Ultrasonically Activated Oxidation of Hydroquinones to Quinones Catalysed by Ceric Ammonium Nitrate Doped on Metal Exchanged K-10 Clay

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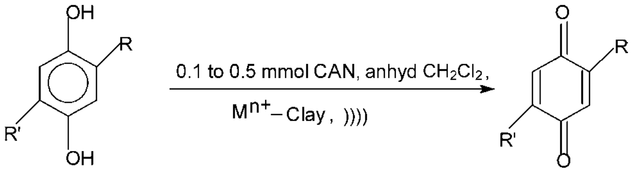
Abstract: We have accomplished the oxidation of hydroquinones to quinones in quantitative yields using catalytic quantity of ceric ammonium nitrate doped on various metal-exchanged K-10 clay, as a mild and efficient reagent, by ultrasonic activation. The exchanged cations examined were Fe^{3+}, Cu^{2+}, Ce^{4+} and K-10 clay itself. The best results were obtained using Fe^{3+}-Mont. K-10 clay.

Key words: ultrasound, Fe^{3+}-Mont. K-10 clay, ceric ammonium nitrate, hydroquinones, quinones

The advantageous use of ultrasound irradiation technique for activating various reactions proceeding via SET mechanism or radical route is well documented in the literature.[1] One of the most notable oxidants among lanthanide reagents is cerium ammonium nitrate (CAN), a one-electron oxidant whose chemistry is dominated by radical and radical cation chemistry. It has been utilised extensively for a variety of oxidative transformations.[2] However, the earlier work on Ce(IV) promoted oxidations was carried out in strongly acidic media using stoichiometric to large excess of CAN.[3] In continuation of our work on developing new methodologies in organic synthesis using non-conventional energy sources we herein report an effective conversion of hydroquinones to quinones in quantitative yields using ultrasonic activation in the presence of catalytic quantity of CAN doped on various cation exchanged K-10 montmorillonite clay as a mild catalyst (Scheme 1).



Scheme 1

Environmental problems has led to an increased interest in the study of heterogeneous reactions that involve solid reagents supported on high surface area inorganic materials.[4] Clays and its modified forms are known to have Lewis and Brönsted acid sites along with radical cation centers in them.[5] The radical cations are formed by the transition metal ions present in clay. The ion exchange increases the metal ion content and hence enhances its activity. The nature of the ion also affects its reactivity and the ions also serve as excellent support materials.

Our rationale here was to try and take advantage of the presence of easily reducible cations in clay which were increased by ion exchange for generating the radical cations and its acidity to promote the reaction using only catalytic quantity of CAN. The efficient and harsh mixing system due to ultrasonic activation further accelerates the reaction. When the parent hydroquinone was oxidised with CAN-doped Fe^{3+}-Mont. K-10 clay under 'silent' (without ultrasound) conditions, the reaction gave after 6 hours the desired quinone in only 45% yield.

Substituted quinones are not only present as common units in natural products but also used as very useful intermediates in organic synthesis. A wide variety of reagents oxidise hydroquinones to quinones. Among the common methods, the stoichiometric oxidation methods use chromium trioxide,[6] sodium hypochlorite,[7] iron(III) chloride,[8] and silver oxide[9] as oxidants. Catalytic oxidations using nitrogen oxides/O_2,[10] alumina supported copper sulfate/O_2,[11] and $VO(acac)_2/O_2$[12] have been reported recently. These methods require either stoichiometric amounts of catalyst or tedious reaction conditions.

The cation (Fe^{3+}, Cu^{2+}, Ce^{4+}) exchanged K-10 clay were prepared according to the method reported in the literature.[13] The best results were obtained with Fe^{3+}-Mont. K-10 clay and is given in Table 1 and was used in the oxidation of all other derivatives (see Table 2). The Fe^{3+}-Mont. K-10 clay can be recycled after the reaction by washing with water, and drying at 120 °C for 5 hours.

