Degradation of 1,3-Diphenyl Thiourea by Cetyltrimethylammonium Permanganate in Solvent Free State: Reaction Kinetics and Mechanistic Aspects

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ABSTRACT

The kinetics of oxidation of 1,3-diphenyl thiourea by Cetyltrimethylammonium permanganate was studied in solvent free condition. The reaction shows first order dependence in cetyltrimethylammonium permanganate and 1,3-diphenyl thiourea which supports the derived rate law. Increase in ionic strength has no significant effect on reaction rate. The effect of temperature on the rate of reaction has also been studied and the activation parameters have been evaluated. The reaction constants involved in the mechanism were computed. A probable mechanism has been suggested on the basis of experimental observations. The stoichiometry of the reaction was found to be 2:3 and the oxidation products were identified as 1,3-diphenyl urea and sulfur.

INTRODUCTION

Thiourea derivatives are important chemical building blocks that have numerous pharmaceutical and chemical applications. They are used as efficient guanylating agents both in solution and on solid support [1-2]. N, N[1]-disubstituted thioureas are commercial substrates used in ore flotation process, isomerization process as catalyst, intermediate for the synthesis of dyes, in primary or secondary vulcanization process as accelerator, in photographic film, elastomers, plastics, textiles, metal refining as corrosion inhibitor and in metal cleaning process [3-10].

1,3-diphenyl thiourea commercially used in dyes, elastomers, plastics, textiles and certain substituted 1,3-diphenyl thioureas are insecticides, preservatives, rodenticides and pharmaceuticals [11-12]. N,N[1]-disubstituted thioureas are generally toxic in nature and their toxicity is because of presence of –N=C=S group and generally they decomposed to hazardous gaseous products like carbon monoxide, carbon dioxide and sulfur dioxide [13]. But the oxidation of N,N[1]-disubstituted thioureas results in corresponding ureas which are non-toxic in nature. Thus, the conversion of thioureas into ureas has attracted the interest of chemists since long. Solvents in organic reactions are believed to be responsible for global warming and climate changes. The toxicity and volatile nature of many solvents that are widely used in huge amount for chemical reactions have posed a serious threat to the environment. Based on above considerations chemists are expending much effort in developing solvent-free synthetic procedures that yield good result [14]. Thus, design of solvent-free reactions received tremendous attention in recent time in the area of green synthesis [15-16].
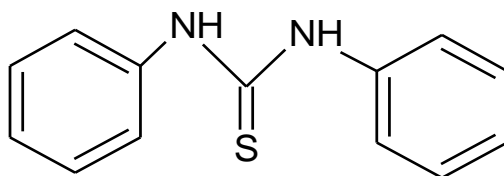

Fig.1: Structure of 1, 3-diphenyl thiourea

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MATERIALS AND METHODS

Experimental

Instrument and Reagents used

Spectrophotometer (Systronics Double beam 2203 smart) was used for absorption studies. 1, 3-diphenyl thiourea (Sigma-Aldrich), KNO3, Ethyl alcohol, Acetonitrile was of analytical reagent grade and were used as received.

Preparation of cetyltrimethylammonium permanganate:

