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Mechanism of Ru (III) catalysis in acid bromate oxidation of dimethyl diethylene glycols: A kinetic study

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ABSTRACT

Ru(III) catalyzed Oxidation of dimethyl diethylene glycol (DMDG) by potassium bromate in acidic media in the presence of mercuric acetate shows zero order dependence on dimethyl diethylene glycol $[H^+]$ *ions while it is first order for [bromate] and Ru(III). Addition of mercuric acetate has no effect on the reaction. The real reactive species of Ru (III) chloride has been proposed as* $(RuCl_2(H_2O)_4]^+$ *in the acid range. The reaction product is the corresponding aldehyde. Various activation parameters have been computed.*

Keywords: Kinetic, Ru (III) chloride, oxidation, DMDG, potassium bromate

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INTRODUCTION

In the oxidation of alcohols [1], cyclonols [2,3], phenols [4], α– hydroxyl acids [5] , aldehydes [6-8], tartaric acid [9], labile substances [10] and ketones [11], a powerful oxidizing agent potassium bromate with redox potential 1.44V is used, but very little work is done on the Ru (III) catalysed reaction involving potassium bromate as oxidizing reagent. This prompted us to investigate the catalytic role of Ru (III) chloride in oxidation of DMDG by acidic solution of potassium bromate in the presence of mercuric acetate as scavenger.

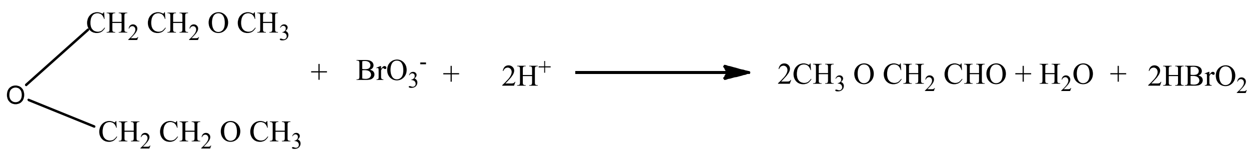
MATERIALS AND METHODS

Potassium bromate (BDH, LR), dimethyl diethylene glycol (BDH, LR) sodium perchlorate (E. Merck) perchloric acid (60%) and E. Merck (Germany) grade of mercuric acetate were used as such. Aqueous solutions were prepared by using double distilled water.

To avoid any photochemical reaction, the reaction stills were blackened from the outside. Except Dimethyl diethylene glycol, requisite amount of all reactants were allowed to mix and thermo stated at 35ºC for thermal equilibrium. Measured amount of DMDG also thermo stated at the same temperature is rapidly added to the reaction vessel containing other reactants. The progress of reaction was monitored by estimating the unconsumed bromate idiomatically, in a measured aliquot of the reaction mixture at different intervals of time. All the observations were taken at constant temp (± 0.1ºC).

STOICHIOMETRY AND PRODUCT ANALYSIS

Reaction mixture containing varying proportion of DMDG and bromate kept at 35ºC in the presence of 1×10^{-3} M perchloric acid for twenty four hour. Estimation of unreacted bromate shows that in dimethyl diethylene glycol, one mole of glycol consumed two moles of bromate according to the following stoichiometry equation.



The end product corresponding aldehydes were confirmed by TLC and also through di nitro phenyl hydrazine (DNP) derivative [12].

