Evaluation of Adsorbent supported Metal nitrates for Heterogenous Catalytic Oxidation of Isopropanol to Acetone

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Summary: Catalytic effects of several solid adsorbents on the adsorbed metal nitrates towards oxidation (dehydrogenation) of isopropanol to acetone in the absence of any co-solvent have been studied. The efficacies of some commercial adsorbents as well as some indigenously available natural clays as catalytic supports have been evaluated. Transition metal nitrates have been found to be better supported oxidizing reagents than the alkali and alkaline-earth metal nitrates. A simple spectrophotometric method has been developed to monitor the amount of acetone formed during isopropanol oxidation.

Introduction

The use of adsorbent supported reagents for organic transformations is an intriguing area of current research [1]. Impregnation of inorganic salts as reagents on solid adsorbent provides larger effective surface area for interaction with the organic substrate molecules. Interaction of the impregnated inorganic reagent with the adsorbent surface generally has been found to activate the inorganic reagent towards the transformation of the organic substrate. Moreover, predisposition of the organic substrate molecules in close proximaty with the supported inorganic reagent causes decrease in the entropy of activation for the reaction. In some adsorbents, the presence of acidic and basic sites on the adsorbent surface may also play a synergistic role in the transformation of the organic substrate molecules. The above mentioned factors have made the supported reagents as reagents of active research interest for imporvement of the yields as well as regio and stereoselectivities of already known organic reactions and to discover novel organic transformations.

Clay supported reagents have been used in cycloaddition reactions [2-4], oxidation of alcohols to aldehydes and ketones [5,6], oxidative couplings [7], nitration of aromatic rings [8], and other valuable organic transformations [9-12]. The present paper describes the evaluation of metal nitrates as oxidizing agents when supported on various commercial and indigenous natural adsorbents. The effectiveness of the supported metal nitrates and the supporting solids has been compared by the oxidation of isopropanol to acetone.

Results and Discussion

A number of oxidizing reagents are knwon for oxidation of alcohols to aldehydes and ketones in homogenous conditions. Heterogenous catalytic oxidations of alcohols are also known [13], but these methods generally require the use of co-solvent which makes the work up and separation procedures cumbersome. The aim of this work was to

develop a convenient and cost effective method for oxidation of liquid secondary alcohols using cheaper inorganic nitrates supported on commercial as well as indigenously available adsorbents under heterogenous condition using the alcohol in neat form with out adding a co-solvent. The effectiveness of the supported metal nitrates as oxidizing species and the catalytic activities of the supporting adsorbents have been compared. A simple spectrophotometric method has been developed to monitor the extent of formation of acetone through the oxidation of isopropanol. The extent of acetone formation from isopropanol has been taken as a criterion for comparison of the effectiveness of metal nitrates and the supporting adsorbents.

Spectrophotometric determination of acetone in isopropanol

The spectrophotometric method used for the determination of acetone in isopropanol utilized Janovsky's reaction [14]. Acetone in the presence of a base adds to m-dinitrobenzene to form a Meisenheimer complex giving a distinct purple coloration. The Janovsky's reaction is used for qualitative detection of α-methylketones. With acetone in the presence of isopropanol, the reagent gave purple color solution showing a λ_{max} at 360 nm (Fig. 1). The color intensity was found to increase with the increase in the amount of acetone. For the purpose of quantitative determination of acetone in isopropanol, different concentrations of acetone ranging from 0 to 60% (V/V) were made. After reacting with m-dinitrobenzene in the presence of sodium hydroxide solution, the absorbance were read at 360nm on spectronic-20. A linear relationship between the concentration of acetone and the absorbance was observed (Fig. 2). The calibration curve obtained was used for the determination of acetone formed during the oxidation of isopropanol.

