Effective Ruthenium-catalysed Oxidation of Chlorinated Olefins by Monopersulfate in Aqueous Medium

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In aqueous medium, in the presence of a surfactant agent and of catalytic amounts of ruthenium derivatives, monopersulfate effectively oxidizes α-chlorinated olefins to hydrochloric acid and the appropriate carboxylic acid and/or carbon dioxide, with rates in excess of 100 turnover min^{-1} at room temperature.

The deep oxidation of chlorinated organics to carbon dioxide and hydrochloric acid with no emission of undesirable materials is a major question addressed by environmental chemistry research. Oxidation catalysts, which operate in the gas phase at lower temperatures than are required for thermal combustion, can be an important tool in overcoming the chemical inertness and thermal stability of this class of compounds.[1] A number of catalysts comprising high-valent metal oxides promote the complete oxidative degradation of chlorinated organics at temperatures as low as 250 °C.[2] Also homogeneous transition-metal catalysts, which are close models to mono-oxygenase enzymes used by the biological systems for the oxidation in the liquid phase of a wide variety of xenobiotics, including chlorinated organics,[3] have been successfully tested in the liquid phase[4] and may become a mild alternative to the present energy-spending technology of disposal.

As a continuation of our previous studies on the use of ruthenium complexes for the oxygenation of unsaturated hydrocarbons,[5] we describe herein a novel effective procedure for the oxidation at ambient temperature of a representative series of α-chloro-olefins by aqueous monopersulfate in the presence of catalytic amounts of the dimethyl sulfoxide-'solvated' $[Ru^{II}(H_2O)_2(Me_2SO)_4](BF_4)_2$ ion,[6] a convenient chlorine-free and water-soluble precursor of ruthenium tetraoxide.† Our investigations were typically conducted with $KHSO_5$ 50 mmol dm^{-3} in aqueous medium (pH *ca.* 3) in the presence of the catalyst (0.1 mmol dm^{-3}) and an appropriate amount of the surfactant agent cetyltrimethylammonium hydrogensulfate (usually 2.5% m/m),[7] which was added in order to 'dissolve' the hydrophobic substrates completely at 10 mmol dm^{-3} concentration.‡ To the contrary the presence of an apolar organic phase such as carbon tetrachloride or dichloromethane,[8] results in a dramatic decrease of the rates of the oxidation of the α-chloro-olefins up to three orders of magnitude. Note that in the aqueous emulsion conditions described above oxidations of the substrates proceed at exceedingly high rates even in the absence of the ruthenium catalyst, contrary to that observed with the two-phase systems, where no reaction is observed under the same concentration conditions (Fig. 1).

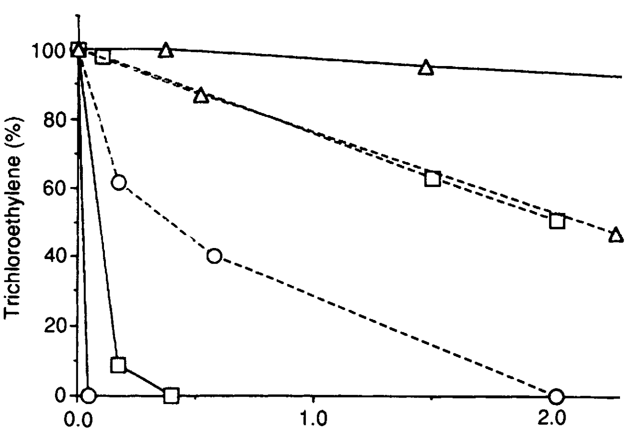
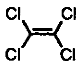
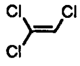
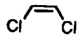
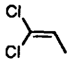
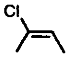
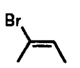


Fig. 1 Time courses for the oxidation of trichloroethylene, 10 μmol, with 1 cm^3 of aqueous $KHSO_5$ 50 mmol dm^{-3} (——) or NaClO 50 mmol dm^{-3} (– – –) in the presence of: □, surfactant (25 mg); ○, surfactant (25 mg) and catalyst (0.1 μmol); △, catalyst (0.1 μmol) and CCl_4 (1 cm^3). Surfactant: cetyltrimethylammonium hydrogensulfate; catalyst: $[Ru^{II}(H_2O)_2(Me_2SO)_4](BF_4)_2$; 20 °C.

