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Kinetics and Mechanism of Oxidation of *m*-Anisidine by Periodate Ion

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The kinetics of the oxidation of *m*-anisidine (MMA) by periodate ion has been followed by monitoring the increase in the absorbance of reaction intermediate, C. The reaction followed second order behaviour, being first order in each reactant. The rate of reaction decreases with decrease in dielectric constant of the medium. Free radical scavengers do not affect the reaction rate. The stoichiometry has been found to be 1 mol MMA:2 mol of periodate. Thermodynamic parameters evaluated are: $E_a = 8.8$ kcal mol^{-1}, A = 3.4.2 × 10^4 dm^3 mol^{-1} s^{-1}; $\Delta S^\# = - 39.9$ kcal mol^{-1}, $\Delta G^\# = 20.8$ kcal mol^{-1} and $\Delta H^\# = 8.2$ kcal mol^{-1}. Results under pseudo first order conditions, [*m*-anisidine] >> [IO_4^-], are in agreement with the rate law:

$$d[C]/dt = kKK_w\,[S]_0[IO_4^-][H^+]\,/\{K_2\,K_w + (K_w + K_b\,K_2)\,[H^+] + K_b\,[H^+]^2\}$$

where kK is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$, K_b is base dissociation constant of MMA and $[S]_0$ represents the concentration of MMA that has been taken in excess. In agreement with the rate law the $1/k_2$ *versus* [H^+] profile passes through the minimum. Main reaction product isolated and characterized is methoxy-1,4-benzoquinone.

Key Words: kinetics, Periodate oxidation, *m*-Anisidine, Rate-pH profile, Methoxy-1,4-benzoquinone.

INTRODUCTION

Keeping in view the contradictory and only few reports available on the non-malapradian periodate oxidation of aromatic amines[1-5], the kinetic-mechanistic studies on the periodate oxidation of *m*-anisidine (MMA) in acetone-water medium were undertaken. The already available reports are contradictory in regard to the ionic or free radical mechanism being followed[6]. Recent reports include the periodate oxidation of 3,3',5,5'-tetramethylbenzidine and oxidation of L-proline by *bis*(hydrogen periodato) argentate(III) complex anion[7]. In continuation to our earlier studies[8-17], the results of studies on periodate oxidation of *m*-anisidine in acetone-water medium aimed to decide the mechanism of the reaction and rate law particularly for seeking an explanation for the unique rate-pH profile observed are being presented and discussed in the present communication.

EXPERIMENTAL

Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[18], consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH. Systronics digital pH-meter-802 was used for measuring the pH of reaction mixture. Sodium meta periodate (Loba Chemie), *m*-anisidine (Sigma-Aldrich), acetone (E. Merck) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/recrystallization. The reactions were initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing the *m*-anisidine and buffer and maintained at the desired temperature (± 0.1 ºC). High precision thermostatically controlled water bath with an accuracy of ± 0.1 ºC was employed for maintaining the desired temperature.

The progress of the reaction was followed by recording the absorbance of reaction mixture at different time on Schimadzu double beam spectrophotometer (UV Pharmaspec-1700), at 470 nm, *i.e.*, the λ_{max} of the yellow reaction mixture. λ_{max} was found to remain unchanged during the period of study of the reaction as well as on changing the pH.

Product analysis: Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially the solution turned yellow, thereafter wine red and finally the product was precipitated on standing. It was filtered and the filtrate was extracted with petroleum ether (40-60 ºC). The extract was evaporated at room temperature. On separation of a droplet (due to moisture), solid residue was left on the watch glass. This residue was dissolved in petroleum ether and subjected to TLC (plate thickness = 0.5 mm, stationary phase = silica gel G, eluent = mixture of chloroform and benzene in the volume ratio 60:30, elution time = 40 min) to get three components scarlet, violet and yellow in colour. Only yellow coloured compound could be collected in sufficient amount by preparatory TLC and recrystallized in ethanol before subjecting to the characterization studies. It was characterized as methoxy-1,4 -benzoquinone on the basis of positive test for quinone[19], m.p. 146 ºC (literature value 145 ºC[20]), UV spectrum (in $CHCl_3$ giving absorption maxima at 250 and 352 nm, which suggested the presence of quinonoid structure in the compound (literature values 254 and 357 nm for methoxy-1,4-benzoquinone[21]).