Preparation of supported reagents

The oxidizing reagents supported on various adsorbents (catalysts) were prepared by dissolving metal nitrates in water and then adding the adsorbent to the solution with subsequent stirring of the solution magnetically at room temperature for 1 hour. The solid was filtered out with suction, and the air dried material was further dried in an oven
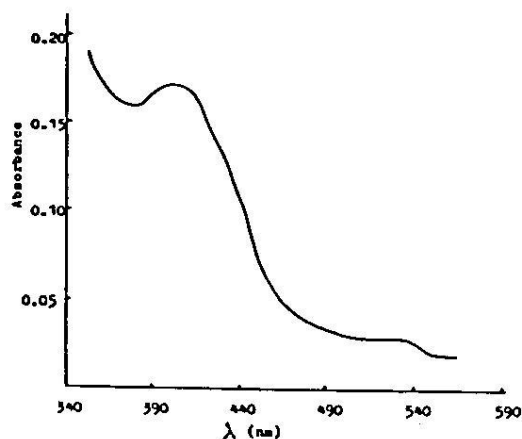

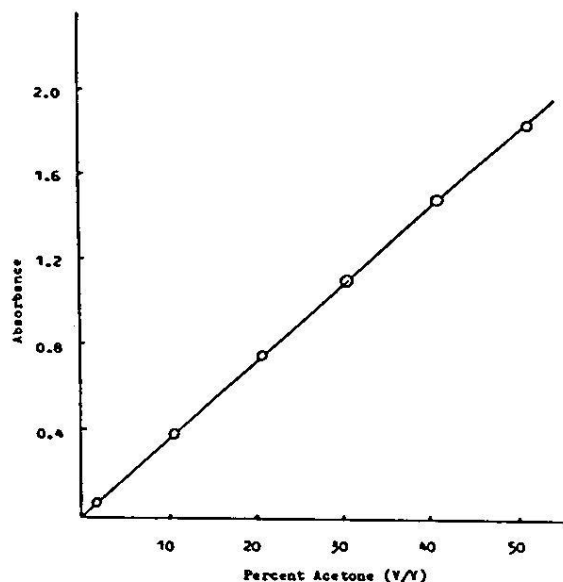Fig. 1: Absorption spectrum of acetone-m-dinitrobenzene complex.

Fig. 2: Calibration curve for acetone determination in isopropanol.

at 150°C, till a free flowing powder was obtained. The dried reagent was kept under anhydrous condition in a desiccator. It was observed that insufficient as well as excessive drying caused decrease in the oxidizing activity of the supported reagent. Similar observation has been reported by Nishiguchi et al. [12]. The effect of the amount of water content in similar supported reagents has been extensively investigated [15,16].

The metal nitrates supported in this study were $Ca(NO_3)_2$, $Pb(NO_3)_2$, $NaNO_3$, NH_4NO_3, $Zn(NO_3)_2$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$. Nishiguchi et

al., [13] have recently reported their results on the oxidation of a variety of alcohols using some metal nitrates supported on chromatographic grade silica gel. Alumina and Montmorrilonite clay have also been investigated as catalytic adsorbents for organic transformations [17,18]. In this study we have investigated indigenously available aluminosilicates (i.e., clay, sand, kaoline and slate), and Multani clay for evaluation of their catalytic activities in the oxidation of isopropanol to acetone and compared the catalytic effeciencies with those of commercially available adsorbents, i.e. Montmorrilonite K-10, chromatographic grade silica gel and alumina, as well as titanium oxide, celite and kieselguhr.

Evaluation of metal nitrates and supported oxidants

The oxidizing powers of some metal nitrates supported on chromatographic alumina was evaluated by the amount of acetone formed in 4 hr at the reflux temperature in isopropanol (Table 1). It was observed that ionic alkali and alkaline earth metal nitrates exhibited poor oxidizing power. However, ammonium nitrate was found to be a better supported oxidizing agent for the conversion of isopropanol to acetone. Among the covalent transition metal nitrates, viz. Zn, Cd and Cu nitrates, the highest oxidizing power observed was for the $Cu(NO_3)_2$ supported reagent (Table 1). Similar reactivity trend has been reported by Nishiguchi et al., [13] for the oxidation of various alcohols with metal nitrates supported on chromatographic silica in CCl_4 as solvent. These observations suggest that covalent transition metal nitrates are superior to ionic metal nitrates as supported oxidation reagents not only because of their higher oxidation power but also because of being safer as the later tend to explode with shock and at higher temperature. In order to evaluate the catalytic activities of the adsorbents, zinc nitrate was chosen as the resulting reagent was more stable than those from Cd and Cu nitrates.

