

Kinetics and Oxidation of an Organic substrate with Quinolinium Fluorochromate

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ABSTRACT

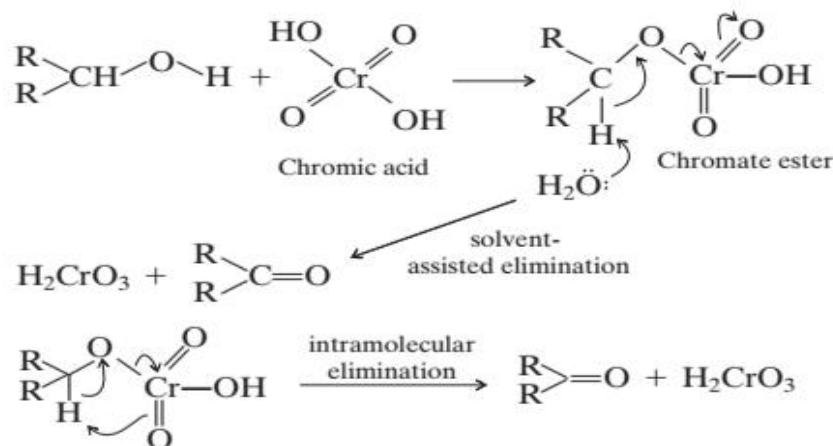
Chemical kinetics deals with the study of factors that affect the rate of the reaction and also the mechanism of the reaction, in the field of chemistry. In our environment chromium occurs in different valence states chromium (Cr III) and chromium Cr (VI). Exposure to hexa valent chromium is more toxic compared to trivalent chromium. It mainly affects the respiratory tract. The Oxidation reaction between Quinolinium Fluorochromate and cyclohexanol has been studied. The medium used for this reaction is acetonitrile and nitrobenzene in the ratio of 1:1 and 5:5. The product of oxidation is the formation of cyclohexanone. on the basis of the experimental data, an appropriate kinetics has been proposed.

Keywords:

Oxidation, cyclohexanol, quinolinium fluoro chromate and kinetics.

1. Introduction

A number of Cr(VI) compounds have been developed to oxidize 1° and 2° alcohols, more generally the 2° alcohols, to respective carbonyl compounds. For example, Jones reagent, that is CrO₃ in 8NH₂SO₄ using acetone as the solvent. In this case, acetone serves the following two purposes. (i) It acts as an excellent solvent for the substrate. (ii) It prevents overoxidation of the primary product formed. The oxidation involves the formation of an inorganic ester, the chromate ester of the alcohol as an intermediate, which may decompose either in a solvent-assisted or an intramolecular elimination of chromous acid to give the ketone.

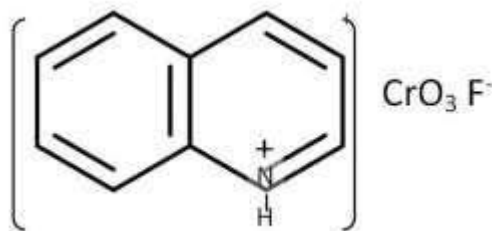


The strongly acidic condition of Jones reagent is unsuitable for oxidizing acid sensitive substrates. So, a number of Cr(VI) reagents have been developed. During the oxidation of alcohol or aldehyde Cr(VI) is reduced to Cr(III). The highly toxic chromium (VI) compounds are converted to chromium (III) compounds. Due to lack of complete understanding of the deposition mechanism, the chemistry of chromium in various forms is discussed, which include polymerization and related mechanisms.

In organic chemistry, oxidation is an important reaction. Primary and secondary alcohols are converted to aldehydes and ketones. Quinolinium Fluorochromate is a mild oxidising agent in synthetic organic chemistry. Primary and secondary alcohols may be converted to aldehydes and carbonyl compounds.

Some of the chromium (VI) reagents developed so far include Pyridinium chlorochromate, Pyridinium dichromate, Pyridinium fluorochromate, Pyridinium bromochromate, Quinolinium chlorochromate, Quinolinium dichromate, [imidazolium dichromate. A new Cr (VI) reagents together with special reaction conditions have been developed. The chromium (VI) reagents developed so far all suffer from at least one of the following drawbacks : high acidity, photosensitivity, instability or requirement of large excess of reagent. Therefore, a new reagent was synthesized -Quinolinium Fluorochromate.