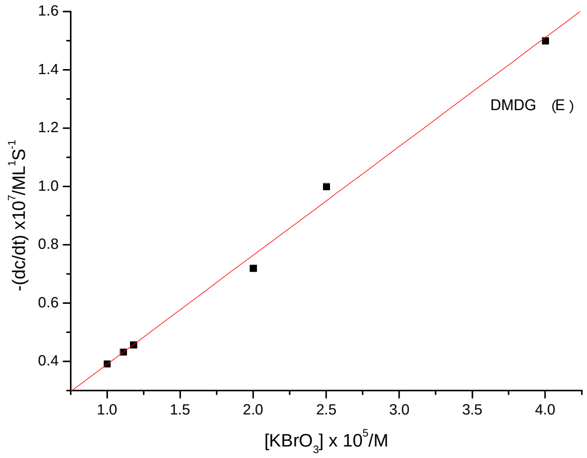
RESULTS AND DISCUSSION

First order dependence on bromate and zero order on DMDG and perchloric acid were obvious from the data (table 1). First order rate constant (-dc/dt) or (K.) were calculated from the slopes of plots of unconsumed bromate verses time for different initial concentration zero. First order kinetics in Ru (III) and Zero order dependence on ionic strength are also obvious from the results (table 2). Successive addition of mercuric acetate (table 2)**,** chloride ions had insignificant effect (table 3). Successive addition of acetic acid increased the reaction rate showing a negative dielectric effect on the rate (table 3). A plot of log K**,** against log [Ru (III)] in case of DMDG also yields a straight line with slope 1.01 confirming thus first order in the Ru (III) fig. (2).

TABLE 1: EFFECT OF REACTANTS RATE ON THE REACTION RATE:

Bromate 10^{-4} M	[DMDG] 10^{-1} M	[$HCLO_4$]10^{-1} M	(-dc/dtx10)$ML^{-1}S^{-1}$	K x 10 Mol^{-1} S^{-1}
4.00	1.00	20.00	1.50	5.64
2.50	1.00	20.00	1.00	5.72
2.00	1.00	2.00	0.72	5.54
1.18	1.00	2.00	0.458	5.40
1.11	1.00	2.00	0.433	5.41
1.00	1.00	2.00	0.392	5.70
2.00	2.00	2.00	.73	5.46
2.00	1.00	2.00	.72	5.54
2.00	0.50	2.00	.74	5.69
2.00	0.33	2.00	.69	5.31
2.00	0.20	2.00	.73	5.62
2.00	0.10	2.00	.72	5.54
2.00	1.00	2.00	.72	5.54
2.00	1.00	5.00	.70	5.39
2.00	1.00	10.00	.74	5.64
2.00	1.00	20.00	.73	5.62
2.00	1.00	100.00	.70	5.39
2.00	1.00	111.11	.69	5.31

Fig. (1)



The values of energy of activation ΔE entropy of activation ΔS**,** free energy of activation Δ*F* are calculated from the rate measurements at 30**,** 35, 40 and 45°C and are found as 66.61 KJ mol^{-1} and 81.24 KJ mol^{-1} respectively.

The number of possible chloro species of Ru (III) present in the solution can be represented by the general formula [Ru (III) (6 – x) (H_2O) Cln] $^{3-x}$ where n = 1- 6. All these species are highly pH dependent. The species present in the pH range [13,14], studied is however $(RuCl_2(H_2O)_4]^+$ This was confirmed by the reported absorption spectra of Ru (III) solution from 1 x 10^{-3} M to 1x10^{-5} M in the pH range 1.00 to 3.00 at constant ionic strength (μ=0.1 M KNO_3).

K_1 at different initial conc. of bromate remains practically constant indicating first order dependence of the reaction on potassium bromate (table 1).The value of K_1 has been determined by the formula K_1 = (-dc/dt)/ [$KBrO_3$].

Where $KBrO_3$ is the concentration of potassium bromate at which (- dc/dt) has been determined by the slope of the curve obtained on protting unconsumed [$KBrO_3$] against time.

Table 2: Effect of Variation of Ru (III) and ionic strength *(μ) of the medium on the reaction rate

[DMDG] 10^{-2} M	Ru (III) x 10^{-6} M	(-dc/dtx10^7)$ML^{-1}S^{-1}$	K_1x10^2 S^1	K_2x10^3
1.00	1.92	0.21	1.09	5.50
1.00	7.62	0.32	4.22	5.60
1.00	15.36	1.25	8.14	5.30
1.00	19.20	2.00	10.40	5.40
1.00	28.80	4.39	15.26	5.30
1.00	38.40	8.49	21.80	5.60
1.00	7.68	0.95	4.80	-
1.00	7.68	2.00	5.00	-
1.00	7.68	5.23	5.20	-
1.00	7.68	9.98	5.00	-
1.00	7.68	26.41	5.30	-
1.00	1.92	49.02	4.90	-
0.50	1.92	0.89	1.11	-
0.50	1.92	2.00	1.00	-
0.50	1.92	3.50	1.18	-
0.50	1.92	3.96	0.98	-
0.50	1.92	6.38	1.27	-