Evaluation of catalytic activities of the adsorbents

A number of both commercial and indigenous adsorbents were investigated to evaluate their catalytic effect on the rate of oxidation of isopropanol to acetone using zinc nitrate as the supported oxidizing agent. Montomorrilonite K-10, a commercial acidic clay was used as a reference catalyst. The adsorbents investigated were, chromatographic grade silica gel and neutral

Table 1: Comparison of alumina supported nitrates as oxidants. (2 g of each nitrate was adsorbed on 10 g of chromatographic neutral alumina. Reactions were carried out with 2.5 g of the supported reagent and 10 mL of isopropanol for 4 hr at the reflux temperature).

Nitrates	Absorbance (360 nm)	Acetone formed % (V/V)
Sodium nitrate	0.00	0.00
Calcium nitrate	0.05	1.25
Ammonium nitrate	0.20	6.00
Lead nitrate	0.07	2.00
Zinc nitrate	0.51	13.50
Cadmium nitrate	0.73	18.50
Copper nitrate	0.80	20.00

alumina, kieselguhr, slate, celite, Warsak series soil, kaoline, Multani clay, titanium oxide and charcoal.

Titanium oxide and charcoal were found to have negligible catalytic effect on the oxidation of isopropanol, while among the aluminosilicates investigated as the adsorbents, the catalytic activity was found to decrease in the order, Montmorrilonite K-10, silica, Risalpur sand, alumina Warsak series soil slate, kieselguhr, celite, koaline (Table 2). Multani clay, a non-aluminosilicate, exhibited a reasonable catalytic activity. The catalytic activity shown by Multani clay might be due to iron as it is in much greater percentage than silica (65.27% vs 0.361%).

Table 2: Comparison of catalytic activities of adsorbents. (2 g of zinc nitrate was adsorbed on 10 g of each adsorbent. 2.5 g of the supported reagent was used, carrying out reaction with 10 mL of isopropanol at reflux for 4 hr).

Adsorbent	Absorbance (30 nm)	Acetone formed % (V/V)
Kaoline	0.02	0.25
Charcoal	0.06	1.50
Celite	0.07	1.75
Titanium oxide	0.08	2.00
Kieselguhr	0.14	3.00
Slate	0.21	6.00
Warsak soil	0.22	6.50
Alumina	0.45	11.20
Risalpur sand	0.49	12.00
Multani clay	0.52	14.00
Silica gel	0.79	20.50
Montmorrilonite K-10	1.00	26.00

The type of alumina used as catalytic adsor-
bent also affected the rate of isopropanol oxidation.
Zinc nitrate supported on α-alumina and γ-alumina
were used for the oxidation of isopropanol (Fig. 3)
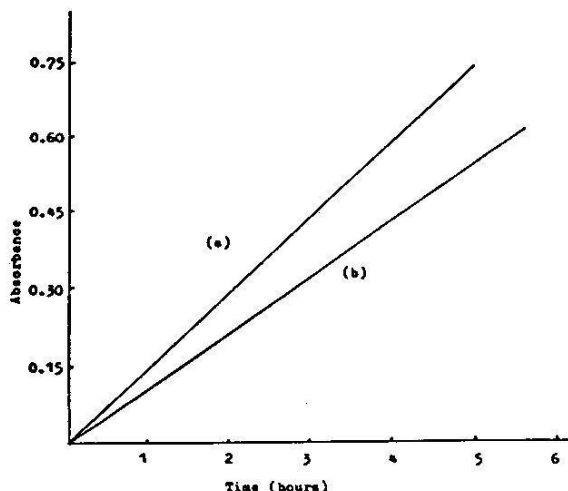Higher catalytic activity was observed with α-type.

Fig. 3: Effect of the type of alumina used as adsorbent; a.
α-alumina b. γ-alumina.

