). It is also known that aromatic hydrocarbons can be oxidized in the presence of a Lewis acid by Cl_2 or Br_2 to give the corresponding halogenated compounds.[4] However, it is obviously of interest to use HCl (HBr) or halide salts as sources for the halogen atoms in such reactions and to employ oxidizing agents that are more easily prepared and handled than Cl_2 and Br_2. Some groups have therefore used reactive metal halides as sources for halogen.[5] Others employed stoichiometric amounts of nitrate, nitrite, NO, and NO_2 as oxidizing equivalents in the presence of HCl (HBr) and catalytic amounts of certain metal compounds to halogenate aromatic compounds.[6] The latter process can also be performed in a way that makes the addition of a metal catalyst redundant.[7] All these procedures have the disadvantage of the aggressive gases NO and NO_2 being present in the reaction vessel, however, as they are either used as oxidants or liberated from nitrite or nitrate, and this in turn often leads to contaminations by the corresponding nitro compounds. Thus, having made the finding described above, naturally the question arose, whether $RuCl_3$ can act as a precatalyst in hydrochloric acid for the oxidation of benzene to chlorobenzene, when O_2 is used as the oxidizing agent.[8]

An experiment as outlined above was therefore performed in an atmosphere of *pure oxygen*, i.e., $RuCl_3$ dissolved in concentrated hydrochloric acid was placed into a high pressure tube, benzene was added and the atmosphere above the two phases was replaced by oxygen gas. After closing the tube and heating it to 145 °C for 17 h an analysis of the organic phase showed that 1.5 moles (Table 1) of benzene per mole of ruthenium had been oxidized to give chlorobenzene (Scheme 1)![9] If the aqueous and organic phases are separated, the aqueous phase can be reused to oxidize a fresh sample of benzene; there are no signs of catalyst deactivation. Other aromatics can be oxidized as well. Toluene, for instance, reacts even faster than benzene (Table 1): applying the same procedure as for benzene 9 moles of toluene per mole of Ru are chlorinated giving *ortho*- and *para*-chlorotoluene in a ratio of 2.6:1 within 15 h (Scheme 1), i.e.,

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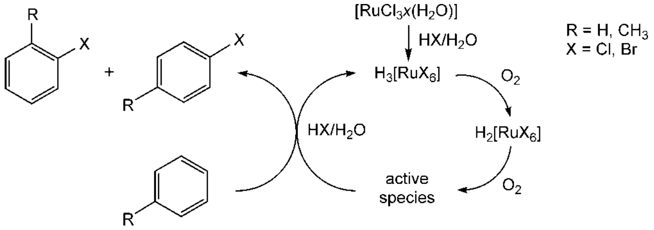
Table 1. Turnover numbers in moles per mole of Ru employed as observed for the halogenation of the given substrates under the conditions specified in the experimental part.

Substrate/Acid/Time/Atmosphere	Turnover	Products
17.4 mmol benzene/HCl/17 h/air	0.3	chlorobenzene
17.4 mmol benzene/HCl/17 h/O_2	1.5	chlorobenzene, dichlorobenzene[a] (*ortho/para* = 0.5) 32% conversion
47.4 mmol toluene/HCl/15 h/O_2	9.0	chlorotoluene (*ortho/para* = 2.6) 70% conversion
17.4 mmol benzene/HBr/17 h/O_2	9.4	bromobenzene,[a] dibromobenzene (*ortho/para* = 0.4) quantitative conversion

[a] Formed only in insignificant amounts (< 1% of the converted substrate).



Scheme 1. Catalytic halogenations of aromatic compounds with the system $HX/H_2O/O_2$.

the turnover frequency is calculated to 0.6 h^{-1}. The radical-derived products benzyl chloride and phenyltolylmethane are obtained in addition, but amount to only 3 and 6%, respectively, of the converted toluene. Although no problems were encountered during our experiments, working in a pure O_2 atmosphere naturally bears certain risks, and it should be noted in this context, that alternatively diluted O_2 (e.g., in form of air) can be used when the pressure is increased to 4 bar; the reaction then has to be performed in an autoclave but comparable results are obtained.

Olefins can be chlorinated within this system, too: Under our standard conditions, cyclododecene is quantitatively converted to chlorocyclododecane (the HCl addition product), 1,2-dichlorocyclododecane (the formal Cl_2 addition product), and higher chlorinated products (which are formed as *main* products, when this olefin is treated directly with free Cl_2 in the absence of $RuCl_3$) in the ratio 2.4:3.8:1.3. *trans*-5-Decene gives 5-chlorodecane as well as *meso*-5,6-dichlorodecene in a ratio of 1:1.3. The stereochemistry of the dichlorination is thus identical with that of a Cl_2 oxidation, which excludes a mechanism involving radicals and argues for an electrophilic transfer of a chloronium ion in the primary step.

Further experiments showed that (i) saturated hydrocarbons are not oxidized, (ii) the addition of $CuCl_2$ to the system is disadvantageous, and (iii) in contrast to $RuCl_3$, $FeCl_3$ fails to catalyze the reaction efficiently. On the other hand, $RuCl_3$ can also affect *brominations* if hydrobromic acid is used as a solvent instead of hydrochloric acid (Scheme 1, Table 1): Under the standard conditions as outlined above (with benzene as the substrate) 9.4 moles of bromine atoms are incorporated per mole of Ru yielding bromobenzene and dibromobenzene (*ortho/para* = 0.4); if benzene is employed only in a five-fold excess with respect to $RuCl_3$ (as in the corresponding experiment specified in Table 1) *para*-dibromobenzene becomes the main product of the reaction, crystallizing in pure form at the bottom of the reaction vessel after cooling to room temperature. *In the absence of $RuCl_3$ hardly any bromination of the benzene is observed!*