Simple Mont. K-10 clay did not work efficiently. Metal ion content of Fe^{3+}-Mont. K-10 clay was determined by an electro-disperse X-ray microscope (EDX) connected to a

Table 1 Variation in Yield of Quinone Using CAN Doped on Different Metal Ion Exchanged Clays

Entry	Catalyst	Yield (%)
1	Cu^{2+}-Mont. K-10 Clay	55
2	Ce^{4+}-Mont. K-10 Clay	70
3	Fe^{3+}-Mont. K-10 Clay	98

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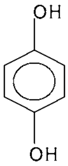
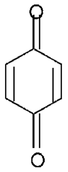
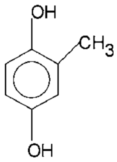
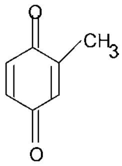
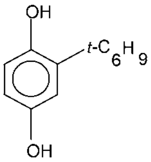
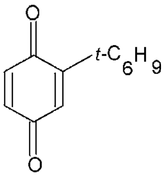
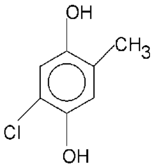
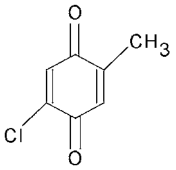
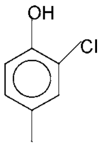
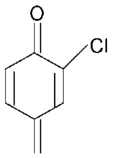
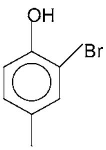
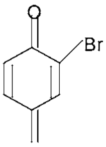
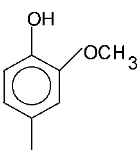
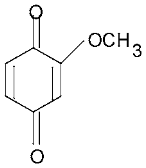
Table 2 Oxidation of Hydroquinone and its Derivatives to the Corresponding Quinones Catalysed by CAN-Doped Fe^{3+}-Mont. K-10 Clay

Entry	Reactant	Product[a]	Yield (%)	Time (min)	CAN (mmol/ mmol of Substrate)	Mp (°C) Found	Reported
1			98	30	0.5	112	115
2			93	30	0.1	66	68–69
3			90	90	0.1	57–59	59
4			90	90	0.1	104	105–106.5
5			92	60	0.1	54	55–56
6			97	60	0.1	47	–
7			85	120	0.2	142	144–146

[a] The products were purified by crystallisation from Et_2O, except for entry 4, which is purified from $CHCl_3$–toluene. All Products are known and were characterised by spectral (^1H NMR and IR) analyses.

Jeol scanning electron microscope. The Fe content in the exchanged clay was found to be 13.83 wt% and in the original clay 10.38 wt%.

^1H NMR spectra were recorded in $CDCl_3$ or CCl_4 on a 300 MHz Bruker instrument using TMS as internal standard. IR spectra were recorded on a Perkin Elmer 337 spectrometer. Branson Ultrasonic cleaning bath model 3150 DTH was used in all the experiments. The metal content of the clay was determined using electron-disperse X-ray microscope (EDX) connected to a Jeol, scanning electron microscope. CH_2Cl_2 was dried by distilling over P_2O_5. K-10 Montmorillonite clay was purchased from Aldrich. Metal salts used were purchased from S. D Fine Chemicals, India.

Preparation of Metal-Exchanged Clays

The metal exchanged clays were prepared by slowly adding the clay (1.0 g) to dilute solutions of $CuCl_2$ (1 M, 12.5 mL), $FeCl_3$ (1 M, 12.5 mL), and $Ce(SO_4)_2$ (0.25 M in 1 M H_2SO_4,16.7 mL), respectively, and stirring for a period of 24 h. After exchange, suspensions were filtered and washed with deionised H_2O to free from anions. The resultant solids were dried on a thin bed at 120 °C for 12 h and ground to a powder. The metal content of the most active clay was determined and is reported in Table 1. X-Ray diffraction spectra of these samples show they are crystalline with no significant changes in structure.

Oxidation of Hydroquinones to Quinones; Quinone (Table 2, entry 1); Typical Procedure

Metal-exchanged clays Fe^{3+}-Mont. K-10, Ce^{4+}-Mont. K-10, Cu^{2+}-Mont. K-10 (0.5 g each) were doped with catalytic amount of CAN (0.274 g, 0.5 mmol) by stirring in CH_2Cl_2 (20 mL) for 10 min followed by evaporation of the solvent to get a dry powder. Hydroquinone (0.11 g, 1.0 mmol) dissolved in anhyd CH_2Cl_2 (10 mL) was added dropwise while sonicating (Branson ultrasonic bath) the reaction mixture at r.t. for various time intervals as shown in Table 2. TLC monitoring of the reaction was done till completion of the reaction. The mixture was filtered, washed with H_2O (2 × 10 mL) and dried ($CaCl_2$). Removal of the solvent followed by recrystallisation from Et_2O gave the desired product as pure yellow crystalline material; yield: 98%; mp 112 °C (Table 2). The spectral data (^1H NMR and IR) of the compounds were in agreement with that reported in literature.[14]

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