Structure of Quinolinium Fluorochromate

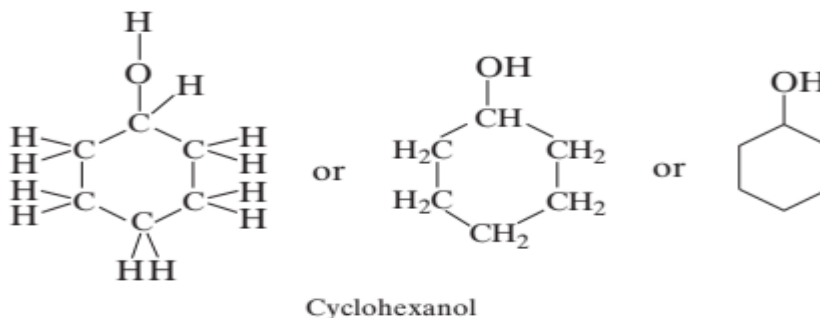


Molecular formula $C_9H_7NH CrO_3F$

Cyclohexanol :

It is an organic compound with the formula $C_6H_{12}O$. It is a secondary alcohol. It is an irritant. Hence contact with skin and eyes has to be avoided. Solubility of cyclohexanol in water is more when compared to cyclohexanone.

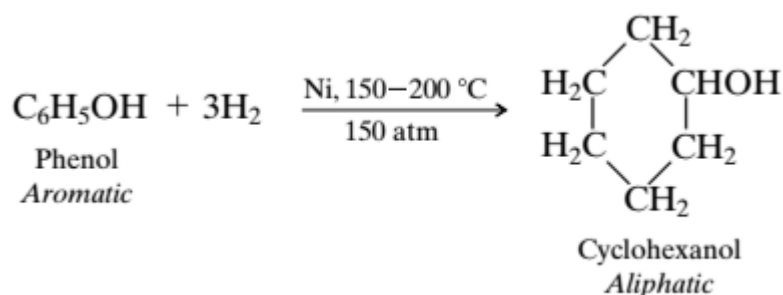
Structure of Cyclohexanol



It is slightly soluble in water. oxidation of cyclohexanol gives the non-volatile adipic acid $HOOC(CH_2)_4COOH$. From cyclohexanol many other cyclic compounds containing a six-membered ring can be made.

Hydrogenation of phenol yields substituted cyclohexanes.

For example



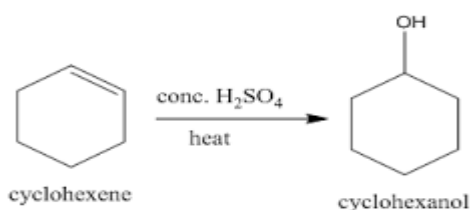
2. Experimental Methods

Preparation of Quinolinium Fluorochromate

Quinolinium Fluorochromate was prepared from quinoline, chromium trioxide and aqueous hydrofluoric acid. Add Chromium trioxide to water, then add 40% hydrofluoric acid drop by drop and stir it.

It was added in the molar ratio of 1:1:5:1. Add Quinoline and heat the mixture on a water bath. Cool the solutions at room temperature. Separate the Quinolinium fluorochromate by filtration. It is a crystalline complex, and non-hygroscopic. It is an air-stable reagent. It can be stored in a sealed polythene bag for longer periods.

Preparation of cyclohexanol



Add concentrated sulfuric acid of 7.0 ml to 3.4 ml of water in a 50 ml, ground-glass stoppered Erlenmeyer flask. Cool the solutions to room temperature. Add 10.1 ml of cyclohexene, stopper the flask and the mixture should be shaken or stirred, till a clear solution is formed.

At this point, pour the mixture into a 250 ml, boiling flask and rinse the Erlenmeyer flask with a total of about 120 ml of water, adding the rinsings to the boiling flask. Distillation adapter is fitted to the flask and a condenser set for distillation. Heat the mixture to hydrolyse the intermediate and to distill the product upto 50 or 60 ml of distillate and is collected.