The strong acidic character of aluminosili-
cates is believed to be a major factor manifested in
the form of catalytic effect in organic reactions. The
acidic character in these binary oxides arises due
to the presence of SiO_4^{4+} tetrahedra in which
each oxygen shared with two tetrahedra. Substitu-
tion of an aluminum for silicon gives the AlO_4^{5-} ion;
so for each aluminum atom introduced there is one
excess negative charge that needs to be balanced
by a proton (Scheme -1). Equivalently, it may be
said that if the aluminum atom remains triply coor-
dinated, a neighbouring SiO_4^{4+} will carry an excess
negative charge, which may be balanced by a
proton in the form of silanol hydroxyl group. The
earlier mentioned arrangement represents a
Bronsted acid while the later represents a Lewis
acid. These protons could catalyze reactions that go
through a carbonium ion mechanism. Additional
factors giving catalytic effect to aluminosilicates in-
clude; (a) the regular crystalline structure and
uniform pore size which provide microenviron-
ments for the reactant molecule to interact effec-
tively, (b) the presence of very large electrostatic
fields in the microenvironments surrounding the or-
ganic intermediate cations or radicals which en-
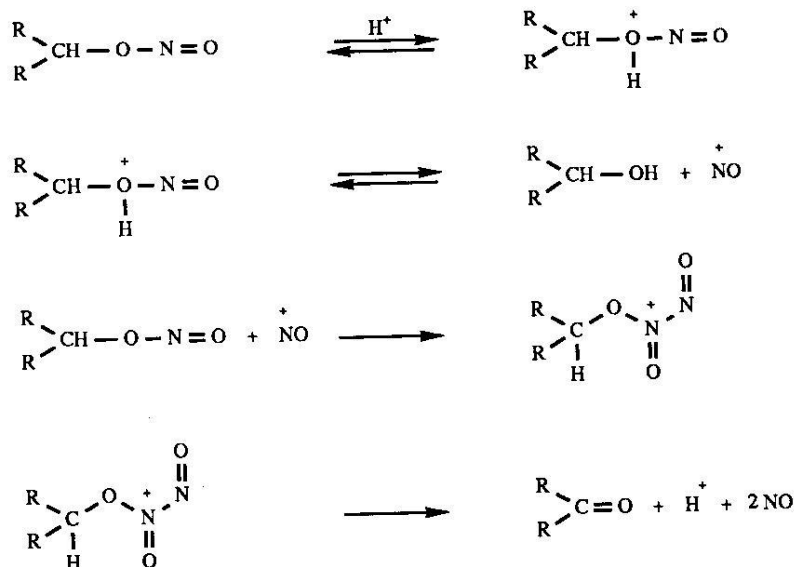hance the overall reaction rate, (c) the high acidity
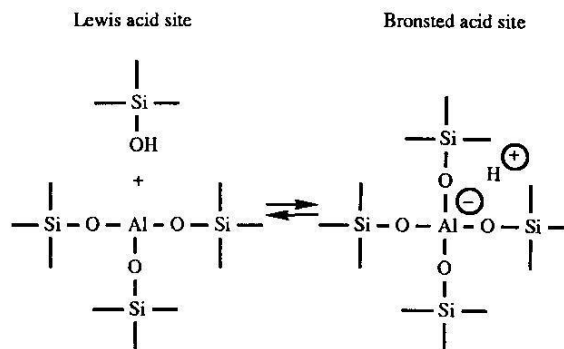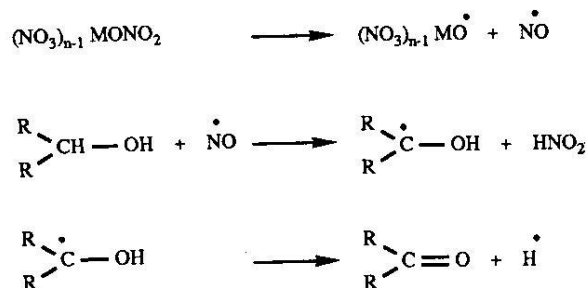

Scheme - I

due to the presence of exchangeable cations which
helps in the polarization of entrapped water
molecules and induce their dissociation and (d) the
presence of siloxane groups O_3Si-O-SiO_3 or some-
times its peroxodimer, O_3-Si-O-O-SiO_3, giving rise
to siloxy radicals which are highly reactive oxidizing
species.

