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



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A R T I C L E I N F O

ABSTRACT

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Keywords: Ultrasonic irradiation Ruthenium Catalytic oxidation Organic compounds $\label{eq:K2} K_2[RuCl_5(H_2O)] \mbox{ were hydrated to} amides by the same catalyst system at 100 °C. The oxidation of two arenes and four alkenes to their aldehydes, ketones or acids by K_2[RuCl_5(H_2O)] with excess KIO_4 using ultrasonic irradiation technique was also reported. Cyclic voltammetric, electronic and Raman spectroscopic techniques have been used to elucidate the nature of the active species present in these catalytic oxidation reactions. \end{tabular}$

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 K₂S₂O₈ in 1 M KOH and/or with excess KIO₄ in biphasic solvent system (H₂O/CH₂Cl₂/CH₃CN) at room tem-

perature. Dehydrogenation of some primary amines to nitriles and primary alcohols to their respective acids by

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}Cl₂(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)₂O₃]²–/S₂O₈^{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 KIO₄ in biphasic solvent system (H₂O/CH₂Cl₂/CH₃CN) 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 d₆-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 WinLabversion 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 cm³ 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

$$NH_{2} = 5\% \text{ mole } K_{2}[RuCI_{5}(H_{2}O)]$$

$$K_{2}S_{2}O_{8} / \text{ molar KOH, RT}$$

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[RuO₃(OH)₂], an aqueous solution of BaCl₂·2H₂O (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 [RuO₄]

A solution of 50 cm³ 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 cm³ of *trans*-[RuO₃(OH)₂]²⁻/S₂O₈²⁻ 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 (3×25 cm³). The ether extracts were dried over anhydrous MgSO₄ 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 $2 \text{ M H}_2\text{SO}_4$ to

Table 1

Ultrasonic-assisted catalytic dehydrogenation of primary amines to nitriles.

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 cm³ 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 MgSO₄ 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 cm³ 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*-[RuO₃(OH)₂]²⁻ ion in less than 2 min.



Reaction conditions: 50 cm³ 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 × time.

0

Scheme 2. Ultrasonic-assisted catalytic hydration of nitriles to amides.

Once primary amine (2 mmol) was added, the reaction mixture gave a transient green nitrile complex. When the reaction was completed, the original orange color returns (i.e. self-indicating). Other co-oxidants BrO_3^- , $[Fe(CN)_6]^{3-}$, NaOCl and HCO₄⁻ were used instead of K₂S₂O₈, they gave benzonitrile in 75, 67, 70 and 30% yields, respectively (Table 2, entries 2a-5a). Therefore, $K_2S_2O_8$ is considered the best co-oxidant and HCO₄⁻ is the worst one, since it is formed with $t_{1/2} \approx 5 \text{ min } [10,11]$. However, when the reaction is also conducted at 60 °C, benzonitrile was obtained in 80% yield and benzamide in 19% vield (Table 2, entry 6a). This indicates that at high temperature selectivity of benzonitrile decreased and that of benzamide increased. Benzonitrile was not formed in the absence of $K_2[RuCl_5(H_2O)]$ or in the presence of K₂S₂O₈ only (Table 2, entries 7a and 8a). To examine the scope of benzylamine dehydrogenation reaction with $K_2[RuCl_5(H_2O)]/K_2S_8O_8$, we extended our studies to various parasubstituted benzylamine derivatives. We noticed that benzylamine derivatives containing electron-donating groups (Table 1, entries 1-4) were smoothly converted to their respective nitriles in better yields than those containing electron-withdrawing groups (Table 1, entries 5–7). In all reactions, yield and turnover frequency (TOF) were calculated and the produced nitriles were identified by measuring their melting point and recording their IR and ¹H NMR spectra where appropriate. As can be seen, the catalyst system, $K_2[RuCl_5(H_2O)]/$ $S_2O_8^{2-}$ can be used efficiently and simply for direct dehydrogenation of these primary amines to their respective nitriles at room temperature by using ultrasonic irradiation technique in a short reaction time (0.5 h).

Table 3

Ultrasonic-assisted catalytic hydration of nitriles to amides.



Scheme 3. Ultrasonic-assisted catalytic dehydrogenation of primary alcohols to carboxylic acids.

3.2. Ultrasonic-assisted catalytic hydration of nitriles to amides

Typical results of the ultrasonic-assisted catalytic hydration of nitriles to amides (Scheme 2) are shown in Table 3.