A solution of 4.25 g (27.0 mmol) of $KMnO_4$ in 25 ml of water placed in a 250 ml two-necked flask equipped with a mechanical stirrer and a dropping funnel was cooled in an ice–water bath to 8–10°C. A solution of 9.10 g (25.0 mmol) of cetyltrimethylammonium bromide in 50 ml of dichloromethane was added in about 10 min. The mixture was stirred at 8–10°C for 3–4 h when most of the permanganate had passed into the organic layer, which was separated and the solvent was recovered under reduced pressure. The purple colored crystalline CTAP precipitated before the solvent was completely removed, which was collected by filtration, washed with water (50 ml) and ether (20 ml) and dried over P_2O_5 under vacuum in a desiccator; yield, 8.6 g (85%); decomposes above 115°C [14].
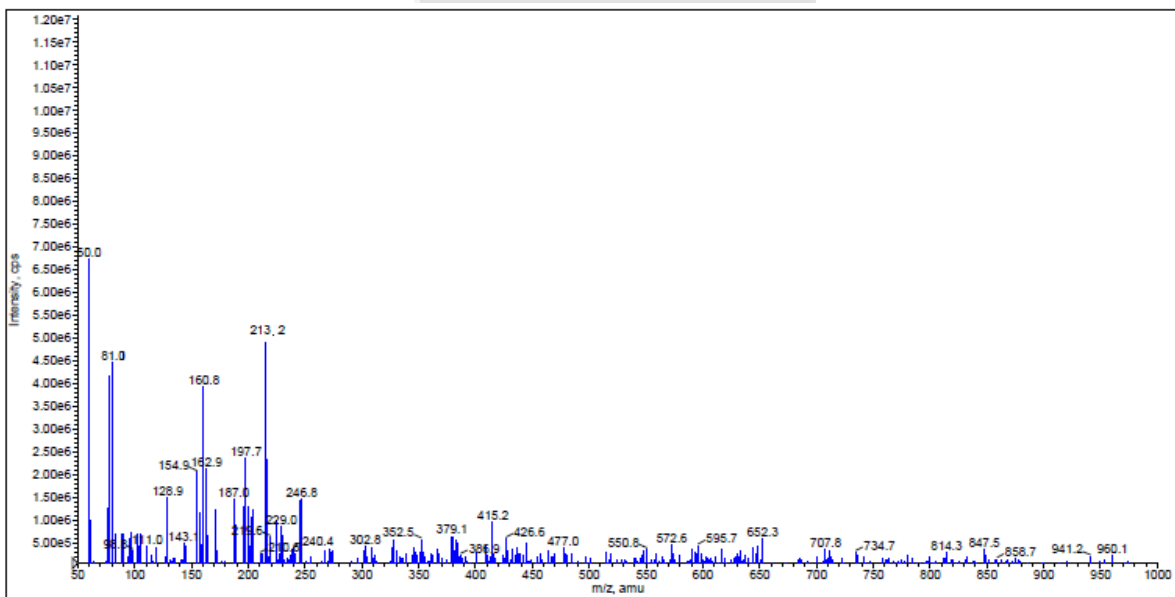

Fig.2: LC-MS which gives intense molecular ion peak at 213.2 MHz for 1,3-diphenyl urea.

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Kinetic Measurements

The reactions were studied under pseudo-first order conditions by keeping an excess of 1,3-diphenyl thiourea over cetyltrimethylammonium permanganate at constant temperature and were followed by monitoring the decrease in concentration of CTAP spectrophotometrically at 527 nm for up to 80% completion of reaction. The pseudo-first order rate constants 'kobs' were determined from the log (absorbance) versus time plots. The plots were linear up to 80% completion of reaction and the orders for various species were determined from the slopes of plots log kobs versus respective concentration of species. The kobs values were reproducible within $\pm 5\%$.

Stoichiometry and Product Analysis

Different sets of reaction mixture containing various ratios of CTAP to DPTU in presence of constant amount of KNO_3 were kept for 24 hours at 25 ± 1.0^0C. The remaining amount of CTAP was estimated spectrophotometrically which indicates the stoichiometric ratio 2:3 for CTAP/DPTU. The oxidative products were identified as 1,3-diphenyl urea which gives molecular ion peak at 213.2 MHz as shown in Fig.2 and Mn (IV) is identified by qualitative test [17].

RESULT AND DISCUSSION

Reaction Order

The cetyltrimethylammonium permanganate concentration was varied from 0.5×10^{-4} mol dm^{-3} to 4.5×10^{-4} mol dm^{-3} at fixed concentrations of DPTU (2.5×10^{-3} mol dm^{-3}) and KNO_3 (1.0×10^{-2} mol dm^{-3}). Pseudo first order plots were made as shown in Fig.3 and pseudo first order rate constants (k) were found to be independent of concentration of CTAP.

The DPTU concentration is varied from 0.5×10^{-3} mol dm^{-3} to 4.5×10^{-3} mol dm^{-3} at fixed concentrations of CTAP (2.5×10^{-4} mol dm^{-3}) and KNO_3 (1.0×10^{-2} mol dm^{-3}). From the pseudo first order rate constants as shown in Table 1 indicates first order dependence in DPTU.

