An investigation of potassium μ-oxobis[pentachlororuthenium(IV)] in hydrochloric acid solution under microwave irradiation

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A study of the ruthenium(IV) and (III) species in HCl solution under microwave irradiation shows a decrease in hydrolysis time, depolymerisation and reduction of ruthenium(IV) to ruthenium(III) by an order of magnitude, as compared with conventional heating of solutions in a boiling water bath.

A knowledge of the forms of existence of platinum group metals in solution is fundamental to any elaboration of their photometric, luminescence, chromatographic or electrochemical properties. In this study, the parameter tested depends on the initial form of the metal in solution. The main difficulties in an investigation of the hydrolysis, depolymerisation, redox- and other processes involving the platinum-group metals arise from their low transformation rates, rather than the variety of their forms. We supposed that such processes would be intensified in a microwave field as with the well-known solid matrix decomposition reaction.[1] In the present work, ruthenium(IV) and (III) states in HCl solution were studied as a model.

A freshly-prepared 8×10^{-5} M solution of potassium μ-oxobis[pentachlororuthenium(IV)] $K_4[Ru_2OCl_{10}]$ in 6 M HCl was studied. Irradiation of the solution ($V = 10$ ml) was carried out in a MLS-1200 MEGA microwave unit from Milestone (Italy) in fluoropolycarbon autoclaves ($C_{HCl} = 0.6, 2, 4, 6, 8, 10$ M). The process was controlled by UV-VIS molecular absorption spectroscopy.

The percentage recovery of the ruthenium complexes was calculated by well-known approaches to the analysis of multicomponent mixtures.[2] This is based on a comparison of the absorption characteristics of irradiated solutions and literature data on the absorption spectra of previuosly identified states. The data for ruthenium(IV) and (III) states in HCl solution under microwave irradiation, involving heating of the solutions with a boiling water bath (98 °C) and at room temperature (20 °C), are summarized in Table 1. Only the existence of forms of ruthenium with a percentage > 15% are presented. The areas of predominance of certain forms (≥ 90%), and therefore methods and C_{HCl}, are marked. It was shown that hydrolysis time, depolymerisation and reduction of ruthenium(IV) decreased to several minutes as compared with hours (heating the reaction mixture with a boiling water bath), or even months and years (20 °C). Moreover, an increase in the power and/or time of microwave irradiation results in an increase in the rates of the processes studied (depolymerisation at a higher degree) and their proceeding to completion.

To intensify the processes in a microwave field, an increase in irradiation power with a simultaneous increase in irradiation time seems reasonable. However, in closed working systems, autoclaves are automatically exposed (to provide safe functioning) which results in wastage of part of the sample. We proposed a new microwave irradiation procedure that increases microwave irradiation efficiency in closed systems, which we term 'multistep irradiation'. This consists of conventional irradiation of a solution at the maximum possible power of the unit and time (*i.e.*, conditions of maximum recovery of the products), at which autoclave exposure does not take place. The autoclaves are then cooled and repeatedly irradiated under extreme conditions. This increases the recovery of the products and decreases the reaction time. The proposed procedure allows an increase in the recovery of $[RuCl_6]^{3-}$ (10 M HCl) and the 'cationic form' of ruthenium(IV) (0.6 M HCl) from 70% to 95% and from 60% to 98%, respectively, at maximum possible power (1000 W) and duration of experiment (5 min) using a (5+5+5) min mode. A change in microwave irradiation parameters and HCl concentration allowed us to obtain solutions with predominant forms, such as $[RuCl_6]^{2-}$ (95%) and $[(RuOH)_2(OH)_2]^{4+}$ (98%). This is impossible when heating initial solutions with a boiling water bath.