Hydration of nitriles was investigated at 100 °C since we noticed the formation of amides as side-product during the dehydrogenation of benzylamine at 60 °C (Table 2, entry 6a). Griffith et al. [9] reported that during the dehydrogenation of benzylamine and *p*-methoxybenzylamine to nitriles, benzamide and *p*-methoxybenzamide were produced as side products in relatively small yields (ca. 10%), this does not occur in the absence of $S_2O_8^{2-}$.

Recently, Kathó et al. [12] reported the catalytic hydration of benzonitrile to benzamide in 99% yield by the ruthenium(II) complex, $[RuCl_2(DMSO)_4]$, with the various water-soluble phosphines at reflux temperature. This really encourages us to investigate our catalyst system for hydration of some nitriles to their respective amides. The composition of the catalytic system here is exactly the same as that used for dehydrogenation of primary amines and alcohols, but reactions were performed at 100 °C.

When benzonitrile (2 mmol) was added to the solution of $K_2[RuCl_5(H_2O)]$ in 1 M KOH containing 10-fold excess of $S_2O_8^{2-}$, an immediate dark red color is formed, probably due to the coordination of benzonitrile to ruthenium center. Attempts to isolate this complex were unsuccessful. Benzamide was obtained in 95% yield from benzonitrile (Table 3, entry 1). No formation of by-products (e.g., benzoic acid) was observed. Other benzonitrile derivatives gave their respective amides in 90–93% yields. All reactions were also conducted in the absence of ultrasonic irradiation, in this case, vigorous



Reaction conditions: 50 cm³ of 1 M KOH, K₂S₂O₈ (1.4 g, 5 mmol), K₂[RuCl₅(H₂O)] (0.0374 g, 0.1 mmol) and nitrile (2 mmol). Irradiation at 100 °C for 0.5 h. TOF = moles of product/mol of catalyst × time.

Table 4

Ultrasonic-assisted catalytic oxidation of primary alcohols to acids.

Entry	Alcohol	Carboxylic acid	Yield % (TOF, h^{-1})
1	СН	ОН	95 (38)
2	H ₃ C	ОН	93 (37.2)
3	H ₃ CO	Пас С С С С С С С С С С С С С С С С С С С	94 (37.6)
4	но	Пассо с о	92 (36.8)
5	CI	НО. ОН	85 (34)
6	O ₂ N OH	CI- OH	80 (32)
7	ОН		94 (37.6)

Reaction conditions: 50 cm³ 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 alcohols (2 mmol). Irradiation at room temperature for 0.5 h. TOF = moles of product/mol of catalyst \times time.

stirring of the reaction mixture for 24 h yielded similar results with only minor changes in the isolated yields.

In all reactions, yield and turnover frequency (TOF) were calculated and the produced amides were identified by measuring their melting point and recording their IR and ¹H NMR spectra where appropriate. 3.3. Ultrasonic-assisted catalytic dehydrogenation of primary alcohols to acids

Typical results of the ultrasonic-assisted catalytic dehydrogenation of primary alcohols to carboxylic acids (Scheme 3) are shown in Table 4.

Table 5

Ultrasonic-assisted catalytic oxidation of alkenes and arenes to aldehydes, ketones or acids.



Reaction conditions: alkene or arene (2 mmol), KIO₄ (2.3 g, 10 mmol), K₂[RuCl₅(H₂O)] (0.0374 g, 0.1 mmol) and solvents (5 cm³ of CH₂Cl₂, 10 cm³ of H₂O and 5 cm³ of CH₃CN). Irradiation at room temperature for 2 h. TOF = moles of product/mol of catalyst × time.



Scheme 4. Mechanistic catalytic cycle for ultrasonic oxidation of arenes and alkenes.

We also studied the use of the same catalyst system prepared as mentioned in Section 3.1 and under the same conditions for direct dehydrogenation of some primary alcohols to their respective carboxylic acids. To optimize the reaction conditions, the catalytic oxidation of benzyl alcohol was selected as model reaction. Concerning the amount of catalyst, it was found that increasing the catalyst amount to 0.2 mmol did not affect the yield (Table 2, entry 2b), but by decreasing the catalyst amount to 0.01 mmol the yield was reduced to 20% (Table 2, entry 3b), therefore, the best yield was obtained with 0.1 mmol of catalyst (Table 3, entry 1). We noticed that longer reaction time than 0.5 h had no obvious effect on the yield (Table 2, entry 4b) while, shorter reaction time than 0.5 h, the yield decreased significantly (Table 2, entry 5b).

We found that when the reaction conducted at 60 °C, the yield was not effected (Table 2, entry 6b). Finally, when we used KBrO₃, K_3 [Fe(CN)₆] and NaOCl as co-oxidants instead of $K_2S_2O_8$, the yield was 83, 75 and 44%, respectively (Table 2, entries 7b–9b). We found that benzoic acid was not detected when the reaction was conducted in the absence of K_2 [RuCl₅(H₂O)] or in the presence of $K_2S_2O_8$ only.

