



Kinetic Studies of Reduction of Tris-(1,1,1,5,5,5-hexafluoroacetylacetonato) ruthenium(III) in Methanol, Ethanol and Propanol

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Abstract: The complex tris-(1,1,1,5,5,5-hexafluoroacetylacetonato-) ruthenium(III), hereafter referred to as Ru(hfacac)₃, has been synthesized. Ultraviolet and visible spectroscopic measurements of the complex in ethanol revealed three prominent absorption bands at 287, 374 and 525 nm with molar absorptivity coefficients of 4.113, 3.885 and 3.59 respectively. Magnetic susceptibility measurements between 78 and 296 K revealed the complex to assume a low spin configuration of $e^0t_{2g}^5$ and an oxidation state of +3 as inferred from a value of 1.92 Bohr magneton. Kinetic investigation of the reduction of the complex in methanol, ethanol and propanol indicate the reduction to proceed in the order methanol > ethanol > propanol. The energies of activation of the reduction in methanol and ethanol were found to be 85.4 and 108 kJ/mol respectively.

Keywords: Ruthenium(III), Ruthenium(II), Kinetics, Hexafluoroacetylacetonato, Ru(hfacac)₃

Introduction

The reactions of metals with β -diketones have been known for well over a century¹. During this period, several researches have been conducted the world over on the synthesis², catalytic activity³⁻⁵ mass spectroscopy⁶, gas chromatography⁷, x-ray⁸ solvent dynamics⁹ and in a wide range of subjects¹⁰ concerning ruthenium β -diketonates⁴. Complexes of fluorinated β -diketones have been investigated¹¹⁻¹³ for its solvent extraction capabilities and as NMR shift reagents. Most studies have been carried out in solvents such as acetonitrile while a few have been in alcohols.

Ruthenium(II) and ruthenium(III) form low spin d^5 and d^6 complexes with numerous derivatives of the ligand acetylacetonone¹⁴. Metal 1,3-diketone systems behave as sensitive heterocycles possessing at least some aromatic character. Holm and cotton¹⁵ have expressed doubt in such aromaticity but collman *et al*¹⁶ and other workers have recognized their quasi-

aromatic character and have reported electrophilic substitution reactions in these systems. β -Diketones have the property of forming stable anions as a result of enolization followed by ionization. The ketoenolate ions form very stable chelate complexes with a variety of metal ions¹¹.

The 1,1,1,5,5,5-hexafluoro-2,4-pentane dione complex of ruthenium(III) has a characteristically strong oxidizing property compared to other β -diketones. Studies of fluorinated β -diketone complexes of ruthenium(III) show these compounds to undergo reduction in alcoholic solutions of alkali hydroxides¹²⁻¹³. These studies were conducted with compounds of ruthenium β -diketonates such as tris-(1,1,1-trifluoro-2,4-pentanedionato-) ruthenium(III), 4,4,4-trifluoro-1-(phenylbutane-1,3-dione), 4,4,4-trifluoro-1-(2-naphthyl)-butane-1,3-dione and 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione¹².

A survey of available literature¹⁷⁻²⁰ indicate that no studies have been undertaken as regards the action of alcoholic alkali hydroxide solutions on the hexafluoroacetylacetonate (hfacac) of ruthenium(III).

This complex is not very stable probably because of the large number of fluorine atoms it possess and also because it is difficult to synthesize. The objective of this work was to measure the rate of reduction of tris-(1,1,1,5,5,5-hexafluoroacetylacetonato) ruthenium(III) in methanol, ethanol and propanol as well in the presence of alcoholic alkali hydroxide solutions.

Experimental

Analytical grade reagents were used throughout this work. 1,1,1,5,5,5-Hexafluoroacetylacetonate (hfacac) was purchased from Eastman Kodak Company. Ru(hfacac)₃ was prepared and purified according to ruthenium blue² method with modifications as described in the synthesis procedure. Magnetic susceptibility measurements were carried out on a magnetic susceptibility balance (Sherwood Scientific) at room temperature by Gouy's method. Ultraviolet-visible spectroscopy was measured on a Cary 50 spectrophotometer.

