Kinetic Study of Oxidation of Aniline Derivatives by Selenium Dioxide in Aqueous Acetic Acid Medium

Abhilash Kumar Verma[1], Akash Kumar Gupta[2]
[1,2]*Department of Chemistry, S.G.S. Govt. P.G. College, (NAAC B+) Sidhi-486661 (M.P.) India*

***Abstract*—This paper reports the results of our initial work on the oxidation of ortho-methoxy aniline and þara-methoxy aniline by selenium dioxide under lack of free radical conditions to yield corresponding industrially important products dimethoxy azobenzenes as dyes. The rate of reactions exhibits duo first-order kinetics with respect to oxidant and substrate and is subject to acid catalysis. The stoichiometrically (1:2) reaction is believed to be proceeded by H_2SeO_3 and $H_3SeO_3^+$ the prime active species of SeO_2 in presence of strong mineral acid with substrate. The dominancy of positive inductive and +M effects, orientation (influence of directing group) and role of thermodynamic parameters in support of proposed coupling type reaction mechanism was assessed.**

***Index Terms*—ortho-methoxyaniline, para-methoxyaniline, seleniumdioxide, stoichiometry, oxidation.**

I. INTRODUCTION

Selenium dioxide is a rare earth compound Riley's *et al.* [1] were the first to introduce SeO_2 as an oxidant. Since then, considerable progress has been made in the application of SeO_2 as a selective reagent in organic synthesis [2] and most commonly oxidizes C-H bonds attached to various activating groups of organic compounds [3-10] which have received much attention, and attracted national and international laboratories.

In presence of mineral acid [11] such as H_2SO_4, SeO_2 produces H_2SeO_3 and $H_3SeO_3^+$ various species which are readily reduced by a variety of substances to Se, but their properties were not studied systematically.

Aromatic amines are derived form ammonia in which nitrogen is directly attached to the benzene nucleus in $-NH_2$ group and are weaker bases as compared to the aliphatic amines due to the presence of lone pair of electrons at nitrogen atom which is in conjugation with π electron of the ring, Hence, the tendency of aromatic amines for protonation is hindered and is less available for coordination with proton. Thus, in order to show the influence of $-NH_2$ group, inductive effect on its reaction mechanism and causes of methoxy group direct influence on rate, widened new vision and utility of SeO_2 in applied field, the task of oxidation of ortho- and þara-methoxy anilines have been taken for investigation. Although, a closely related reaction of oxidation of nucleo substituted halo amines and analogous studies have already been made by different oxidants. [12-14]

The study of methoxy aniline derivatives is one of the most important classes of intermediates used in the production of dyes, pharmaceutical products, pesticides and in valuable synthesis of a number of heterocyclic compounds.

II. EXPERIMENTAL

All the chemicals and solvents used in the experiment were purified [15] by double distillation. The oxidizing agent, SeO_2 (Loba) and o- and þ-methoxy nucleus substituted aniline derivatives of Across reagent grade were used as such obtained. SeO_2 solution was standardized iodometrically [16] before use.

III. KINETIC STUDY

The kinetic experiments were carried out in the presence of excess of methoxy aniline derivatives, a small correction was introduced to account for the slow oxidation of the solvent by SeO_2 in typical experiment. A 50 ml volumetric flask containing solutions of methoxy aniline derivatives in aqueous acetic acid was held about 30 minutes in a thermostat at 35^0 C and 30^0 C. Definite calculated quantity of SeO_2 was then added and the solution was vigorously stirred until homogeneous, about 2 ml of the aliquot

was immediately transferred to another flask maintained at same respective temperatures kept in the thermostat. The reaction kinetics were periodically estimated volumetrically by iodometric technique until the reaction was completed. Pseudo first-order rate constants were obtained by using integration method and also from the slopes of ln $[SeO_2]_0 / [SeO_2]_t$ vs. time (t) plots graphically.

IV. RESULTS AND DISCUSSION

Plots of -ln (a-x) vs. time are linear, thus indicating that the reaction rates are first-order with respect to oxidizing agent (SeO_2). This was confirmed by measuring the initial rates of o-methoxy and þ-methoxy anilines at several SeO_2 concentrations. The initial rates are found proportional to the initial SeO_2 concentrations.

The pseudo first-order rate constants were observed to be proportional to the substrate concentrations. Thus, it may be concluded that the reactions are also first-order with respect to the reductants. The plots of k_{obs} vs. [substrate] (Fig. 1) were linear in all cases for the oxidation of aniline derivatives. The kinetic data are summarized in Table 1.