The IR spectrum of compound (in KBr) showed the presence of bands at 2700 cm^{-1} (s) (due to ring C-H stretch), 1635 cm^{-1} (s) (indicating the presence of C=O on 1,4-benzoquinone pattern with the possibility that the position of this band got lowered due to +I effect of methoxy group[22]), 3250 cm^{-1} (s) (may be due to overtones of C=O stretch as the frequency is about twice that of C=O stretch). Further, the bands at 1393 cm^{-1} (s), 1492 cm^{-1}(s) may be due to C=C ring stretch. The bands at 1245 cm^{-1} (m) to 1041 cm^{-1} (m) may be due to asymmetric and symmetric C-O-C strech and at 831 cm^{-1} (m) (due to out of plane C=C bending mode). The observed values are in good agreement with those reported/expected for methoxy-1,4 -benzoquinone.

The NMR spectrum of this compound in $CDCl_3$ showed the peaks at $\delta = 7.260$, s, (1H); at $\delta = 7.000$, d, (2H) and at $\delta = 4.080$, s, (3H). A singlet at $\delta = 4.080$ may be due to $-OCH_3$ group attached to the ring. The other signals in spectrum at $\delta = 7.260$ and $\delta = 7.000$ were due to protons of the ring.

RESULTS AND DISCUSSION

Preliminary observations: On mixing the reactants, the solution becomes yellow which later changes in to wine red. On keeping for long time it finally gives the product. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. The rapid scan of the yellow solution showed the λ_{max} of the intermediate C to be 470 nm. The UV-visible spectra of IO_4^- and *m*-anisidine indicated these to show no absorption in visible region. Hence for following the kinetics the absorbance changes were recorded at 470 nm at which only the intermediate C absorbs. Plane mirror and Guggenheim's methods, respectively were used for evaluation of initial rates, (dC/dt) and pseudo first order rate constants, k_{obs}.

Stoichiometry: Stoichiometry of the reaction was determined by allowing a known excess of $NaIO_4$ to react with substrate. At suitable intervals of time, the reaction mixture was pipetted out and the product, either in turbid or in precipitated form was extracted with chloroform. Now the reaction mixture was estimated for the unconsumed $NaIO_4$ iodimetrically. The graphical plot obtained in this way, followed the pseudo first order behaviour upto a point after which inflexion was obtained in the curve. It was taken as the point corresponding to the completion of the first stage of the reaction for which the kinetic studies were made. The results indicate the stoichiometry to be 1 mol MMA:2 moles periodate as in eqn. 1.

$$CH_3OC_6H_4NH_2 + 2IO_4^- + 2H^+ \rightarrow CH_3OC_6H_3O_2 + 2HIO_3 + NH_3 \qquad (1)$$

Rate law: The kinetics was studied under pseudo order conditions, *viz.*, $[IO_4^-]_0 >> [S]$ and $[S]_0 >> [IO_4^-]$. Under these conditions, the reaction displayed first order. Under the condition, $[S]_0 >> [IO_4^-]$, the results (Table-1) were defined by the eqn. (2) and pseudo first order rate constant, k_{obs}, was equal to $k_2\,[S]_0$.

$$d[C]/dt = k_2\,[IO_4^-]\,[S]_0 \qquad (2)$$

where k_2 is a pH-dependent second order rate constant.

On the other hand under the condition $[IO_4^-]_0 >> [S]$, the rate was defined by eqn. 3 and k_{obs} was equal to $k_2\,[IO_4^-]_0$.

$$d[C]/dt = k_2\,[IO_4^-]_0\,[S] \qquad (3)$$

In eqns. 2 and 3 $[IO_4^-]_0$ and $[S]_0$ represent the initial concentrations of reactants in excess. The values of k_2 determined from k_{obs} values clearly indicate first order in each of periodate and anisidine.