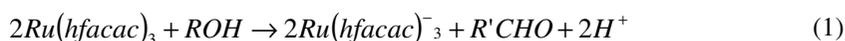
Synthesis

0.0025 moles of ruthenium(III) chloride (RuCl₃·3H₂O) were weighed and dissolved in 10 mL of 3 M hydrochloric acid. The solution of ruthenium chloride in HCl was then evaporated to dryness indirectly on a heating mantle at 80 °C. When completely dried, a few drops of ethanol was added to dissolve the solid material and again evaporated to dryness. Solid materials obtained at the end of the evaporation process were then dissolved in 50 mL of ethanol in a 250 mL round bottom flask giving a greenish solution. 0.0031 moles of the ligand hexafluoroacetylacetonate (hfacac) was then added. The mixture was then warmed under reflux for about one hour. During reflux, 0.0025 moles of potassium hydrogen carbonate (KHCO₃) was added. The refluxing was then continued for 24 h. Another portion of 0.000125 moles of potassium hydrogen carbonate was again added with 10 mL of ethanol. Heating was then continued for a further 48 hours. At the end of the synthesis, the reaction mixture was filtered on a sintered glass funnel No 3. The filtrate obtained was evaporated to dryness with *n*-pentane added to hasten evaporation. An oily liquid resulted which was washed with chloroform and filtered at the pump. Dark brown crystals were obtained which weighed 0.43 g. The crystals were again washed with double distilled water at the pump and evaporated to dryness. Reddish crystals obtained were purified by sublimation. A yield of 48.8 mg of ruthenium(III) hexafluoroacetylacetonate Ru(hfacac)₃ was obtained. Melting point of the crystals was found to be 98-99 °C which is in agreement with literature¹².

Kinetic measurement

Kinetic measurement of the rate of reduction of $Ru(hfacac)_3$ in methanol, ethanol and propanol at various temperatures was followed spectrophotometrically with a Cary 50 spectrophotometer. These measurements were based on the absorbance wavelength due to ruthenium(III) at 374 nm. A 0.1 M solution of potassium hydroxide was prepared in ethanol and standardized against a standard 0.1 M potassium hydrogen phthalate solution. A 1.4×10^{-4} M solution of $Ru(hfacac)_3$ was reacted with 0.1 M solution potassium hydroxide. The two solutions were mixed and quickly transferred to a 1 cm quartz cell in a thermostated compartment of the UV Vis spectrometer. The UV Vis absorption spectrum 300-800 nm was then scanned at specific time intervals. Maintenance of isosbestic point throughout the entire reaction was an indication of a simple reaction.

Rate measurements for the reduction of $Ru(hfacac)_3$ in the alcohols were made under pseudo-first order conditions with the alcohol in excess. The reaction equation is as follows:



Where, $R' = H, CH_3, C_2H_5, C_3H_7$

$$-\frac{d[Ru(hfacac)_3]}{dt} = k_o[ROH][Ru(hfacac)_3]^2 \quad (2)$$

Where, k_o is the observed rate constant.

$$-\frac{d[Ru(hfacac)_3]}{dt} = k_{exp1}[Ru(hfacac)_3]^2 \quad (3)$$

Where, $k_{exp1} = k_o[ROH]$

Results and Discussion

Spectral measurements of the complex in chloroform and ethanol in the ultraviolet and visible region gave three prominent absorption bands at 287, 374 and 525 nm. The band at 287 nm has a molar absorptivity coefficient of 13000 L/mol cm. The band at 374 nm and 525 nm have molar absorptivity coefficient of 7667 and 3889 L/mol cm respectively. This band at 287 nm is found in all β -diketones and their complexes for which upon chelation with a metal ion may be shifted either to longer or shorter wavelength with respect to the ligand. Barnum²⁰ attributed these among others to the effect of metal- ligand π -interactions in trivalent transition metal complexes, for which ruthenium is in the trivalent state. The observed band at 287 nm has been assigned as a π - π transition originating from the ligand hexafluoroacetylacetone (Hhfacac), holm and cotton, and Barnum^{15,20} and other researchers have stated that the origin of these bands are not known since they also occur in iron(III) β -diketones. Despite the controversy surrounding these bands, they could be said to be charge transfer transitions between the metal and ligand and metal. Electronic configuration of ruthenium(III) is known to be d^5 and low spinned with an unfilled orbital on the 4d orbital in the t_{2g} degenerate level, it is possible for a transition from the π -orbital of the ligand to the metal to occur. However, for a low spinned ruthenium(II) with an orbital electron distribution in which the t_{2g} level is filled, it cannot accept any electron from the ligand to the t_{2g} level rather, it would most likely produce a transition from metal to ligand. Since the splitting energy of the octahedral field is large, transition to the e_g level is not possible.