[Bromate] = 2 x 10^{-4} M [Hg $(OAc)_2$] = 4 x 10^{-4} M

$HClO_4$ = 2 x 10^{-4} M

[Hg $(OAc)_2$] = 2 (a), 4.00 (b), 5.23 (c) , 9.98 (d), 26.4(e), 49.02(f),
At U = 8.00 x 10^3 M (g), 20.00 x 10 ^{3} M(h),
= 30.00 x 10^3 M (i), 40.00 x 10^3 M(j), 50.00 x 10 ^{3} M(k)

Fig. 2:

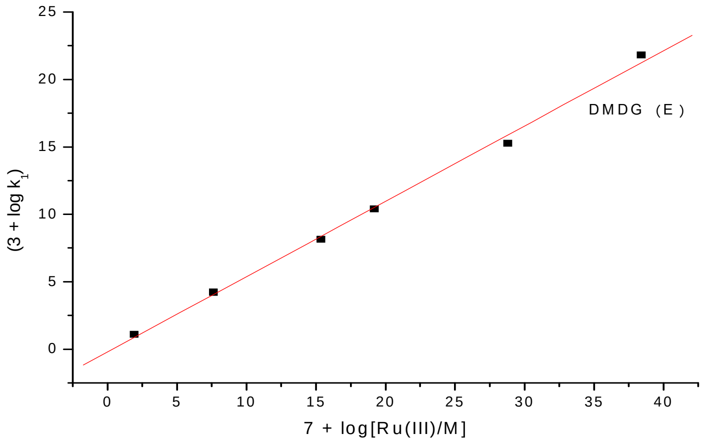


Table 3 : Effect of acetic acid and chloride ion

[DMDG] X 10 M	(-dc / dt.)	K 1 x 10³ S
33	1.56	
33	2.50	
33	3.00	
33	3.66	
33	5.00	
1.00	3.56	1.78
1.00	8.52	1.70
1.00	18.30	1.83
1.00	85.44	1.71
1.00	150.81	1.51
1.00	254.03	1.91