Hydrolysis of $[Ru_2OCl_{10}]^{4-}$ (20 °C, 0.6 M HCl) without microwave irradiation and with heat removal with flowing cold water and liquid nitrogen was studied. The composition of solutions after 1 h is: $[Ru_2OCl_{10}]^{4-}$ (80%), $[Ru_2O(H_2O)_2Cl_8]^{2-}$ (20%); $[Ru_2O(H_2O)_2Cl_8]^{2-}$ (80%), $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ (20%) and $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ (90%), $[Ru_2O(H_2O)_2Cl_8]^{2-}$ (10%). Based on the difference in recovery of the most hydrolysed form, $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ (*i.e.*, 90% in the case of heat removal with nitrogen; 20% in the case of heat removal with water; 0% without irradiation), we conclude that microwave irradiation directly affects (*i.e. via* non-thermal effects) the process under investigation.

Thus, hydrolysis, depolymerisation and reduction of ruthenium(IV) were accelerated dozens of times under microwave irradiation, as compared with traditional convection heating of

Table 1 Proposed states of ruthenium(IV) and (III) in hydrochloric acid solution with respect to C_{HCl}, power of microwave irradiation, temperature and time. Initial form $K_4[Ru_2OCl_{10}]$, $C_{Ru} = 8\times10^{-5}$ M.

Conditions	Concentration of HCl/M					
	0.6	2	4	6	8	10
5 min, 150 W	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ 80% $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 20%	$[Ru_2OCl_{10}]^{4-}$ 95%	$[Ru_2OCl_{10}]^{4-}$ 95%	$[Ru_2OCl_{10}]^{4-}$ 95%	$[Ru_2OCl_{10}]^{4-}$ 95%	$[Ru_2OCl_{10}]^{4-}$ 95%
5 min, 500 W	$[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 85%	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ 65% $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 35%	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ **90%**	$[Ru_2OCl_{10}]^{4-}$ 80% $[RuCl_6]^{2-}$ 20%	$[Ru_2OCl_{10}]^{4-}$ 70% $[RuCl_6]^{2-}$ 30%	$[RuCl_6]^{3-}$ 35% $[RuCl_6]^{2-}$ 35% $[Ru_2OCl_{10}]^{4-}$ 30%
5 min, 1000 W	Cationic form of ruthenium(IV) 60% $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 40%	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ 40% $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 40%	$[RuCl_6]^{2-}$ 75% $[Ru(H_2O)Cl_5]^{2-}$ 25%	$[RuCl_6]^{2-}$ **90%**	$[RuCl_6]^{2-}$ 45% $[RuCl_6]^{3-}$ 35% $[Ru_2OCl_{10}]^{4-}$ 20%	$[RuCl_6]^{3-}$ 70% $[RuCl_6]^{2-}$ 20%
1 month, without irradiation, 20 °C	$[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ **100%**	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ 50% $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 50%	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ **95%**	$[Ru_2OCl_{10}]^{4-}$ **100%**	$[Ru_2OCl_{10}]^{4-}$ **95%**	$[Ru_2OCl_{10}]^{4-}$ **95%**
9 h, without irradiation, 98 °C	$[RuCl_n(H_2O)_{6-n}]^{(3-n)+}$ (n = 1, 2) 60% Cationic form of ruthenium(IV) 20%	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ 50% $[Ru_2O_2(H_2O)_2Cl_6]^{2-}$ 50%	$[Ru_2O(H_2O)_2Cl_8]^{2-}$ 75% $[Ru(H_2O)Cl_5]^{2-}$ 25%	$[RuCl_6]^{3-}$ 35% $[RuCl_6]^{2-}$ 25% $[Ru_2OCl_{10}]^{4-}$ 25%	$[RuCl_6]^{3-}$ 65% $[RuCl_6]^{2-}$ 18% $[Ru_2OCl_{10}]^{4-}$ 17%	$[RuCl_6]^{3-}$ **90%**

solutions, though the transformation principles may be different in some cases. It is likely that the role of non-thermal effects is significant. An appropriate selection of the conditions can provide rapid synthesis of the predominant forms.

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