Therefore, the band at 374 nm is π - t_{2g} transition in ruthenium(III) while the band which occurs at 525 nm is a t_{2g} - π^* transition for ruthenium(II). Again, in the region under discussion, the existence of d - d transition in metal ion cannot be excluded. If they do occur, they are overlapped by the intensity of the charge transfer transition.

The effective magnetic moment μ_{eff} for ruthenium(III) from magnetic susceptibility measurement of the synthesized complex using Gouy method was found to be $\mu_{eff} = 1.92$ BM. This approximates to the presence of one unpaired electron since the magnetic moment of a single unpaired electron has a value of 1.73 BM.

Kinetic measurements were carried out at room temperature, approximately 25 °C, in alcohols. The reaction kinetics was monitored spectroscopically at λ_{max} 374 nm which decreases due to reduction of ruthenium(III) or at 525 nm which increases due to oxidation of ruthenium(II).

The reduction reaction in methanol, ethanol and propanol were initiated by the dissolution of the $Ru(hfacac)_3$ in the respective alcohols. $Ru(hfacac)_3$ is not stable in the lower alcohols, instability being attributable to the large number of fluorine atoms. Studies by a number of researchers indicate that the substitution of methyl ($-CH_3$) influences complex stability, increases volatility and decreases thermal stability⁵.

In methanol, the reduction reaction was complete within one hour which indicates a single set of reactants producing a single set of products as may be deduced from the single isosbestic point produced at 437 nm (Figure 1). The rate of the reaction at 25, 30 & 35 °C produces straight lines when plotted as pseudo-first order kinetic reaction (Figure 2). Rate constants for the reaction at various temperatures are tabulated in Table 1.

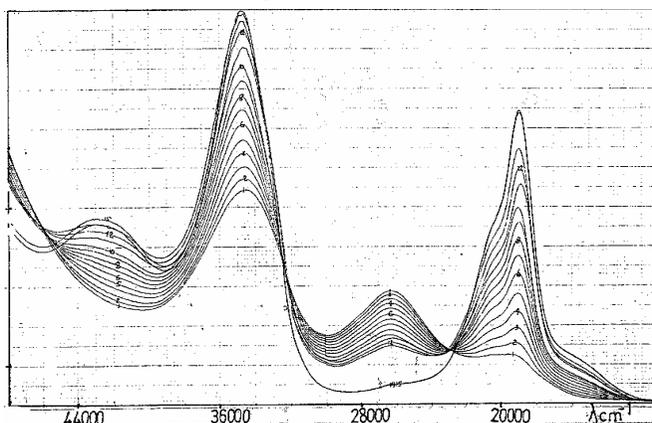


Figure 1. Absorbance measurement of $Ru(hfacac)_3$ in methanol

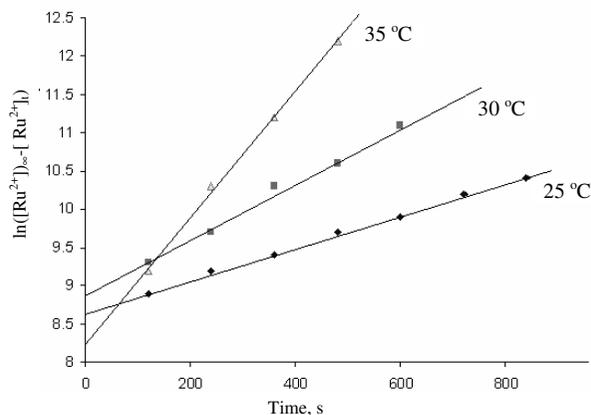


Figure 2. Rate measurement of $Ru(hfacac)_3$ in methanolic KOH solution at 25, 30 and 35 °C

Table 1. Rate constants and half life for kinetic measurement in methanol

Temperature, K	$k/\text{mole} \times 10^4$	$\ln k$	$t_{1/2}$ (s)
288	0.521	-9.86	1300.8
298	1.23	-9.00	5620
303	2.95	-8.13	2349.65
308	5.38	-7.53	1287.58

In ethanol, the reduction reaction process was complete in less than four hours at 25 °C. This reaction also produces a well defined isobestic point at 433 nm which indicates a single set of reactants giving rise to a single set of products (Figure 3). The rate of the reaction at 25, 30 & 35 °C produces straight lines when plotted as a pseudo-first order kinetic reaction (Figure 4). Rate constants for the reaction at various temperatures are tabulated in Table 2.