TABLE-1
EFFECT OF VARIATION OF CONCENTRATION OF REACTANTS, IONIC STRENGTH, DIELECTRIC CONSTANT AND pH ON THE REACTION RATE; Temp. = 35 ± 0.1 ºC

[$NaIO_4$] (mol dm^{-3})	[MMA] (mol dm^{-3})	Acetone % (v/v)	pH	$k_{obs} \times 10^4$ (s^{-1})	$k_2 \times 10^2$ (dm^3 mol^{-1} s^{-1})
0.001	0.010	10	7.0	1.92	1.92
0.001	0.012	10	7.0	2.30	1.92
0.001	0.014	10	7.0	2.69	1.92
0.001	0.016	10	7.0	3.07	1.92
0.001	0.018	10	7.0	3.45	1.92
0.001	0.020	10	7.0	4.00	2.02
0.010	0.001	10	7.0	1.25	1.25
0.012	0.001	10	7.0	1.49	1.24
0.014	0.001	10	7.0	1.73	1.23
0.016	0.001	10	7.0	1.92	1.20
0.018	0.001	10	7.0	2.12	1.18
0.020	0.001	10	7.0	2.35	1.18
0.001	0.01	10	5.0	1.34	1.34
0.001	0.01	10	5.5	1.63	1.63
0.001	0.01	10	6.0	2.02	2.02
0.001	0.01	10	6.5	2.50	2.50
0.001	0.01	10	7.0	1.92	1.92
0.001	0.01	10	7.5	1.50	1.50
0.001	0.01	10	8.0	1.15	1.15
0.001	0.01	10	8.5	0.96	0.96
0.001	0.01	10	9.0	0.86	0.86
0.001	0.01	5.0	7.0	2.30	2.30
0.001	0.01	7.5	7.0	2.11	2.11
0.001	0.01	10.0	7.0	1.92	1.92
0.001	0.01	12.5	7.0	1.63	1.63

Effect of pH, dielectric constant of the medium, free radical scavengers and temperature: The effect of pH was examined in the range 5.0-9.0. Rate-pH profile indicates a maximum at pH = 6.5 (Table-1, Fig. 1), which could be due to change in the nature of species and their relative reactivity when the pH is changed.

An increase in dielectric constant increased the rate of reaction as indicated by a linear plot between log k_2 *versus* 1/D, where D is the dielectric constant of the medium. Free radical scavengers acrylamide and allyl alcohol had no effect on the reaction rate. This effect (Table-1) indicates an ion-dipole type interaction in the rate-determining step and that the reacting ion is possibly an anion.

The thermodynamic parameters evaluated by determining the rate constants at four different temperatures ranging from 35.0 to 50.0 ºC (Table-2) are: E_a = 8.8 kcal mol^{-1}, A = 3.4×10^4 dm^3 mol^{-1} s^{-1}, $\Delta S^{\#}$ = -39.9 cal mol^{-1}, $\Delta G^{\#}$ = 20.8 kcal mol^{-1} and $\Delta H^{\#}$ = 8.2 kcal mol^{-1}.

Initially, there is appearance of yellow colour which continues to darken with increase in the concentration of the intermediate, C and finally the product settles on standing for long time. Obviously, the coloured intermediate is formed on a time scale of minutes and the final product on a time scale of hours. It appears that the overall reaction involves several steps and possibly several transient intermediates, in addition to comparatively stable one C, are formed during the oxidation of *m*-anisidine into benzoquinone. Further, the kinetic order of one in periodate but requirement of the two periodate molecules for each anisidine molecule as per stoichiometry indicates the involvement of only one periodate in the rate determining step and second IO_4^- ion is consumed in a fast step in the formation of the intermediate, C. It also indicates the yellow coloured intermediate is quite stable and its concentration is not in steady state. There should be no change in its concentration with time. On the contrary, concentration of C increases continuously with time and reaches a limiting value - the happening that was used in following the kinetics of this reaction. Moreover, k_2-$[H^+]$ profile indicates the presence of at least three differently reactive reactant species in the pH region chosen for study.