Multani clay and Risalpur sand ranked third
and fourth respectively in their catalytic activities
preceeded by silica and Montmorrilonite. This ob-
servation is quite unexpected, as Multani clay being
a non-aluminosilicate has proven to be a better
catalytic adsorbent than some aluminosilicates like
kaoline, kieselguhr, slate, soil and sand. Work on
either the composition, crystal lattice or catalytic
property of Multani clay is heretofore not reported
in the literature. Structural characterization, sur-
face properties and other studies on Multani clay
would be needed before pondering over the
mechanistic mode of its catalytic actvity in such
oxidations. Among the indigenous clays inves-
tigated, Multani clay, Risalpur sand and Warsak
series soil proved to be prospective candidates for
their use as catalytic supports in metal nitrates
mediated heterogenous catalyhtic oxidation of al-
cohols to aldehydes and ketones.

Mechanistic investigations of the supported
metal nitrate oxidations of alcohols have shown the
intermediacy of nitrous esters [17]. In the presence
of strongly acidic clay like Montmorrilonite, a
nitrosonium ion (NO^+) mediated mechanism has
been proposed as shown in Scheme - 2 [18]. While
in the cases of adsorbents with lower surface
Bronsted acidities and possibility of the presence of
siloxyl radicals, like in chromatographic silica, a
nitro radical (NO) as intermediate has been impli-

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} CH-O-N=O \quad \xrightleftharpoons{H^+} \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} \overset{+}{CH-O}-N=O$$

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} CH-\overset{+}{O}-N=O \quad \underset{H}{|} \quad \rightleftharpoons \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} CH-OH \; + \; \overset{+}{NO}$$

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} CH-O-N=O \; + \; \overset{+}{NO} \quad \longrightarrow \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} \underset{H}{\overset{|}{C}} - O - \overset{+}{N} \overset{O}{\underset{O}{\parallel}} N$$

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} \underset{H}{\overset{|}{C}} - O - \overset{+}{N} \overset{O}{\underset{O}{\parallel}} N \quad \longrightarrow \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} C=O \; + \; \overset{+}{H} \; + \; 2NO$$

Scheme - II

$$(NO_3)_{n-1} MONO_2 \quad \longrightarrow \quad (NO_3)_{n-1} \overset{\bullet}{MO} \; + \; \overset{\bullet}{NO}$$

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} CH-OH \; + \; \overset{\bullet}{NO} \quad \longrightarrow \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} \overset{\bullet}{C}-OH \; + \; HNO_2$$

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} \overset{\bullet}{C}-OH \quad \longrightarrow \quad \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} C=O \; + \; \overset{\bullet}{H}$$

Scheme - III

cated [14] with the reaction following a radical pathway as shown in Scheme 3.
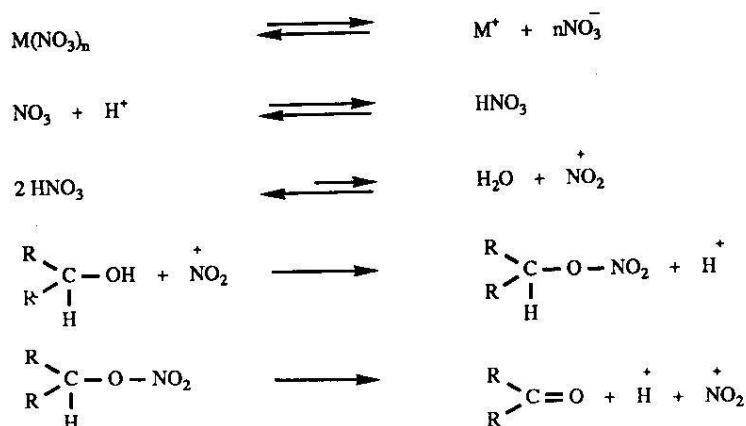
The lower oxidizing ability of the ionic metal nitrates (alkali and alkaline earth metal nitrates) compared to the covalent metal nitrates (transition metal nitrates) could be explained by invoking the participation of nitronium ion (NO_2^+) as the oxidizing species. Assuming the nitronium ion as the rate limiting reagent in the case of oxidation by the supported ionic metal nitrates, the lower rate of oxidation of isopropanol could be explained by the mechanism proposed in Scheme 4.