[Bromate] = 2 x 10^{-4} M, [Hg $(OAc)_2$] = 4 x 10^{-4} M,

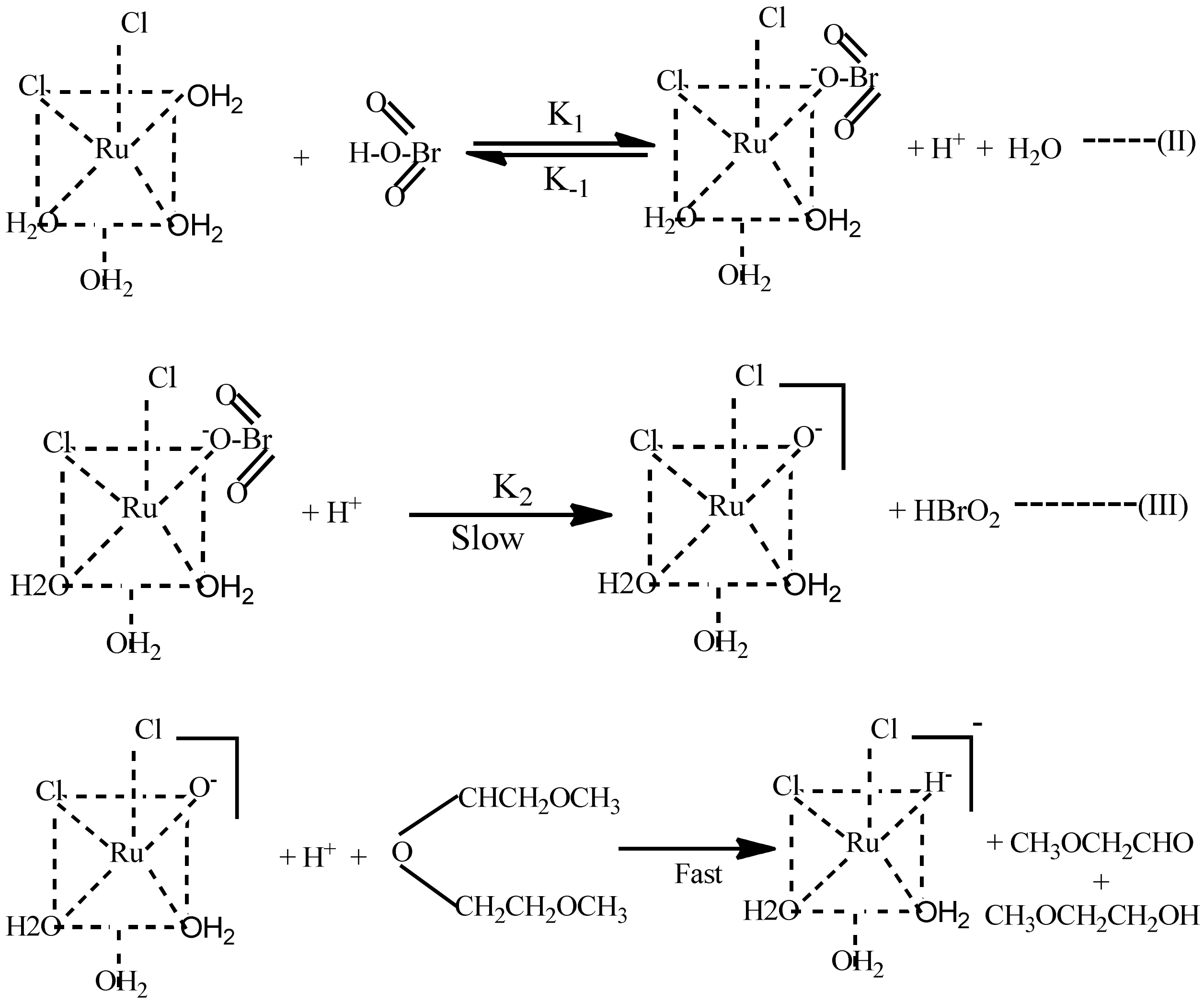
[$HClO_4$] = 2 x 10^{-4} M, Ru (III) = 19.20 x 10 M

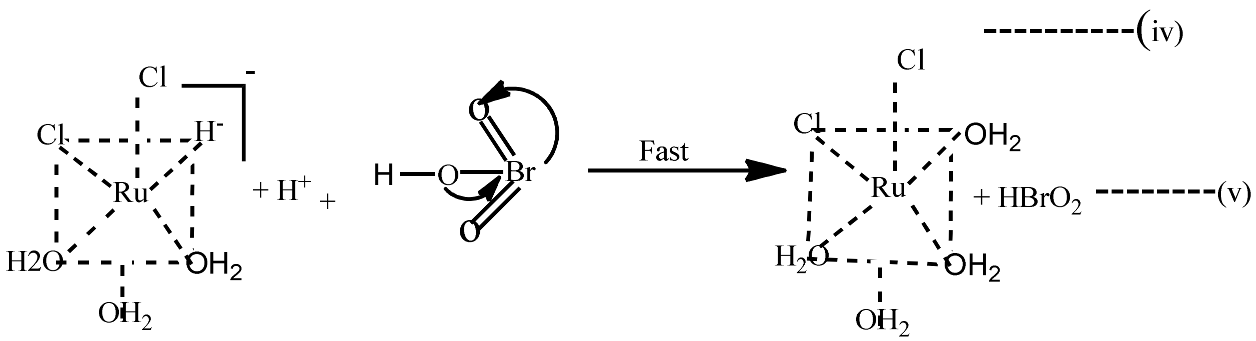
Acetic acid = 5 (e), 10(m), 20(n), 40(o), 50(p)

