



Ultrasonic-assisted ruthenium-catalyzed oxidation of some organic compounds in aqueous medium



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ABSTRACT

Ultrasonic generation of ruthenium complexes $K_2[RuO_3(OH)_2]$ and $[RuO_4]$ is reported from $K_2[RuCl_5(H_2O)]$ with excess $K_2S_2O_8$ in 1 M KOH and/or with excess KIO_4 in biphasic solvent system ($H_2O/CH_2Cl_2/CH_3CN$) at room temperature. Dehydrogenation of some primary amines to nitriles and primary alcohols to their respective acids by $K_2[RuCl_5(H_2O)]$ with excess $K_2S_2O_8$ at room temperature was reported. A number of nitriles were hydrated to amides by the same catalyst system at 100 °C. The oxidation of two arenes and four alkenes to their aldehydes, ketones or acids by $K_2[RuCl_5(H_2O)]$ with excess KIO_4 using ultrasonic irradiation technique was also reported. Cyclic voltammetric, electronic and Raman spectroscopic techniques have been used to elucidate the nature of the active species present in these catalytic oxidation reactions.

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1. Introduction

Many organic transformations which involve ruthenium species as catalyst are known and well documented [1,2]. Ruthenium(III) complexes are also well known to catalyze a variety of organic transformations [3–7]. Recently, we have reported the catalytic dehydrogenation of benzylamine, *p*-methylbenzylamine and *p*-nitrobenzylamine to their respective nitriles by using $[Ru^{III}Cl_2(8-hq)_2]Cl$ in DMF as a solvent and in the presence of *N*-methyl morpholine-*N*-oxide (NMO) as co-oxidant [8]. It has been reported that the reagent $trans-[Ru^{VI}(OH)_2O_3]^{2-}/S_2O_8^{2-}$ in aqueous base dehydrated primary amines to nitriles at room temperatures and longer reaction time resulted in hydrolysis of produced nitriles to amides [9].

Herein, we report the ultrasonic generation of $K_2[RuO_3(OH)_2]$ and $[RuO_4]$ from $K_2[RuCl_5(H_2O)]$ with excess $K_2S_2O_8$ in 1 M KOH and/or with excess KIO_4 in biphasic solvent system ($H_2O/CH_2Cl_2/CH_3CN$) at room temperature, respectively. We found that ultrasonic irradiation accelerates the catalytic oxidation of some organic compounds (primary amines, nitriles, primary alcohols, arenes and alkenes) by the in situ generated ruthenium complexes. Different spectroscopic techniques were used to establish the nature of the active catalytic intermediates formed in these catalytic oxidation reactions.

2. Experimental

2.1. Chemicals and physical measurements

All chemicals and solvents were of analytical grade and used without further purification and purchased from Sigma-Aldrich Chemicals Company (USA). The IR spectra were recorded as KBr discs ($4000-400\text{ cm}^{-1}$) on a

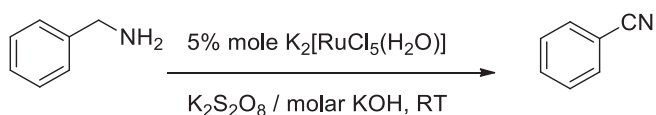
JASCO 410 spectrophotometer. Raman spectra were measured on a PerkinElmer 1760X Fourier Transform Raman instrument with 1064 nm Nd-YAG excitation with a power of 2 W, and on a Dilor LabRam Infinity instrument with 632 nm He-Ne excitation and 532 nm frequency doubled Nd-YAG excitations, as appropriate, each at 5 mW. Ultrasonication was performed in thermostated ultrasonic cleaner with a frequency of 28 kHz and a normal power of 300 W (Delta sonic 920 N° 484 (France)). The reaction flask was located in the water bath of the ultrasonic cleaner. Melting points were measured on a Buchi Melting Point B-540 instrument.

1H NMR spectra in d_6 -DMSO were recorded on a Varian Unit plus 300 MHz model using TMS as an internal standard. A computerized voltammetric analyzer CHI610C Electrochemical Analyzer controlled by CHI Version 9.09 software (CH Instruments, USA) was used for the voltammetric measurements. Home-made three printed electrodes: a working screen-printed carbon electrode (3.1 mm diameter) printed from a carbon-based ink (Electrodag 421, Acheson); a silver-silver chloride pseudo-reference electrode made from a silver-based ink (Electrodag 477, Acheson) and the auxiliary electrode from a carbon ink, were used. The UV spectra were performed by a PerkinElmer UV-VIS double beam spectrophotometer equipped with a PC for data processing UV WinLab-version 2.80.03 (PerkinElmer, USA). The spectra were recorded over the wavelength range from 200 to 650 nm at a scan speed of 240 nm/min. A quartz cell with a 1.0 cm path length was used.