It is believed that in pure hydroxylic organic medium, the nitronium ion will play a rate limiting role. However, further studies are needed to validate the nature of association of nitrate ion (NO_2^-) with the adsorbent as a proof for the involvement of nitronium ion as an intermediate oxidizing species.

Experimental

Material

Isopropanol and acetone were obtained from BDH and were used without any further treatment. Silica gel (kiesselgel 60, 35-70 mesh) and m-dinitrobenzedne were obtained from E. Merck. Alumina (neutral), celite-535 and kieselguhr (chromatrographic grade) were supplied by BDH. Montmorrilonite K-10 was from Hanssen Chemica, Belgium. Multani clay, slate (Chirat), sand (Risalpur), soil (Warsak series), and kaoline (Swat) were either collected from the place indicated in parentheses or purchased from the local market. The adsorbents were screened on mesh and material having mesh size 60-70 and lower were used in this study. Spectronic-20 (Milton Roy) was used for the absorbance measurements.

$$M(NO_3)_n \rightleftharpoons M^+ + nNO_3^-$$

$$NO_3 + H^+ \rightleftharpoons HNO_3$$

$$2\,HNO_3 \rightleftharpoons H_2O + \overset{+}{N}O_2$$

$$\begin{array}{c}R\\ \diagdown \\ C-OH + \overset{+}{N}O_2 \\ R'\diagup \;|\\ H\end{array} \longrightarrow \begin{array}{c}R\\ \diagdown \\ C-O-NO_2 + \overset{+}{H}\\ R\diagup \;|\\ H\end{array}$$

$$\begin{array}{c}R\\ \diagdown \\ C-O-NO_2 \\ R\diagup \;|\\ H\end{array} \longrightarrow \begin{array}{c}R\\ \diagdown \\ C=O + \overset{+}{H} + \overset{+}{N}O_2\\ R\diagup\end{array}$$

Scheme - IV

Method

Absorption spectrum of acetone-m-dinitrobenzene complex

To 1.00 ml solution of isopropanol and acetone (1:1) was added 1.00 ml of sodium hydroxide solution (10%) and 1.00 ml of m-dinitrobenzene solution (1%). On mixing a dark red solution was formed which was diluted by addition of 5.30 ml of distilled water. Absorbance was recorded in the wavelength range of 340 nm to 600 nm on spectronic-20 using the appropriate blank. The recorded absorbance were plotted against the respective wavelengths (Fig. 1). Calibration studies for isopropanol-acetone system was subsequently done using λ_{max} (360 nm).

Calibration study for the determination of acetone in isopropanol

To 1.00 ml of various concentration (0 to 50%) of acetone in isopropanol was added 1.00 ml of the sodium hydroxide solution (10%) and 1.00 ml of 1% ethanolic solution of m-dinitrobenzene. The resulting solution was quickly mixed and diluted with 5.30 ml of distilled water. The absorbance was read at 360 nm after 5 min. of mixing. Calibration plot was obtained by plotting absorbance versus concentration of acetone in isopropanol (Fig. 2).

Preparation of catalyst supported metal nitrate reagents

Metal nitrate (2 g) was dissolved in 10 ml of distilled water. The adsorbent (10 g) was added to this solution and the slurry was stirred magnetically for 1 hr at 25°C. The solid was filtered on suction and air dried. The air dried reagent was further dried in oven at 105°C. The oven dried reagent was kept in a vacuum desiccator over anhydrous $CaCl_2$ under nitrogen atmosphere.

General method for oxidation of isopropanol

Isopropanol was refluxed with supported reagent (2.5 g) alongwith magnetic stirring. Aliquots (1.0 ml) were taken out with a glass syringe through a serum cap after intervals of 1 hr. To each aliquot was added 1.0 ml of the sodium hydroxide solution (10%) and 1.0 ml of the m-dinitrobenzene solution (1% ethanolic). The solution was diluted with 5.3 ml distilled water. The absorbance of the solution was read at 360 nm against an appropriate blank. The change in absorbance with time was plotted.

Acknowledgement

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