Table 1: Dependence of rate constants on the concentration of o-methoxy aniline and þ-methoxy aniline

k $s^{-1} \times 10^4$		
[Aniline derivative] mol $dm^{-3} \times 10^3$	o-methoxy aniline (1)	þ-methoxy aniline (2)
0.50	-	0.91
1.00	1.31	1.85
1.66	-	2.84
1.88	2.34	-
2.00	2.65	3.14
2.50	3.15	4.11
3.33	4.10	5.41
4.00	4.91	-
5.00	6.21	-

$[SeO_2] \times 10^3$ (mol dm^{-3}) = 2.50 (2), 3.33 (1) ; $[H^+] \times 10^3$ (mol dm^{-3}) = 0.40 (1, 2) ;
Acetic acid-water, % (v/v) = 15 (2), 20 (1); Temperature K = 303 (2), 308 (1)

The results presented in Table 2 indicate that reaction is subject to acid catalysis.

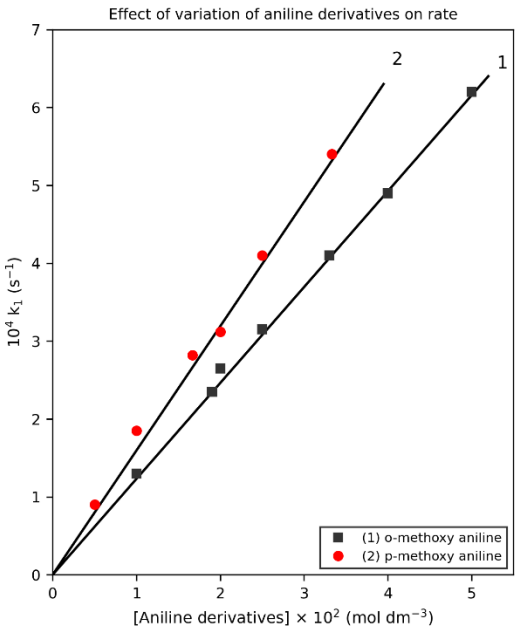


Fig. 1 Plot of k_1 vs. [Substrate]

$[SeO_2] \times 10^3$ (mol dm^{-3}) = 2.50 (2), 3.33 (1);
$[H^+] \times 10^3$ (mol dm^{-3}) = 0.40 (1, 2);
CH_3COOH-H_2O, % (v/v) = 15 (2), 20 (1);
Temperature K = 303 (2), 308 (1)

It is instructive to consider possible points in the reaction sequence where acid catalysis could logically occur. Plots of ln k vs. ln $[H^+]$ are linear with unit slope value (Fig. 2) exhibited first-order kinetics with respect to H^+.

It is known that protonation of SeO_2 / H_2SeO_3 produces a powerful oxidant could therefore account for the observed catalysis.

Table 2: Dependence of the rate constants on the concentration of acid

k $s^{-1} \times 10^4$		
$[H_2SO_4] \times 10^3$ mol dm^{-3}	o-methoxy aniline (1)	þ-methoxy aniline (2)
0.250	1.31	1.50
0.333	1.83	-
0.400	2.35	2.84
0.500	2.72	3.55
0.666	3.65	4.70
1.000	5.42	6.97
1.250	6.87	8.71

[Substrate] $\times 10^3$ mol dm^{-3} = 1.66(2),1.88(1) ; $[SeO_2] \times 10^3$ mol dm^{-3} = 2.50 (2), 3.33 (1) ;
CH_3COOH: H2O, % (v/v) = 15 (2), 20 (1); Temperature K = 303 (2), 308 (1)

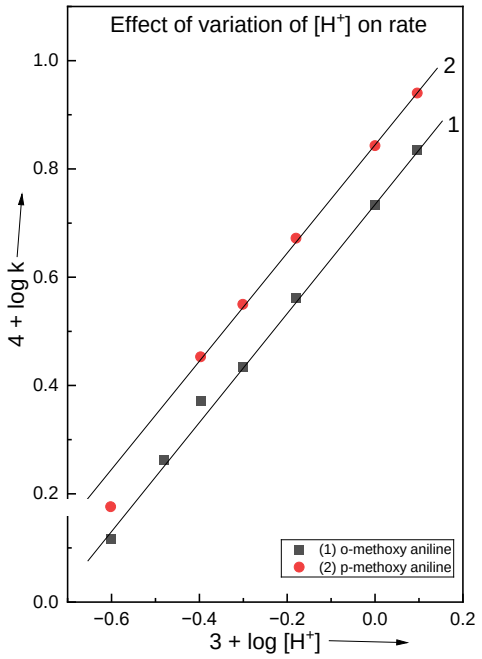


Fig. 2 Plot of log k vs. log [H^+]

[Substrate] ×10^3 mol dm^{-3} = 1.66 (2).1.88 (1) ;
[SeO_2] × 10^3 mol dm^{-3} = 2.50 (2), 3.33 (1) ;
CH_3COOH:H_2O, % (v/v) = 15 (2), 20 (1) ;
Temperature K = 303 (2), 308 (1)

These reactions were studied at different composition of acetic acid-water mixtures (10% to 50%, v/v), with the increase in the percentage of acetic acid there is a slight enhancement of in the reaction rate. The plots of log k versus 1/D are linear with positive slope showing that reaction is a positive ion-dipolar type. The study also satisfies Swain's [17] and Kamlet [18] equations and have negligible effect pointing there by the ion-dipole nature of the reaction.