TABLE-2
ACTIVATION PARAMETERS FOR THE PERIODATE OXIDATION OF *m*-ANISIDINE IN ACETONE-WATER MEDIUM

$[MMA] \times 10^2 = 1.0$ mol dm^{-3}, $[NaIO_4] \times 10^3 = 1.0$ mol dm^{-3}, Acetone = 10.0 % (v/v), pH = 7.0

Temp. ± 0.1 °C	$k_{obs} \times 10^4$ s^{-1}	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}	E_a k cal mol^{-1}	$A \times 10^4$ dm^3 mol^{-1} s^{-1}	$\Delta S^\#$ cal mol^{-1}	$\Delta G^\#$ k cal mol^{-1}	$\Delta H^\#$ k cal mol^{-1}
35	1.92	1.92	8.8	3.4	-39.9	20.8	8.2
40	2.40	2.40	–	–	–	–	–
45	2.97	2.97	–	–	–	–	–
50	3.74	3.74	–	–	–	–	–

It is important to consider and discuss the speciation of anisidine and periodate species in aqueous solutions before proposing a mechanism for the reaction under consideration. In aqueous solutions, periodate exists in three forms represented by the equilibria:

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, K_1 = 2.30 \times 10^{-2} \quad (4)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, K_2 = 4.35 \times 10^{-9} \quad (5)$$

The value of K_1 indicates that in the pH range 5-9, the species H_5IO_6 shall be practically non-existent and hence only species $H_4IO_6^-$ and $H_3IO_6^{2-}$ need be considered for explaining observed pH-dependence. In case of *m*-anisidine[23], in aqueous solution the following acid-base equilibrium with $K_b = 1.58 \times 10^{-10}$ operates.

$$CH_3OC_6H_4NH_2 + H_2O \rightleftharpoons CH_3OC_6H_4NH_3^+ + OH^- \quad (6)$$

In the studied pH-range, both $CH_3OC_6H_4NH_2$ and $CH_3OC_6H_4N^+H_3$ shall exist and both of these have been considered.

Based on the observed kinetic rate laws (2-3) and pH-dependence, the following mechanism, which assumes, $CH_3OC_6H_4NH_2$ and $H_4IO_6^-$ to be the reactive species, is proposed.

$$CH_3OC_6H_4NH_2 + [IO_4^-] \xrightleftharpoons{K} [A] \tag{7}$$

$$[A] \xrightleftharpoons{k} \text{Intermediate [B] (slow)} \tag{8}$$

$$[B] + IO_4^- \longrightarrow \text{Intermediate [C] (fast)} \tag{9}$$

The intermediate, C, appear to undergo very slow reorganization/ hydrolysis to yield the reaction product.

$$\text{Intermediate [C]} \longrightarrow \text{Product} \tag{10}$$

In the mechanism for simplicity, $H_4IO_6^-$ has been written as IO_4^-. Since the elementary reactions in liquid phase are a rarity, the formation of a transient intermediate [C], which could be a collisional complex/reactant pair in a rapid step having a low value of equilibrium constant, K, is assumed in the proposed gross mechanism.

The mechanistic steps (8-9) lead to the rate law:

$$d[C]/dt = k\,[A] \tag{11}$$

$$= kK[CH_3OC_6H_4NH_2]\,[IO_4^-] \tag{12}$$

Since the observed kinetics shows first order in each of $[CH_3OC_6H_4NH_2]$ and $[IO_4^-]$, the value of K must be low.

At affixed pH, under the condition $[S]_0 >> [IO_4^-]$, the rate of formation of intermediate, C, is given by eqn. 13.

$$d[C]/dt = kK[IO_4^-][S]_0/(1 + K[S]_0) \tag{13}$$

Likewise, under the condition $[IO_4^-]_0 >> [S]$

$$d[C]/dt = kK\,[IO_4^-]_0[S]/(1 + K[IO_4^-]_0) \tag{14}$$

Since the reaction shows first order in each of [S] and $[IO_4^-]$, the inequalities $K[S]_0 << 1$ and $K[IO_4^-]_0 << 1$ should operate in eqns. 13 and 14, respectively leading to the rate laws in eqns. 2 and 3.