To check the ability of this catalytic system to cleave the double bond, the oxidation of cinnamyl alcohol was carried out and cinnamic acid was produced in high yield (Table 4, entry 7). We noticed that the para-substituted benzyl alcohol derivatives containing electrondonating groups (Table 4, entries 2–4) were smoothly converted to their respective acids in better yields than those containing electronwithdrawing groups (Table 4, entries 5–6). In all reactions, yield and turnover frequency (TOF) were calculated and the produced acids were identified by measuring their melting point and recording their IR and ¹H NMR spectra where appropriate.



Fig. 1. Electronic spectra of [RuO₄], K₂[RuO₃(OH)₂] and K₂[RuCl₅(H₂O)] complexes.

3.4. Ultrasonic-assisted catalytic oxidation of alkenes and arenes

Typical results of the ultrasonic-assisted catalytic oxidation of alkenes and arenes are shown in Table 5. Here we investigated the use of $K_2[RuCl_5(H_2O)]$ with excess of KIO₄ in a biphasic solvent system for oxidation of two arenes and four alkenes.

A mixture of substrate (2 mmol), KIO_4 (10 mmol) in a biphasic solvent system consisting of H_2O , CH_2Cl_2 and CH_3CN (ratio 2:1:1) and catalytic amount of $K_2[RuCl_5(H_2O)]$ (0.0374 g., 0.1 mmol) was irradiated by ultrasonic radiation for 2 h at room temperature. Naphthalene gave phthalaldehyde in 75% yield as the main product (Table 5, entry 1). This is in contrast with the other reported methods where formation of 1,4-naphthoquinone or naphthols were the predominant products [13, 14].

Treatment of anthracene under the same conditions gave the corresponding 1,4-anthraquinones in 80% yield (Table 5, entry 2). Benzoic acid is obtained in 94 and 92% yields as the main product in the oxidation of styrene and *trans*-stilbene, respectively (Table 5, entries 3 and 4). For comparison with Sharpless results [15], this protocol was applied to the oxidation of cyclopentene and cyclohexene. Glutaric acid and adipic acid were obtained in 94 and 95% yields, respectively (Table 5, entries 5 and 6).

Although the precise mechanism of the reaction awaits further studies, by analogy with the previous works on ruthenium-catalyzed oxidation of olefins [16], a proposed mechanistic catalytic cycle for the oxidation of these substrates which rationalizes the formation of [RuO₄] is presented in Scheme 4. It is noteworthy that the addition of acetonitrile improves the yields of the products as it has long been known in RuCl₃·nH₂O/NaIO₄ system [15], and we have reported a similar effect in *cis*-[RuCl₂(bipy)₂]·2H₂O/IO(OH)₅ system for alkene cleavage [16].

The action of CH₃CN is not clear; Sharpless and co-workers have suggested that in the case of ruthenium complexes, CH₃CN is itself resistant to oxidation and may stabilize lower intermediate oxidation states of ruthenium involved in the catalytic cycle [15]. Yields and turnover frequencies (TOF) were calculated and the products were identified by measuring their melting point and recording their IR and ¹H NMR spectra where appropriate.

3.5. Synthesis and characterization of the complexes

We describe here the preparation of K₂[RuO₃(OH)₂] and [RuO₄] from $K_2[RuCl_5(H_2O)]$ as a water soluble ruthenium precursor using ultrasonic irradiation technique. It has been reported that the trans- $[RuO_3(OH)_2]^2 / S_2O_8^2$ reagent can be made from $RuCl_3 \cdot nH_2O$ and excess K₂S₂O₈ in aqueous 1 M KOH [9]. The single x-ray crystal structures of trans-K₂[RuO₃(OH)₂] [17,18] and of trans-Ba[RuO₃(OH)₂] [19] showed that these complexes contain the trigonal bipyramidal (D_{3h}) trans- $[RuO_3(OH)_2]^{2-}$ anion. During our attempt to use $K_2[RuCl_5(H_2O)]$ as oxidation catalyst for some organic compounds, we found that irradiation of K₂[RuCl₅(H₂O)] with excess K₂S₂O₈ in 1 M KOH produces K₂[RuO₃(OH)₂] in less than 2 min. Since a number of ruthenium(VI) complexes were made by oxidation of ruthenium(III) complexes using H_2O_2 or peracids [20], we used NaOCl in place of K₂S₂O₈ for in situ generation of K₂[RuO₃(OH)₂]. In the latter preparation, the solutions obtained were all unstable and did not show any advantages over K₂S₂O₈. Connick and Hurley [21] reported that [RuO₄] is usually generated in situ from either RuCl₃·nH₂O or RuO₂·nH₂O followed by extraction in CCl₄. We found that [RuO₄] is easily generated from K₂[RuCl₅(H₂O)] with excess KIO₄ in H₂O in less than 1 min using ultrasonic irradiation technique. Electronic spectroscopy was used to characterize the ultrasonically generated complexes K₂[RuO₃(OH)₂] and [RuO₄] and also to establish the nature of intermediate catalytic species in these catalytic oxidation reactions. Comparisons between the electronic spectra of $K_2[RuCl_5(H_2O)]$ with the electronic spectra of the ultrasonically generated complexes K₂[RuO₃(OH)₂] and [RuO₄]