The concentration of KNO_3 is varied from 0.25×10^{-2} mol dm^{-3} to 3.0×10^{-2} mol dm^{-3} at fixed concentrations of DPTU (2.5×10^{-3} mol dm^{-3}) and CTAP (2.5×10^{-4} mol dm^{-3}). The rate constants

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(k) for pseudo first order reaction indicates that the reaction rate was independent of ionic strength as mentioned in Table 1.
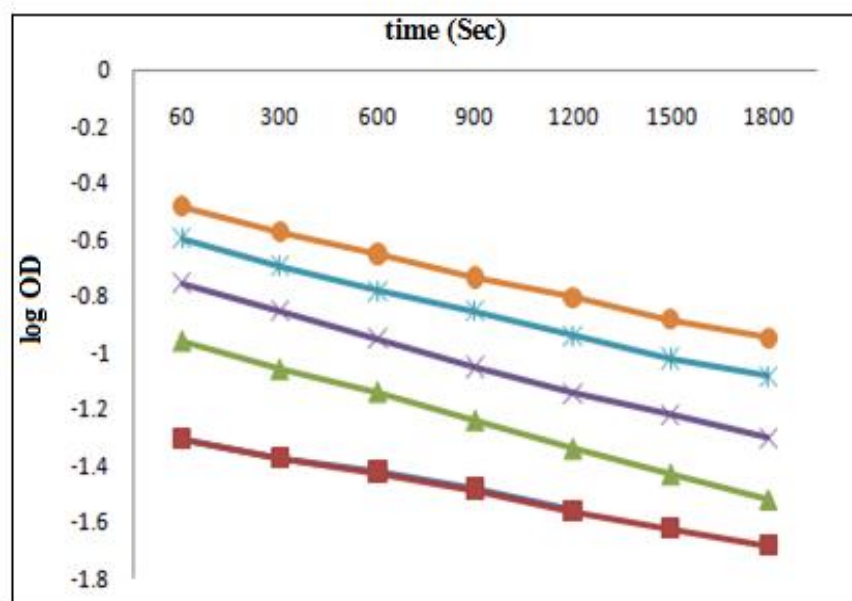
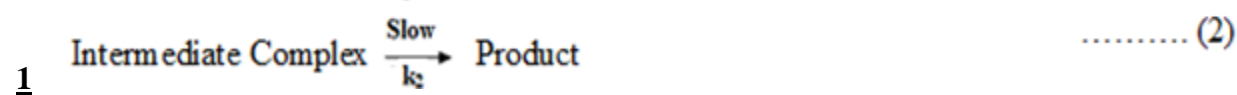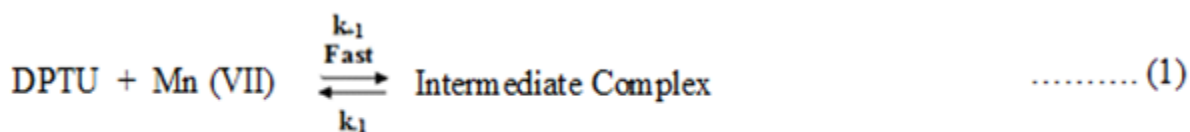**Fig.3: A graph of Log OD versus time shows first order dependence with respect to CTAP.**

POLYMERIZATION STUDY:

Involvement of free radical during oxidation of DPTU by CTAP was studied by adding acrylonitrile (free radical scavenger) followed by methanol dilution result in no precipitation, which clearly indicates reaction path is free from radical mechanism.

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Table 1: Effect of variation of CTAP $(2.5 \times 10^{-4}$ moldm$^{-3})$, DPTU $(2.5 \times 10^{-3}$ moldm$^{-3})$ and KNO$_3$ $(0.01$ moldm$^{-3})$ on the reaction rate.