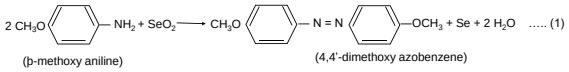
It should be noted that presence of ionic strength (I) of the medium and salts sodium chloride and potassium chloride in reaction does not bring out any change in rate thus overruling the probability of ascribing the suppression in rate logically demonstrating due to salt significant effect.

The rate of oxidation of these compounds is catalyzed by the addition of third series of transition metal ion Cu^{2+} whereas retardation was observed in presence of Mn^{2+}. This fact has already been explained by previous workers. [19]

Free radicals are not generated even after tested by trapping method employing olefinic monomer acrylonitrile. The investigation fails to induce polymerization [20] completely and discarded the involvement of one electron-based mechanism.

V. STOICHIOMETRY

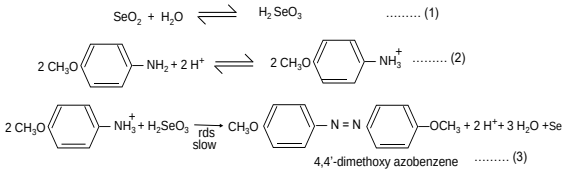
The stoichiometry of these reactions was determined methodically as pseudo first-order condition [SeO_2] >> (anilines) maintaining the concentrations of other participating reagents and temperatures constant. The overall stoichiometry reaction may be formulated as an exemplary equation for þ-methoxy aniline.



The products dimethoxy azobenzenes of the reactions were characterized by azo dyes test and IR spectral analysis.

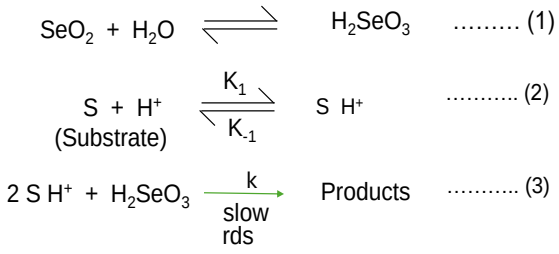
VI. MECHANISM

We propose from the evidence detailed above, the following mechanism for the SeO_2 oxidation of o- and þ-methoxy anilines involving stoichiometry (1:2) at the cost of a rate determining loss of hydrogen.



RATE LAW

The rate expression corresponding to postulated mechanism may be derived as follows:



The rate $\frac{-d}{dt}[H_2SeO_3] = k\,[SH^+][H_2SeO_3]$ ….(4)

Employing mass balance for H_2SeO_3, at steady-state approximation, we obtain equation (5)

$$k_{obs} = \frac{K_1\,K_2[S][H^+][H_2SeO_3]}{K_{-1} + k\,[H_2SeO_3]} \ldots\ldots(5)$$

Under the condition when K_{-1} >> k, after omission of k [H_2SeO_3] from denominator and writing k_1/k_{-1} = k then

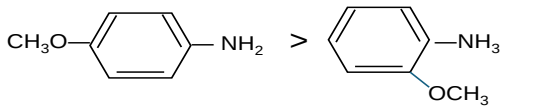
The equation (5) reduces to

$$k_{obs} = k\,K\,[S]\,[H^+][H_2SeO_3] \quad \ldots.(6)$$

Equation (6) justifies all the kinetic features about the first-order each with respect to oxidant substrate and H^+.

VII. STRUCTURE AND REACTIVITY

The rate constant for the two nucleo substituted methoxy anilines studied indicate that the order of reactivity of methoxy aniline is:



(þara-methoxy aniline) (ortho-methoxy aniline)

The justification of above sequence of reactivity among the nucleo substituted methoxy anilines is based on orientation influence of directing group inductive effect, +M mesomeric effect in addition to partition function and thermodynamic parameters. Since in the complied mechanism involves Zwitter ion, the oxidation is due to driving force pausing toward a bond sufficient to expel the proton in the reaction. It has been found that +I and +M effects are more pronounced and dominant in the þara-methoxy group another than ortho-methoxy group. The examination of Table 3, provides ample of evidence that the values of Arrhenius equation was found to be in accordance with reactivity order i.e.