On substituting the values of concentrations of the reactive species $[CH_3OC_6H_4NH_2]$ and $[IO_4^-]$ in terms of equilibria (4-5) and (6), respectively, in eqn. 12, the complete rate law including $[H^+]$-dependence becomes:

$$d[C]/dt = kK\{([S]_0[OH^-]/([OH^-] + K_b)\}\{([IO_4^-][H^+]/(K_2 + [H^+])\} \tag{15}$$

On replacing $[OH^-]$ $[H^+]$ by K_w and $[OH^-]$ by $K_w/[H^+]$ in denominator and on rearranging, we get,

$$d[C]/dt = k\,KK_w[S]_0[IO_4^-][H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b\,[H^+]^2\} \tag{16}$$

On comparing eqns. 2 and 16, we get

$$k_2 = kKK_w[H^+]/\{K_2\,K_w + (K_w + K_b\,K_2)\,[H^+] + K_b\,[H^+]^2\} \tag{17}$$

Equation 17 on rearranging becomes eqn. 18.

$$1/k_2 = (K_2/kK[H^+]) + \{(K_w + K_b\,K_2)/k\,KK_w\} + K_b\,[H^+]/kKK_w \tag{18}$$

The nature of the rate law shows that a plot of $1/k_2$ *versus* $[H^+]$ shall pass through a minimum as discussed in detail in a review by Gupta and Gupta[24]. On differentiating $1/k_2$ with respect to $[H^+]$ in eqn. 18, we get the values of $d^2[1/k_2]/d[H^+]^2$. The value of second derivative is found to be positive showing the plot of $1/k_2$ *versus* $[H^+]$ to pass through a minimum. Thus, on setting $d[1/k_2]/d[H^+]$ equal to zero for obtaining hydrogen ion concentration at which the $1/k_2$ *vs.* $[H^+]$ profile will pass through minimum, we obtain,

$$[H^+]_{min} = (K_2 K_w/K_b)^{1/2}$$

On substituting the values of K_2, K_w and K_b, we get

$$[H^+]_{min} = 5.25 \times 10^{-7} \text{ mol dm}^{-3}$$

It is gratifying to note that the calculated value of $[H^+]_{min}$ is in excellent agreement with the experimental value of $[H^+]_{min}$ of 3.16×10^{-7} mol dm^{-3} obtained from $1/k_2$ *versus* $[H^+]$ plot (Fig. 1).