Perchloroethylene is quantitatively, although slowly, converted into carbon dioxide and hydrochloric acid, whereas the other examined substrates, *i.e.* trichloroethylene and *cis*-1,2-dichloroethylene, 1,1-dichloropropene, 2-chlorobut-2-ene and 2-bromobut-2-ene, also yield substantial amounts of formic or acetic acid, as described in detail in Table 1.§ In no case was carbon monoxide detected among the products.[9] Finally, a number of polychlorinated alkanes have also been detected in trace amounts, together with their oxidized counterparts, which are clearly produced upon addition of Cl_2 across the double bond of the starting unsaturated substrates.

Table 1 Ruthenium-catalysed oxidation of α-chlorinated alkenes by monopersulfate[a]

Substrate	Rate[b]	HCl[c] (%)	CO_2[d] (%)	Other products[d] (%)
	0.03 (0.007)	98	99	
	⩾6 (1.3)	85	40	HCO_2H (55) $CHCl_3$ (5)
	⩾5 (0.4)	85	45	HCO_2H (45) $CHCl_3$ (5) $ClCH_2CO_2H$ (5)
	⩾5 (3.0)	80	42	CH_3CO_2H (35) $CH_3CHClCO_2H$ (16) CH_3COCCl_3 (5) $CH_3CHClCCl_3$ (2)
	⩾6.5 (1.5)	850	30	CH_3CO_2H (60) $CH_3CHClCOCH_3$ (8) $CH_3CHClCCl_2CHO$[e] (1) $CH_3CHClCCl_2CO_2H$[e] (1)
	⩾11 (2.0)	85[f]	30	CH_3CO_2H (60) $CH_3CHBrCOCH_3$ (8) $CH_3CHBrCBr_2CH_3$ (< 0.5) $CH_3CHBrCBr_2CHO$[e] (< 1) $CH_3CHBrCBr_2CO_2H$[e] (< 1)

[a] Reactions run at 20 °C in water (1 cm^3) containing the substrate (10 mmol dm^{-3}), $[Ru^{II}(H_2O)_2(Me_2SO)_4](BF_4)_2$ (0.1 mmol dm^{-3}), cetyltrimethylammonium hydrogensulfate (25 mg), and oxone (15.4 mg, corresponding to 50 mmol dm^{-3} $KHSO_5$). [b] Disappearance rate, units: mmol dm^{-3} min^{-1}. In parentheses conversion rates in the absence of added catalyst. [c] Yields after 2 h reaction (chlorine balance, mol per mol). [d] Yields after 2 h reaction (carbon balance, mol per mol). [e] Products detected after 24 h reaction. [f] HBr.

Indeed, during the oxidation, *i.e.* in the presence of an excess of oxidant, the dominant species for chlorine appears to be Cl_2 and not HCl, as expected on the basis of the large E° value, 1.8 V, reported for the HSO_5^-/HSO_4^- couple.[10] Dichlorine is rapidly and completely replaced by HCl when all of the persulfate is consumed: at this point the yellow solutions of ruthenium tetroxide[11] suddenly turn brown–violet with formation of a strongly reducing ruthenium(IV) species, which can be considered the 'resting' state of the catalyst.[12]

The method described in this paper presents several advantages because it requires easily available reagents and it readily occurs under extremely simple experimental conditions, in high yield and also at very low concentrations of the substrates (oxidations exhibited first-order dependences to the substrates, to the catalyst and to the oxidant in the concentration ranges explored, *i.e.* 10–0.1, 1–0.01 and 500–5 mmol dm^{-3}, respectively); the positive role played by the surfactant may depend on several factors and merits further investigations.

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Footnotes

† In the presence of $KHSO_5$ the $[Ru^{II}(H_2O)_2(Me_2SO)_4](BF_4)_2$ complex is rapidly converted into RuO_4 with complete oxidation of dimethyl sulfoxide to dimethyl sulfone. Direct experiments showed that the catalytic system can be reused several times to promote the conversion of fresh substrate with fresh persulfate at comparable rate.

‡ Under the same conditions the reactions also proceed when oxone is replaced by sodium hypochlorite. Magnesium monoperoxyphthalate and potassium (di)persulfate were completely inactive, whereas hydrogen peroxide underwent rapid disproportionation with little or no oxidation of the substrates. The reactions with sodium hypochlorite have not been investigated in detail, owing to the possible interference by hypochlorous acid, a well-known chlorinating agent.

§ The identities and the quantities of the organic derivatives produced upon the oxidations were determined by GLC- and HPLC-MS analysis of the reaction mixtures; HCl was measured by argentometric titration and the evolved CO_2, previously captated into a $Ba(OH)_2$ solution, was quantitated by retrotitration with HCl.

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