[CTAP] X 10^{-4} (mol dm^{-3})	[DPTU] X 10^{-3} (mol dm^{-3})	[KNO$_3$] X 10^{-2} (mol dm^{-3})	kobs x 10^{-3} Exp	kobs x 10^{-3} Cal
0.5	2.5	1.0	1.748	1.780
1.5	2.5	1.0	1.733	1.780
2.5	2.5	1.0	1.768	1.780
3.5	2.5	1.0	1.724	1.780
4.5	2.5	1.0	1.742	1.780
2.5	0.5	1.0	0.436	0.432
2.5	1.5	1.0	1.036	1.170
2.5	2.5	1.0	1.768	1.780
2.5	3.5	1.0	2.302	2.316
2.5	4.5	1.0	2.714	2.749
2.5	2.5	0.25	1.762	1.780
2.5	2.5	0.5	1.753	1.780
2.5	2.5	1.0	1.768	1.780
2.5	2.5	2.0	1.766	1.780
2.5	2.5	3.0	1.772	1.780

SCHEME-

$$\text{DPTU} + \text{Mn (VII)} \underset{k_1}{\overset{\substack{k_{-1} \\ \text{Fast}}}{\rightleftharpoons}} \text{Intermediate Complex} \quad \dots\dots\dots\dots (1)$$

$$\text{Intermediate Complex} \xrightarrow[k_2]{\text{Slow}} \text{Product} \quad \dots\dots\dots\dots (2)$$

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By applying steady state approximation

Rate = -d [Complex] / dt = k_1 k_2 [DPTU] [CTPA] / 1 + k_1 [DPTU] ....… (3)

-d [Complex] / dt $\times$ 1 / [CTPA] = kobs = k_1 k_2 [DPTU] / 1 + k_1 [DPTU] ....… (4)

1 / kobs = 1 / k_1 k_2 [DPTU] + 1 / k_2 ....… (5)

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Equation (5) is verified by plotting 1/kobs versus 1/[DPTU] as shown in Fig.4, from the slope and intercept of plot, reaction constants k_1 and k_2 were calculated and the values are found to be 109.52 and 0.833×10^{-2} respectively. These constants are used to calculate 'kcal' under different experimental conditions and the values obtained are in close agreement with the experimental results as shown in Table 1.
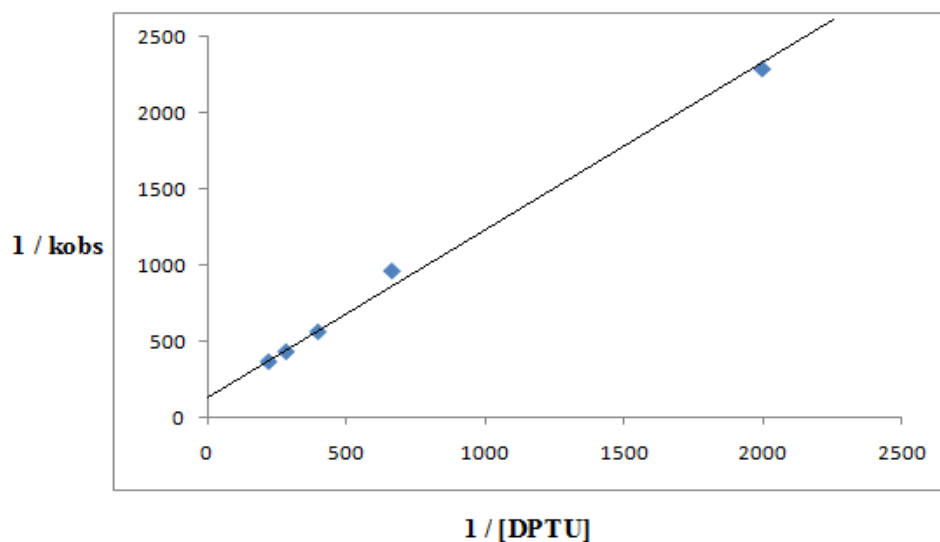

Fig.4: A Graph of 1/kobs versus 1/[DPTU] supporting the verification of rate law.

Table 2: Effect of variation of temperature on the Rate of Oxidation of DPTU by Permanganate (VII).