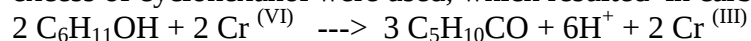
Saturate the distillation with sodium chloride and separate the cyclohexanol by extracting it with ether. Dry the extract, then filter and remove the ether by distillation on the steam bath. Distill the residue and on boiling it between 155 and 162° C, and finally cyclohexanol is produced.

Kinetics

Cyclohexanol, Quinolinium Fluorochromate and other reagents were prepared. Pseudo-first conditions were maintained. A known volume of Quinolinium fluorochromate was added into the flask. The reactions were carried out at constant temperature (303K) by using thermostat. Excess of cyclohexanol were used with respect to Quinolinium Fluorochromate.

3. Result

The rate constants and other experimental data were obtained for alcohol. Oxidation reaction has occurred between cyclohexanol and QFC. As a result, cyclohexanone is formed as the product. Cyclohexanone is readily oxidised by a $K_2Cr_2O_7.H_2SO_4$ mixture to the crystalline adipic acid. Analysis of products, indicated the following reaction. During the oxidation process, excess of cyclohexanol were used, which resulted in carbonyl compound as products.



Effect of oxidant

From the table given below, it is observed that the concentration of oxidant (QFC) is increased from (0.001 to 0.005 mol dm⁻³). For this concentration the reaction rate is increased. The oxidation reaction between the oxidant and substrate was found to be first order reaction. All the other concentration where kept at constant. Change in the rate constant of Quinolinium Fluorochromate (QFC) was found to be inconsiderable.

Table 1 : Dependence of the reaction rate on oxidant: T = 303 k

[QFC] X 10 ⁻³ mol dm ⁻³	[Cyclohexanol] 0.01 mol dm ⁻³	K ₁ X 10 ⁴ Sec ⁻¹
1	8.34	
2	8.60	
3	8.45	
4	8.68	
5	8.71	

Table 2 : Dependence of the reaction rate on substrate concentration : [QFC] = 0.001 mol dm⁻³ :
T = 303 k

[Substrate] mol dm ⁻³	[Cyclohexanol] K ₁ X 10 ⁴ Sec ⁻¹	Rate	Constants
0.01	8.34		
0.02	12.90		
0.03	14.89		
0.04	16.34		
0.05	18.17		

Effect of Substrate

The reaction process was carried out by varying the concentration of substrate. The other variables are kept at constant. With the increase in the concentration of cyclohexanol, the rate of reactions also increased. This indicates a complex formation in the rate determining step.

Effect of solvent

The percentage of concentration of solvent was changed (by increasing the concentration of Nitrobenzene, while decreasing the concentration of Acetonitrile) and was noted for the change. From the table given below, it was also noted that the rate of dielectric constant decreased. This indicates the need for excess reaction times for the polar solvents to carry on the oxidation reactions. It also indicates that an interaction between an ion and dipole occurred in the rate determining step. Thus showing the occurrence of a protonated Cr (VI) species, during the reaction.

Table 3: Dependence of Reaction Rate on Solvent Composition : [Oxidant] = 0.002 mol dm⁻³, T = 303 k

Nitro benzene (%)	Acetonitrile (%)	Dielectric constant	[Cyclohexanol] 0.02 mol dm ⁻³ K ₁ X 10 ⁴ Sec ⁻¹
30	70	36.50	3.61
40	60	36.20	5.98
50	50	35.90	7.62
60	40	35.70	10.89
70	30	35.40	13.17

Effect of temperature

The rate constants were measured by increasing the rate of temperature from (303k to 318k). And a plot between rate of reaction and temperature using Arrhenius equation was made. Thermodynamic, the rate of enthalpy change, the rate of entropy change and the rate of Gibbs free energy have been calculated.