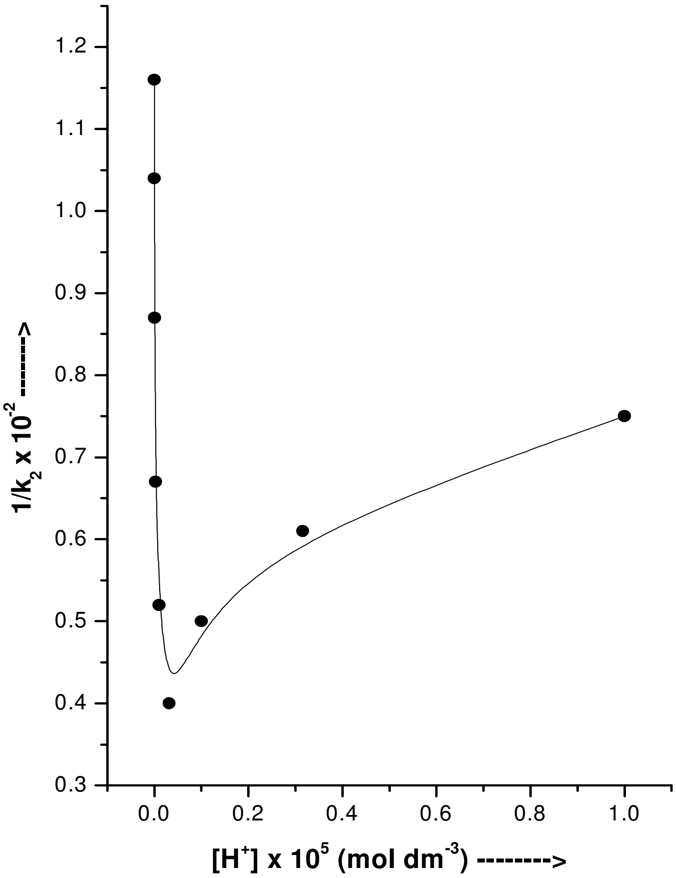
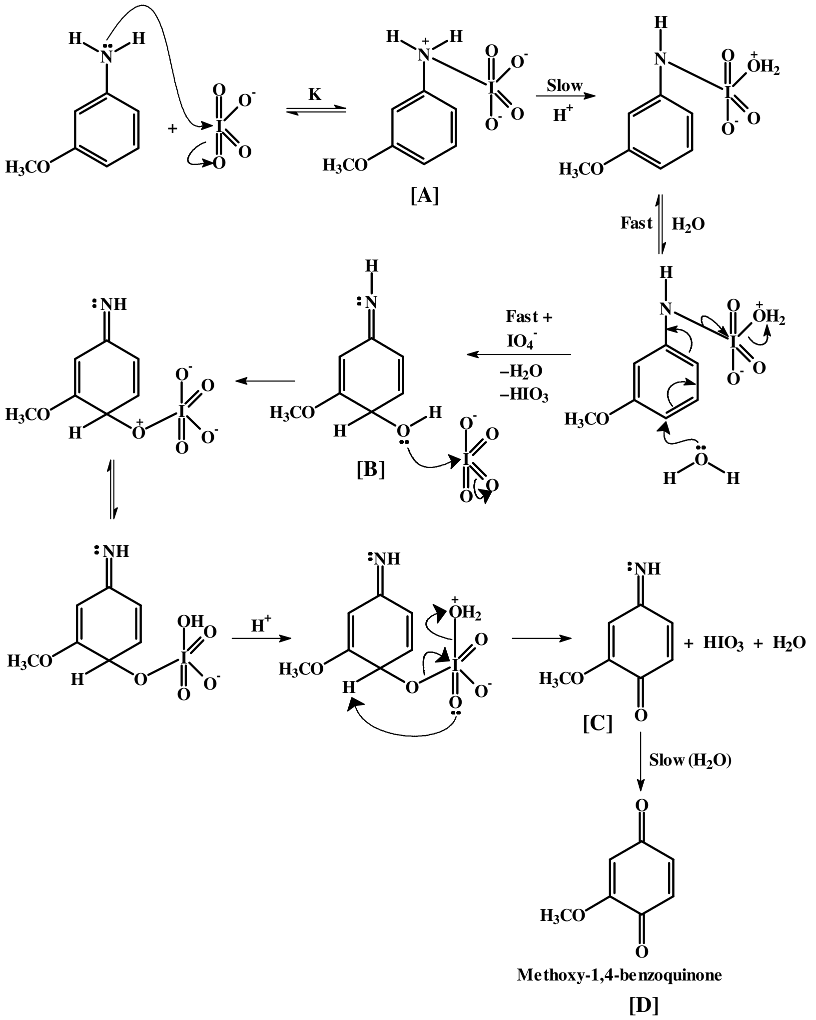


Fig. 1. Effect of $[H^+]$ on reaction rate at $[NaIO_4]$ = 0.001 mol dm^{-3}, [MMA] = 0.01 mol dm^{-3}, acetone = 10.0 % (v/v), Temp. 35 ± 0.1 ºC

It is necessary and interesting to discuss the possible molecular mechanism of the reaction. Mechanism proposed in **Scheme-I** shows the first step as a reversible bimolecular reaction between MMA and [IO_4^-]. The formation of a charged intermediate complex [A] taking place by the attack of [IO_4^-] on the nitrogen of anilino group and stabilization of positive charge on this nitrogen are well supported by our earlier LFER studies on this type of reaction series[12-14]. The high negative value of entropy of activation supports the involvement of solvation effects in this reaction. The formation of another intermediate [B] followed by its reaction with another IO_4^- to form quinoneimine [C] in a fast step are the expected steps of the mechanism involved. The last step (10) seems to be the slow hydrolysis and rearrangement of (C) to give methoxy-1,4-benzoquinone (D), *i.e.*, the main product of the reaction that has been isolated, separated and characterized.



Scheme-I

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