Temperature (K)	kobs x 10^{-3} (s^{-1})
298	1.768
303	2.538
308	3.526
313	5.258
318	7.008

The reaction rates were measured at temperature range 298K – 318K at fixed reactant concentrations with other conditions being constant. As temperature increases, the reaction rate also increases (Table 2). The Arrhenius plot is shown in Fig. 5 of log k against 1/T gives straight

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line and from the slope and intercept, the experimental energy of activation Ea was calculated. The Eyring's parameters $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were calculated and tabulated as shown in Table 3.

Table 3: Activation Parameters of Oxidation of DPTU by Permanganate (VII).

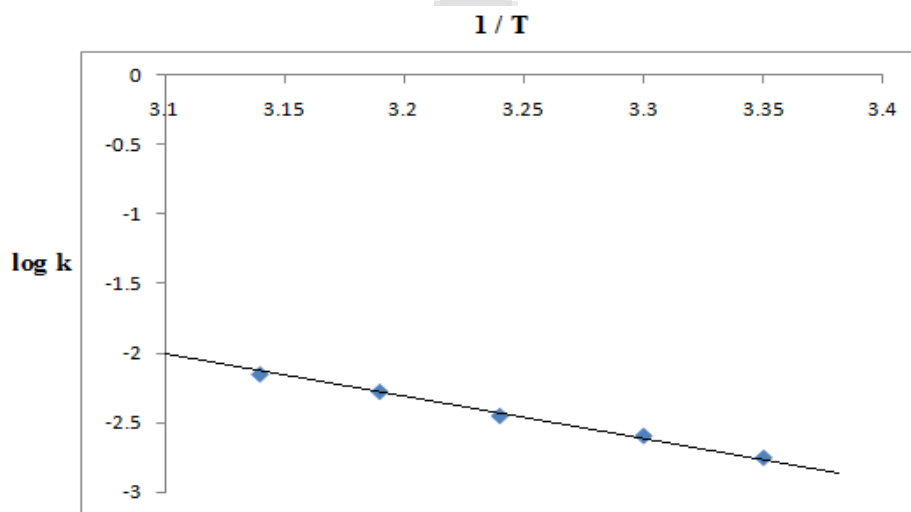| Activation Parameters	Values
Ea (kJ/ mol)	57.03
$\Delta H^{\#}$ (kJ/mol)	54.32
$\Delta S^{\#}$ (J/K/mol)	-123.92
$\Delta G^{\#}$ (kJ/K/mol)	90.84
$\log_{10}A$	2.0