Table 4 : Dependence of rate on temperature

Temperature	k	K ₁ X 10 ⁴ S ⁻¹
303		8.34
308		8.72
313		9.12
318		9.55

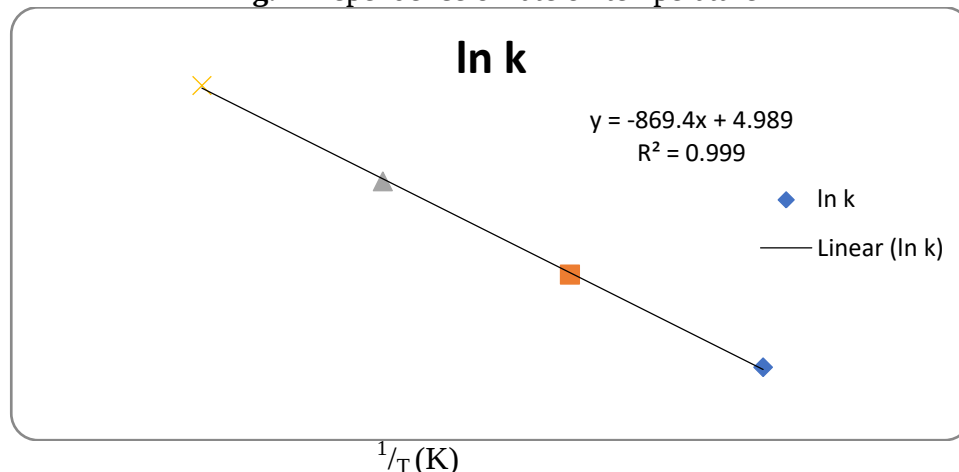
$$[\text{QFC}] = 0.001 \text{ mol dm}^{-3} \quad [\text{Substrate}] = 0.01 \text{ mol dm}^{-3}$$

$$\Delta H^* = 5.22 \text{ (KJ mol}^{-1}\text{)}$$

$$\Delta S^* = -274.12 \text{ (KJ}^{-1} \text{ mol}^{-1}\text{)}$$

$$\Delta G^* = 90.93 \text{ (KJ mol}^{-1}\text{)}$$

The reaction rate increases with increase in temperature. A high negative values of entropy was noted. A negative value of ΔS indicates a decrease in entropy, showing the restrictions in the freedom of the motion of the molecules. When it is impossible for two molecules to move away, then they are joined as a single molecule. Thus the free energy of the products is greater. In such reaction, ΔS will be negative. Hence the solvent acetonitrile does not show any reaction with Cr(VI).

Fig. 1 Dependence of rate on temperature

Activation energy can be calculated from the slope

$$\text{slope} = -E_a / R$$

where E_a is activation energy, R is a constant equal to 8.314 J/mol.k.

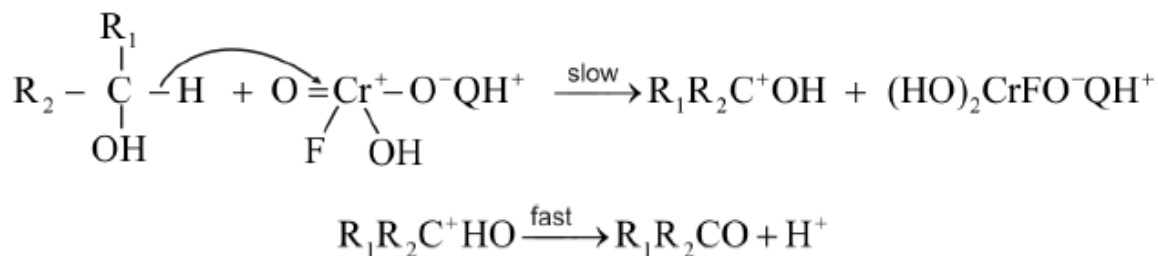
$$E_a = 72.284 \text{ KJ/mol}$$

4. Discussion

Quinolinium Fluorochromate is soluble in water, dimethylformamide, dimethyl sulfoxide and acetone. It is slightly soluble in chloroform and dichloromethane. It is insoluble in benzene, heptane, toluene, ether and ethylacetate. Quinolinium fluorochromate does not show any reaction with acetonitrile, nitrobenzene and dimethyl formamide. QFC is less acidic than PCC. It is quite stable.

Mechanism and rate law

From the above observations, the following mechanism is proposed. It represents the movement of transfer of hydride-ion in the rate determining step, during the oxidation of alcohol to carbonyl compound.



$$\begin{aligned} \text{Rate} &= -d [\text{Cr (VI)}] / dt \\ &= K [\text{S}] [\text{QFC}] \end{aligned}$$

5. Conclusion

we conclude that, the oxidation reaction between the oxidant (QFC) and substrate (cyclohexanol) was found to be first order reaction. This reaction was found to be first order with respect to chromium (VI). The product of oxidation was corresponding carbonyl compound. Thus a suitable mechanism was proposed.

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