

Ruthenium Tetroxide Destroys Dioxin

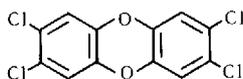
THE OXIDATIVE CONTROL OF AROMATIC POLLUTANTS

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Ruthenium tetroxide is a powerful oxidising agent and has been widely used in laboratories for small scale oxidations as it reacts rapidly with most oxidisable organic functional groups at ambient temperature (1). In such conditions a solution of ruthenium tetroxide in carbon tetrachloride is often employed, the organic solvent taking up the ruthenium tetroxide as it is generated by the oxidation of ruthenium trichloride with aqueous hypochlorite. Initially the ruthenium tetrachloride solution is yellow, and a clear indication that the oxidative reaction is taking place is given by the precipitation of black insoluble ruthenium dioxide. As the hypochlorite is capable of continuously regenerating the ruthenium tetroxide from the hydrated dioxide, only catalytic quantities of ruthenium compounds are required.

Potassium permanganate is used commercially for the oxidative control of air pollutants by wet scrubbing; however a solution of ruthenium tetroxide—being more potent—is an attractive alternative oxidant for persistent aromatic pollutants. An illustration of its effectiveness is provided by the reported destruction of polychlorodibenzodioxins (2), including the now notorious TCDD that was accidentally released at Seveso in Italy in 1976.



2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

The electron-donating oxygen atoms of the ruthenium compound enhance the oxidation of this structure: the simple phenols and their ethers all react extremely rapidly, but chlorosubstituents have a stabilising effect. Clearly the solvent employed must be considerably inactivated; nitromethane can sometimes

be used with advantage. The rate of these oxidations is approximately doubled for every 10°C rise in temperature.

Ruthenium tetroxide is toxic, but less so than osmium tetroxide; its solutions may be safely handled in closed systems or in fume cupboards. A 2 per cent aqueous solution can be safely obtained from warm ruthenium dioxide/hypochlorite by its entrainment in a stream of air followed by collection in a cooled trap. In water there is considerable rate enhancement compared to reactions in carbon tetrachloride.

Potential Industrial Applications

From a practical point of view, two specific examples of aqueous oxidations indicate the industrial possibilities.

Mono- and dichlorophenols are oxidised extremely rapidly. The destruction of pentachlorophenol is best accomplished by the action of the tetroxide on the phenoxide. This reaction requires treatment for 18 hours at 30°C, when complete fragmentation occurs giving carbon dioxide and chloride ions as sole products (3).

A group of thiophene odorants at concentrations of about 10⁻³ grams/litre requires treatment for hundreds of minutes with saturated permanganate at 22°C. When ruthenium tetroxide is used on comparable concentrations the disappearance time is reduced to a few minutes (4).

References

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