Fig.5: Arrhenius plot (log k versus 1/T) of variation of temperature for DPTU oxidation by Permanganate (VII).
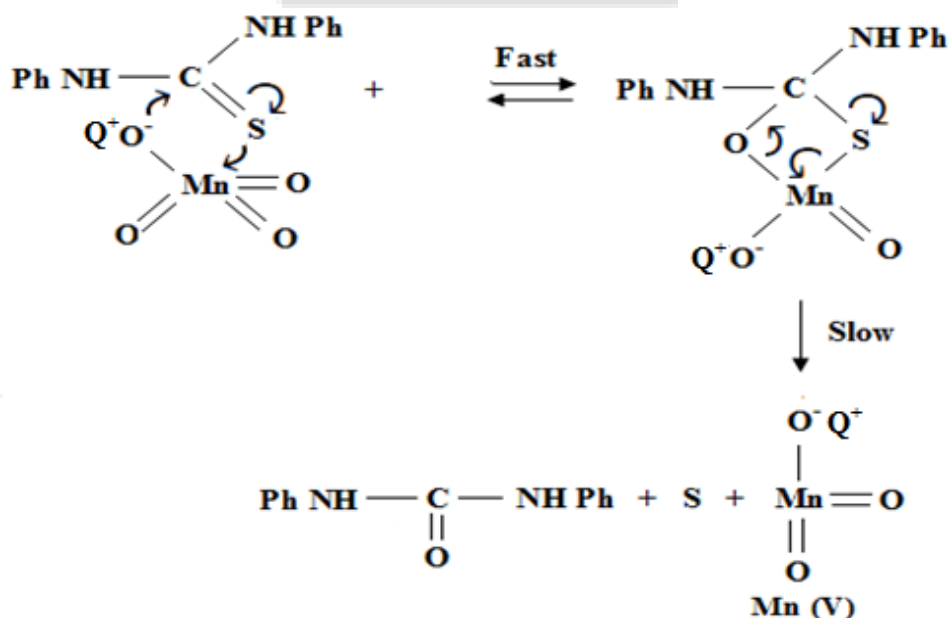
The permanganate ion attacks the sp^2 carbon of the 1,3-diphenyl thiourea to form a complex. The resultant sulfide attacks the electron deficient Mn to form a four-membered cyclic ester, which with a lose of two electrons dissipates to 1,3-diphenyl urea, sulfur and Mn(V). The reactive Mn(V) again reacts with another thiourea in a similar manner to yield respective urea, sulfur and Mn(III). The unstable Mn(III) undergoes disproportionation reacts with Mn(V) to yield two
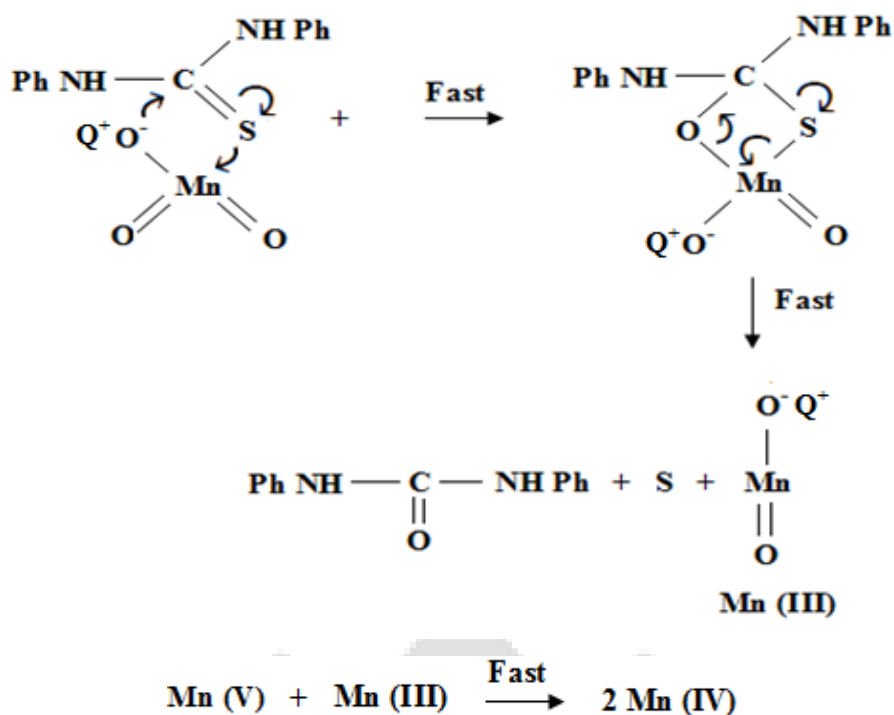
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Mn(IV). In this mechanism, the dissipation of the complex of Mn(VII) to Mn(V) is the rate-determining step.

CONCLUSION

The redox reaction of 1,3-diphenyl thiourea and cetyltrimethylammonium permanganate in solvent free condition shows a stoichiometry of 3:2, order of reaction found to be unity with respect to both DPTU and CTAP. The rate of reaction has no significant effect on ionic strength. Cetyltrimethylammonium permanganate oxidation process is eco-friendly and has gained importance in green chemistry. CTPA possess a long hydrocarbon chain that can draw substrate close to permanganate ion in a micelle-like aggregation, thereby enabling reactant molecules to efficiently interact with oxidizing ion even if a solvent is not present. The moderate values of $\Delta H^{\#}$ and the negative $\Delta S^{\#}$ supports the formation of complex in reaction as shown in scheme-1. The overall sequence described here is consistent with mechanistic studies and kinetic studies. In this article, we reported kinetics and oxidation of 1,3-diphenyl thiourea by cetyltrimethylammonium permanganate in solvent free condition and the method gives the procedure to reduce the toxicity of 1,3-diphenyl thiourea.