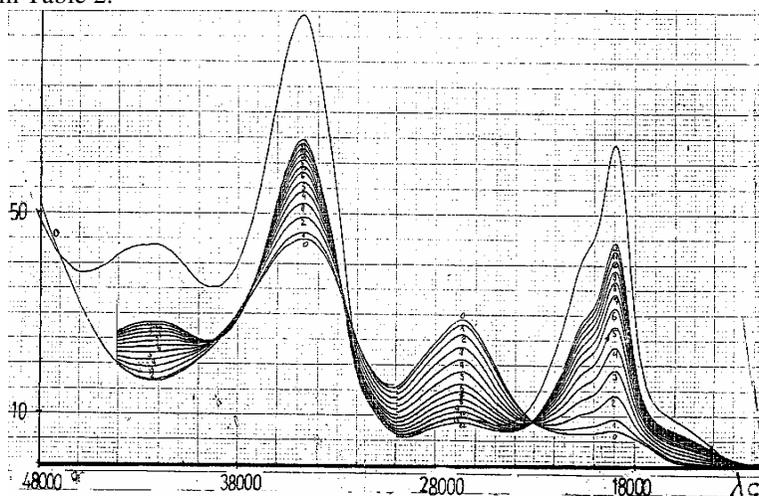
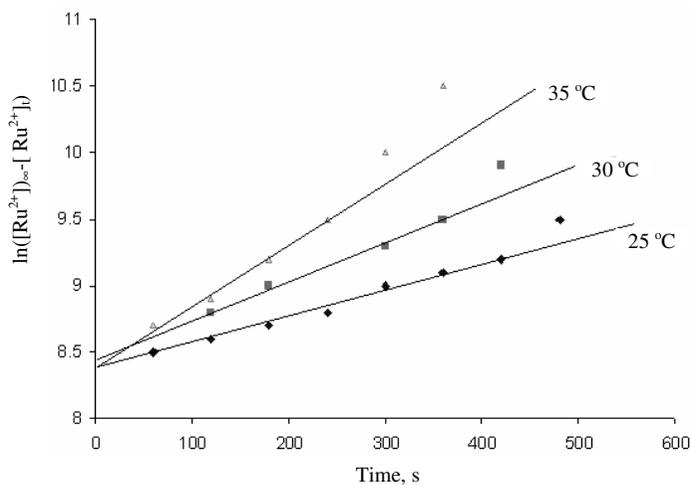
**Figure 3.** Absorbance measurement of $\text{Ru}(\text{hfacac})_3$ in ethanol**Figure 4.** Rate measurement of $\text{Ru}(\text{hfacac})_3$ in ethanolic KOH solution at 25, 30 and 35 °C

Table 2. Rate constants and half life for kinetic measurement in ethanol

Temperature, K	k mole/s $\times 10^5$	ln k	$t_{1/2}$ (s) $\times 10^4$
298	3.07	-10.39	2.26
303	5.55	-9.80	1.25
308	9.67	-9.24	

In propanol however, the reduction reaction process does not go directly to completion. An equilibrium is established somewhere in the system with the production of a diffused isosbestic point between 417 and 434 nm (Figure 5). The rate of the reaction at 30 & 40 °C produces straight lines when plotted as a pseudo-first order kinetic reaction (Figure 6). Rate constants for the reaction at various temperatures are tabulated in Table 3.