2.2. Preparation of ruthenium complexes

2.2.1. Ultrasonic-assisted generation of $trans-[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ ruthenate reagent

A mixture of 50 cm^3 of 1 M KOH containing $K_2[RuCl_5(H_2O)]$ (0.0374 g, 0.1 mmol) and excess $K_2S_2O_8$ (1.4 g, 5 mmol) was irradiated



Scheme 1. Ultrasonic-assisted catalytic dehydrogenation of primary amines to nitriles.

by ultrasonic radiation for 2 min at room temperature after which the orange solution appeared. The orange solution was identified by its electronic spectrum and concentrated under vacuum to give red crystals of $K_2[RuO_3(OH)_2]$ which sealed in melting point tube.

For preparation of the solid $Ba[RuO_3(OH)_2]$, an aqueous solution of $BaCl_2 \cdot 2H_2O$ (0.0244 g, 0.1 mmol) was added to the orange solution of $K_2[RuO_3(OH)_2]$ with stirring until a red precipitate was obtained. It was centrifuged and the residue was washed three times with water and dried *in a vacuum*. Yield: 70%.

2.2.2. Ultrasonic-assisted generation of $[RuO_4]$

A solution of 50 cm^3 of distilled H_2O containing $K_2[RuCl_5(H_2O)]$ (0.0374 g, 0.1 mmol) and KIO_4 (1.1 g, 5 mmol) was irradiated by ultrasonic radiation for 2 min producing the yellow solution in water. The clear yellow solution of $[RuO_4]$ was freshly identified by its electronic spectrum.

2.2.3. Ultrasonic-assisted catalytic dehydrogenation of primary amines to nitriles by $trans-[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$

To 50 cm^3 of $trans-[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent, primary amine (2 mmol) was added, the reaction mixture turned dark green. The reaction mixture was further irradiated for half an hour, after which time, the reaction is completed since the original orange color of ruthenate reappears. The mixture was then extracted with diethyl ether ($3 \times 25 \text{ cm}^3$). The ether extracts were dried over anhydrous $MgSO_4$ then filtered and evaporated to give the product. Similarly, nitriles were hydrated to their respective amides at 100°C .

Also, primary alcohols were oxidized to their respective carboxylic acids. The alkaline aqueous layer was acidified with 2 M H_2SO_4 to

Table 2

Optimization of the catalytic oxidation of benzylamine and benzyl alcohol to benzonitrile and benzoic acid by $K_2[RuCl_5(H_2O)]/K_2S_2O_8$, respectively.

Entry	Benzonitrile (amide) yield %	Entry	Benzoic acid yield %
1a	95 (5)	1b	95
2a	75	2b	95
3a	67	3b	20
4a	70	4b	95
5a	30	5b	50
6a	80 (19)	6b	95
7a	0	7b	83
8a	0	8b	75
–	–	9b	44

Reaction conditions: 50 cm^3 of 1 M KOH, $K_2S_2O_8$ (1.4 g, 5 mmol), $K_2[RuCl_5(H_2O)]$ (0.0374 g, 0.1 mmol) and substrate (2 mmol).

pH 2 and extracted with diethyl ether. The extract was dried over anhydrous $MgSO_4$ then filtered and evaporated to give the product.

3. Results and discussion

3.1. Ultrasonic-assisted catalytic dehydrogenation of primary amines to nitriles

Typical results of the ultrasonic-assisted catalytic dehydrogenation of primary amines to nitriles (Scheme 1) are shown in Table 1.

Oxidation of benzylamine was performed as a model reaction with $K_2S_2O_8$ in 1 M KOH and in the presence of catalytic amount of $K_2[RuCl_5(H_2O)]$. In the catalyst system, $K_2[RuCl_5(H_2O)]/K_2S_2O_8$ catalyst (pH = 14) showed good catalytic activity and selectivity for the transformation of benzylamine to benzonitrile in 95% under ultrasound-assisted irradiation technique at room temperature.

A mixture of $K_2S_2O_8$ (1.4 g, 5 mmol) in 50 cm^3 of 1 M KOH and catalytic amounts of $K_2[RuCl_5(H_2O)]$ (5 mmol%) was ultrasonically irradiated at room temperature until the appearance of the orange color, expected to be $trans-[RuO_3(OH)_2]^{2-}$ ion in less than 2 min.

Table 1

Ultrasonic-assisted catalytic dehydrogenation of primary amines to nitriles.

Entry	Amine	Nitrile	Yield % (TOF, h^{-1})
1			95 (38)
2			94 (37.6)
3			93 (37.2)
4			90 (36.0)
5			80 (32.0)
6			85 (34.0)
7			83 (33.2)

Reaction conditions: 50 cm^3 of 1 M KOH, $K_2S_2O_8$ (1.4 g, 5 mmol), $K_2[RuCl_5(H_2O)]$ (0.0374 g, 0.1 mmol) and primary amine (2 mmol). Irradiation at room temperature for 0.5 h. TOF = moles of product/mol of catalyst \times time.

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