What is the mechanism of this catalysis like? In order to investigate this question, experiments were carried out in the absence of any organic substrate. If $RuCl_3$ is brought into concentrated hydrochloric acid it enters into a complex equilibrium, that contains $H_3[RuCl_6]$ as the main species.[10] It turned out that O_2 oxidizes the ruthenium centers of such solutions to the oxidation state +IV in the primary step: after performance of an experiment under standard conditions, addition of KCl leads to the precipitation of $K_2[RuCl_6]$. However, the Ru(IV) species thus formed ($H_2[RuCl_6]$?) cannot be used as a reagent for the chlorination of any substrate: after treatment of a $RuCl_3/HCl/H_2O$ mixture with O_2 at 145 °C and subsequent degassing, the solution it is not capable of oxidizing toluene or benzene stoichiometrically. This means that the Ru(IV) species is further oxidized at 145 °C in the presence of O_2 to give an active species (Scheme 1), which performs the reaction. This species [possibly a Ru(V) or a Ru(VI) oxychloride or peroxychloride] probably has only a very short life time, decomposing to give the Ru(IV) compound and an oxidized species such as Cl_2 in the absence of any substrate. It proved difficult to detect free Cl_2 during the reactions, but in case of the brominations elemental Br_2 was clearly visible in the gas phase (it should be noted that no Br_2 formation is observed when hydrobromic acid is heated in an O_2 atmosphere in the absence of $RuCl_3$). With regard to the products obtained in the chlorination of toluene, the Cl transfer must be electrophilic (and not radical-like), since only insignificant amounts of benzyl chloride are detected among the products.[11] The same conclusion can be derived from the facts that the reaction rate is increased on going from benzene to toluene and that Cl_2 addition proceeds in the case of *trans*-5-decene stereospecifically in an *anti* fashion.

In summary, it is thus likely, that the active species either transfers Cl^+ or liberates Cl_2 which is, in turn, activated by the Ru(IV) centers in solution to chlorinate the substrates. In the latter case, the $RuCl_3$ could be regarded as a Friedel–Crafts-type catalyst, which, however, is capable of simultaneously catalyzing the O_2-oxidation of HCl to Cl_2 and which consequently has great advantages from economical and practical points of view (see above) in comparison to the Fe salts usually employed in FC-halogenations.

Rather remarkably, the active species can apparently not be formed in the presence of a cation other than H^+, so that, for instance, the potassium salt $K_2[RuCl_6]$ is inactive as a catalyst!

Further research will concern the investigation of the scope of the catalysis as well as its optimization: currently, the system involves three phases (aqueous, organic, and gaseous), and it can be envisaged that the TON will further increase with an enlargement of the interfaces. Moreover, interest focuses on the identification of the active species being formed in concentrated hydrochloric acid at 145 °C in an oxygen atmosphere.

Experimental Section

Typical Procedure

$RuCl_3(H_2O)_x$ (1 g, ca. 3.7 mmol) was dissolved in 50 mL of concentrated hydrochloric (or hydrobromic) acid. The solution was filled into a high pressure tube (350 mL volume, d = 4.5 cm) equipped with a greaseless stopcock and a magnetic stirrer bar. The substrate was added (aromatics in the amounts specified in Table 1; in case of the olefins, 17.4 mmol), the mixture frozen to –196 °C, and the vessel evacuated. The tap of the tube was closed and, after annealing, O_2 gas was allowed to enter the tube until the overall pressure amounted to ca. 1 bar. The tap was closed again and the tube placed into an oil bath (so that the vigorously stirred liquid phase was covered by the oil), which was heated to 145 °C subsequently for 17 h. The mixture was cooled to room temperature, and a part of the organic phase was removed and investigated by means of GC/MS and NMR spectroscopic measurements. To determine yields in the cases of toluene and cyclododecene (or for the bromination of benzene), the two-phase mixtures were extracted with pentane, from which the products were isolated by distillation. The aqueous phase could then be reused for a new experiment.

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References and Notes

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[2] See, for instance: B. A. Aendtsen, R. G. Bergman, T. A. Mobley, T. H. Peterson, *Acc. Chem. Res.* **1995**, *12*, 154; A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; E. L. Muetterties, *Chem. Soc. Rev.* **1983**, *12*, 283; H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. Dubois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. N. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953.

[3] C. Limberg, *German patent application* 10026138.8 (Applicant: BASF Aktiengesellschaft) filed in 2000.

[4] J. March, *Advanced Organic Chemistry*, 3rd ed., John Wiley and Sons, Chicester, **1985**, p. 47.

[5] for a recent summary, see: H. A. Muathen, *Tetrahedron* **1996**, *52*, 8863.

[6] C. M. Selwitz (Gulf Research and Development Company), *US Patent* 3,591,645.

[7] V. A. Notaro, C. M. Selwitz (Gulf Research and Development Company), *US Patent* 3,591,644.

[8] Only recently it was reported that $RuCl_3$ in CF_3CO_2H catalyses the oxidation of alkanes to give ketones and acetates using *peracids* as oxidants: N. Komiya, S. Noji, S.-I. Murahashi, *Chem. Commun.* **2001**, 65.

[9] With increasing yield of chlorobenzene, i.e., with increasing reaction time, enlarged amounts of *ortho*- and *para*-dichlorobenzene are formed in a ratio of ca. 1:2.

[10] A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 91st – 100th edn., Walter de Gruyter, Berlin, New York, 1985, p. 1192.

[11] In agreement with these results, it was found that, after the reaction of Ph_3CH, no Ph_3CCl could be detected.