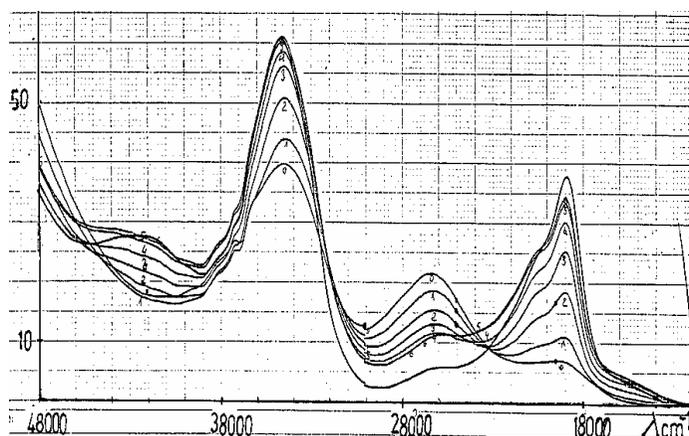
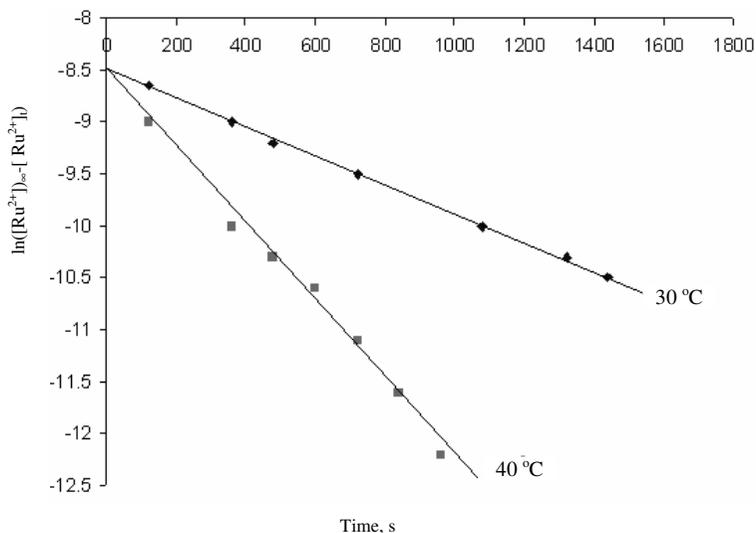
**Figure 5.** Absorbance measurement of $\text{Ru}(\text{hfacac})_3$ in propanol**Figure 6.** Rate measurement of $\text{Ru}(\text{hfacac})_3$ in propanolic KOH solution at 30 and 40 °C

Table 3. Rate constants and half life for kinetic measurement in propanol

Temperature, K	K, mole/s x 10 ⁴	ln k	t _{1/2} (s)
298	1.05	-9.16	6601.4
303	1.417	-8.86	4892.80
313	3.55	-7.94	1952.53
323	13.7	-6.595	507.18

Activation parameters were then determined from the slope of the plot of ln k *versus* 1/T over the temperature range of 15-50 °C for a number of representative reactions. The energies of activation obtained for methanol and ethanol indicate that the reduction is fastest in methanol Table 4.

Table 4. Measured thermodynamic properties

Alcohol	Graphical Evaluation of E _a , kJ/mol	Least square evaluation of E _a , kJ/mol	Error of slope, kJ/mol	Enthalpy of Activation, ΔH	Entropy of Activation, ΔS, J/mol
Methanol	85.34	85.41	1.00	82.86	-42.15
Ethanol	108.1	103.9	0.202	101.446	+22.95
Propanol	94.571	96.890	1.46	94.41	-12.22

Calculated entropies of activation for each of the alcohols gave negative values for methanol and propanol and signify a lack of induced dipole – dipole interaction and also show a separation of ions in the system. However, the positive entropy value for ethanol signifies the presence of dipole - dipole interaction.

Barley & becker²¹ in their study of electron transfer dynamics have stated that solvents in many chemical reactions play a less passive role. In their measurement of a number of polar solvents found that dielectric relaxation time of polar fluids is a measure of the damping or reorientation of the dipole. Man sheung *et al.*¹⁴ studying electron exchange rate between Ru(hfacac)₃ and Ru(hfacac)₃⁻ in different solvents have stated that the main deterrent to electron transfer is probably the necessity of solvent reorganization and that exchange reactions increase with decreasing values of the dielectric constant.

Indicates an electron transfer from alcohol to ruthenium reducing ruthenium(III) to ruthenium(II). The mode of electron transfer for this reaction process has been described by many researchers as an outer sphere process where the transfer of electron proceeds without opening of the chelate rings⁵.

Conclusion

Tris-(1,1,1,5,5,5-hexafluoroacetylacetonato) ruthenium(III) (Ru(hfacac)₃) was synthesized by the ruthenium blue method with a slight modification as stated in the synthetic procedure. Kinetic reduction of (Ru(hfacac)₃) in various alcohols show a conversion to tris-(1,1,1,5,5,5-hexafluoroacetylacetonato) ruthenium(II) (Ru(hfacac)₃⁻). In methanol and ethanol the reduction reaction show a single set of reactants giving rise to a single set of products. The identity of the product have been reported by other researchers as ruthenium(II)¹².

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