That is the value of E_a (Energy of activation) is lowest for fastest reaction and vice-versa as cited in reverse order of reactivity. The minimum value of entropy of activation lowers the disorder of molecules and reducing the translational and rotational freedom of molecule as per order of reactivity. The entire reactions are in well specifically associated by enthalpy controlled.

Table 3: Thermodynamic and Activation Parameters for the Oxidation of Anilines derivatives by Selenium dioxide

Substrate	E_a kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}
o-methoxy aniline [a]	61.22	87.00	59.54	87.90
p-methoxy aniline [b]	58.78	84.42	55.77	93.77

Temperature range 30-45^0 C [(a)] and 25-45^0 C for [(b)]

The entropies of activation are referred to the 1 M standard state.

Average coefficient of temperature (T): 1.47[(a)] and 2.16[(a)] and 1.45[(b)] and 2.11 [(b)] for respective 5^0 and 10^0 C.

VIII. CONCLUSION

The reacting species H_2SeO_3 / $H_3SeO_3^+$ of oxidant in mineral acid postulated has been used in elucidation of the oxidation mechanism of o- and þ-methoxy anilines based on Zwitter ions observing coupling reaction to afford dimethoxy azobenzenes industrially import dyes as the products. The dominancy of +I and mesomeric effects and directing influence of group was observed. The order of reactivity with stoichiometric ratio (oxidant: substrate) 1:2 was assigned. The H^+ ion catalyzed reactions follow first-order each with respect to oxidant and substrates, The proposed mechanism is in conformity with the derived rate law, supported by kinetic data and activation parameters.

ACKNOWLEDGEMENT

The authors are very thankful to principal and Head department of Chemistry, S.G.S. Govt P.G. College, Sidhi (M.P.) India for encouraging and providing laboratory facilities for this work.

CONFLICT OF INTEREST

The authors declare conflicts of no interest whatsoever.

REFERENCES

[1] H. L. Riley and N. A. Friend, *J. Chem. Soc.*, p. 2342, 1932.
[2] N. Rabjohn, Organic Reactions, vol. 5, ch. 8. New York, NY, USA: John Wiley & Sons, 1959.
[3] D. K. Dwivedi and N. Manikpuri, Int. J. Adv. Res. Chem. Sci., vol. 6, no. 2, pp. 1–6, 2019.
[4] N. D. Valechha and A. K. Pandey, J. Indian Chem. Soc., vol. 63, p. 679, 1986.
[5] N. D. Valechha, Indian Chem. Soc., vol. 24A, p. 773, 1985.
[6] H.-S. Kim and J.-H. Kang, Bull. Korean Chem. Soc., vol. 22, no. 12, p. 1390, 2001.

[7] K. B. L. Shrivastava and R. Singh, Asian J. Chem., vol. 7, p. 767, 1995.
[8] S. S. Baghel, S. P. Singh, and S. K. Singh, Int. J. Green Herb. Chem., sec. A, vol. 9, no. 3, pp. 315–322, 2020.
[9] J. P. Schafer, J. Am. Chem. Soc., vol. 84, p. 717, 1962.
[10] K. J. Singh and S. N. Anand, J. Indian Chem. Soc., vol. 56, p. 363, 1979.
[11] S. Tiwari, M. U. Khan, B. M. L. Tiwari, K. S. Tiwari, and N. D. Valechha, Oxid. Commun., vol. 22, no. 3, pp. 416–423, 1999.
[12] P. S. Radhakrishnamurti and M. D. Prasad Rao, Indian J. Chem., vol. 10, pp. 790–792, 1976.
[13] K. B. Subhaiah, P. S. N. Murty, B. A. N. Murty, and P. V. Subba Rao, J. Indian Chem. Soc., vol. 56, pp. 1213–1216, 1979.
[14] P. S. Radhakrishnamurti and M. D. Prasad Rao, Indian J. Chem., vol. 14B, p. 898, 1976.
[15] D. Perrin, W. L. Armarego, and D. R. Perrin, Purification of Laboratory Chemicals. New York, NY, USA: Pergamon Press, 1980.
[16] M. Z. Barkat and A. Waheb, Anal. Chem., vol. 51, p. 764, 1986.
[17] C. G. Swain, S. H. Unger, N. M. R. Rosenquest, and M. S. Swain, J. Am. Chem. Soc., vol. 105, p. 492, 1983.
[18] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham, and R. W. Taft, J. Org. Chem., vol. 48, p. 2877, 1983.
[19] A. C. Chatterjee and S. K. Mukherjee, J. Phys. Chem., vol. 28, p. 287, 1958.
[20] D. S. Mohajer and S. Tangeaninejod, Tetrahedron *Lett.*, vol. 35, p. 845, 1994.