<ins>The detailed mechanism of Scheme-1</ins>

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$$Mn\ (V)\ +\ Mn\ (III)\ \xrightarrow{Fast}\ 2\ Mn\ (IV)$$

REFERENCES

[1] Alan R. Katritzky, Boris V. Rogovoy, Recent development in guanylating agents, ARKAT USA, Inc., 2005, 1424 (6376), 49-87.

[2] Silvio Cunha, Manoel T. Rodrigues Jr., The first bismuth (III) - catalyzed guanylation of thioureas, Tetrahedron Letters, 2006, 47, 6955-6956.

[3] Arifoglu M.A, Marmer W.N, Dudley R.B, Textile Res. 1992, 62, 94–100.

[4] Cagarra J, Gacen J, Caro, M, Pepio, M. J. Soc. Dyers Colour 1988, 104, 273–279.

[5] Ayres J.A, Decontamination of Nuclear Reactors and Equipment; Ronald Press Co., NewYork, 1970, p 177.

[6] Klern H, Lux, J, Noll D, Reider W, Phillips H, A Field Survey of Internal Boiler Tube Corrosion in High-Pressure Utility Boilers, Proceedings of the American Power Conference, Illinois Institute of Technology, Chicago, IL, 1971, 33, 702–709.

[7] Atwood K.L, Hale G.L, A Method for Determining Need for Chemical Cleaning of High-Pressure Boilers, Proceedings of the American Power Conference, Illinois Institute of Technology, Chicago, IL, 1971, 33, 710–720.

[8] Knox J.A, Smith J.A, Stout R.F, US Patent 1973, 3,730,901; Chem. Abstr. 1974, 81, 53183.

Snell F.D, Photometric and Fluorimetric Methods of Analysis, Parts I and II, Wiley, NewYork, 1978.

[9] Okazaki K, Murakami M, Kawada H, Okada, A. Jpn. Kokai. 1975, 394, 7597; Chem. Abstr. 1975, 83, 175159.

[10] Giri, S.N, Combs, A.B, Toxicol. Appl. Pharmacol. 1967, 16, 709–717; Lewis R.J, Sax's Dangerous Properties of Industrial Materials, 1992, Vol. 2064 (8), Von Nostrand, NewYork.

[11] Hans-Wilhelm Eagels, Herrmann-Josef Weidenhaupt, Manfred Pieroth, Werner Hoffman, Rubber chemicals and additives, Ullmann's encyclopedia of industrial chemistry by Wiley-VCH, Weinheim, 2004.

[12] Kristin Samuelsson, Diphenyl thiourea, a common rubber chemical, is bioactivated to potent skin sensitizer, Chemical research in Toxicology, 2011, 24(1), 35-44.

[13] Fourth Annual Report on Carcinogens, 423; US Department of Health and Human Services, GPO:Washington, DC, 1985; Sixth Annual Report on Carcinogens 1991; US Department of Health and Human Services, National Toxicology Program, 1991, 376.

Citation: M. Manju et al. Ijppr.Human, 2016; Vol. 7 (3): 41-51.

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[14] B C Vimala, Gepatur Nagendrappa, Solvent free reactions using cetyltrimethyl ammonium permanganate and cetyltrimethylammonium dichromate-cis-1,2-dihydroxylation of alkenes, oxidation of alcohols and regeneration of aldehydes and ketones from oximes" , J. Saudi Chem. Soc. 2009, 13(2), 169-178.

[15] Hiren M. Marvaniya, Kaumil N. Modi, Dhrubo jyoti sen, Green reactions under solvent free conditions, Int. Journal of Drug Dev. and Res., 2011, 3(2), 34-43.

[16] M Himaja, Das Poppy, Karigar Asif, Green technique – solvent free synthesis and its advantages, Int. Journal of research in ayurveda and pharmacy, 2011, 2(4), 1079-1086.

[17] Svehla, Vogel's qualitative inorganic analysis, 7th Edition, Pearson Edu Ltd. 1996.

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