Fig. 2. Raman spectra of (A) K₂[RuO₃(OH)₂] and (B) Ba[RuO₃(OH)₂].

showed that the complex $K_2[RuCl_5(H_2O)]$ displayed two bands at 224 and 314 nm, these bands are similar to those reported by Viljoen [22]. While the orange solution showed maxima at 369 and 468 nm due to trans-[RuO₃(OH)₂]²⁻ anion (Fig. 1), these data are similar to the data reported by Griffith [23,24]. We also recorded the electronic spectrum for the reaction mixture used in oxidation of alkenes and arenes and found that the electronic spectra of the aqueous layer showed the characteristic peaks of [RuO₄] with attendant vibrational fine structure at 374, 384 and 394 nm (Fig. 1). We have also evaporated and concentrated the orange solution to give dark red solution of $K_2[Ru^{VI}(OH)_2O_3]$ from which Ba[Ru^{VI}(OH)₂O₃] is isolated (see Experimental section). Raman spectrum of these two complexes showed the symmetric Ru=O stretch in the range of $815-820 \text{ cm}^{-1}$ (Fig. 2). It thus seems clear that K₂[RuCl₅(H₂O)] was oxidized by K₂S₂O₈ in 1 M KOH to generate K₂[RuO₃(OH)₂] and by KIO₄ in water/CCl₄/CH₃CN mixture to generate [RuO₄]. We also conclude that these are the effective catalytic species in these catalytic oxidation reactions. Similar results were reported for the oxoruthenate complexes containing [RuO₄] [21–23].



Fig. 3. Cyclic voltammogram of 1.0×10^{-4} M solution of K₂[RuCl₅(H₂O)] in phosphate buffer pH = 4.5. Scan rate: 50 mVs⁻¹.

3.6. Electrochemical properties of $K_2[RuCl_5(H_2O)]$

The electrochemical behavior of K₂[RuCl₅(H₂O)] was investigated by cyclic voltammetry (Fig. 3). The investigation was carried out in phosphate buffer (pH = 4.5) to confirm the possibility for generation of oxidation states higher than three from K₂[RuCl₅(H₂O)]. The complex showed one reduction wave (peaks A and E), one oxidation wave (peaks B and D) and one oxidation peak (C). The reduction wave is quasireversible, characterized by peak-to-peak separation of 240 mV and is assigned to Ru(III)/Ru(II) reduction. The oxidation wave is quasireversible ($\Delta E = 214 \text{ mV}$) versus Ag⁺/AgCl electrode, and assignable to Ru^{III}/Ru^{IV} oxidation. An oxidation peak found at 940 mV, the height of the peak current for this peak is nearly twice that of the height of peak current of the reduction wave. For this reason this peak is assigned to oxidation of Ru(III) to higher oxidation states probably, Ru(VI) or Ru(VIII), respectively. These results are similar to that reported for the perruthenate anion, $[RuO_4]^-$ [25].

4. Conclusions

We concluded that the complex K₂[RuCl₅(H₂O)] is ultrasonically oxidized by K₂S₂O₈ in 1 M KOH to generate K₂[RuO₃(OH)₂] in situ and by KIO₄ in H₂O/CCl₄/CH₃CN mixture to generate [RuO₄] at room temperature in less than 2 min. The complex K₂[RuCl₅(H₂O)] dehydrogenated primary amines to nitriles and primary alcohols to acids at room temperature. It also hydrated some nitriles to amides at 100 °C by using ultrasound-assisted irradiation technique and in the presence of K₂S₂O₈ as co-oxidant. The structures of the generated active species in these catalytic oxidation reactions were elucidated by using cyclic voltammetric, electronic and Raman spectroscopic techniques and found to be potassium ruthenate, $K_2[RuO_3(OH)_2]$ with $K_2S_2O_8$, and ruthenium tetroxide, [RuO₄] with KIO₄.

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