[Cl) = = 0.20(q), 0.50 (r), 1.00 (s), 5.00(t), 10.00 (u), 13.30 (v),

On the basis of nature of reactive species of Ru(III) chloride and the observed kinetic results the following reaction steps are suggested for the little reactions.

$$BrO_3 + H^+ \overset{K}{\rightleftharpoons} HBrO_3 \quad \text{-----------------------------(1)}$$





$$CH_3OCH_2CHO + CH_3OCH_2CH_2OH \xrightarrow{\text{Ru(III) Species/HBrO}_3} CH_3OCH_2CHO \text{ ---------(VI)}$$

The rate of the reaction in terms of consumption of concentration of potassium bromate may be expressed as equation

$$\frac{-\,dBrO_3^-}{dt} = K_2\,[C_2]\,[H^+] \text{ -----------------------------(1)}$$

.
The concentration of the compex formed in step (II) i.e. [C2] may be determined by applying steady state treatement of [C_2]. Hence,

$$\frac{-\,dBrO_3^-}{dt} = K_1\,[C_1]\,[HBrO_3]\ \ -K_{-1}[C_2][H^+]\text{-}K_2[C_2][H^+] \text{ -----------------------------(2)}$$

But at steady state

$$\frac{-\,d[C_2]}{dt} = 0 \text{ -----------------------------(3)}$$

Hence, from equation (2) and (3) we have

$$K_1\,[C_2]\,[HBrO_3]\ \ -K_2[C_2][H^+]\ \ -K_2[C_2][H^+] = 0$$

$$\text{or}\quad K_{-1}[C_2][H^+]\ \ -K_2[C_2][H^+] = K_1\,[C_2]\,[HBrO_3]$$

$$\text{or}\quad [C_2]\{\,K_{-1}\ \ [H^+] + K_2\,[H^+]\} = K_1\,[C_1]\,[HBrO_3]$$

$$\text{or}\quad [C_2] = \frac{K_1\,[C_1]\,[HBrO_3]}{(\,K_{-1} + K_2)\,[H^+]} \text{ ---------(4)}$$

On comparing equation (1) & (4) we have

$$\text{or}\quad \frac{-\,d[BrO_3^-]}{dt} = \frac{K_1K_2\,[H^+]\,[C_1]\,[HBrO_3]}{(\,K_{-1} + K_2)\,[H^+]}$$

$$\text{or}\quad \frac{-\,d[BrO_3^-]}{dt} = \frac{K_1K_2\,[H^+]\,[C_1]\,[HBrO_3]}{(\,K_{-1} + K_2)} \text{ ------(5)}$$

The total concentration of Ru (III) i.e. [Ru (III)] -1 may be determined by equation (6)

$$[\mathrm{Ru\ (III)}]_T = [C_1] + [C_2]$$

By equation (4) and (6) we have equation (7)

$$[\mathrm{Ru\ (III)}]_T = \frac{[C_1] + K_2\ [C_1]\ [\mathrm{HBrO_3}]}{[H^+]\ (K_{-1} + K_2)}$$

$$[\mathrm{Ru\ (III)}]_T = [C_1]\ \{1 + \frac{K_1\ [\mathrm{HBrO_3}]}{(K_{-1} + K_2)\ [H^+]}\}$$

$$\text{or} \quad [\mathrm{Ru\ (III)}]_T = [C_1] \quad \{\frac{([H^+]\ K_{-1} + K_2)\ K_1\ [\mathrm{HBrO_3}]}{(K_{-1} + K_2)\ [H^+]}\}$$

$$\text{or} \quad [C_1] = \frac{[H^+]\ (K_{-1} + K_2)\ [\mathrm{Ru\ (III)}]_T}{([H^+]\ K_{-1} + K_2)\ K_1\ [\mathrm{HBrO_3}]} \quad \text{------(7)}$$

On putting the value of [C_1] in eq. (5) , we have

$$\text{or} \quad \frac{-\ d[\mathrm{BrO_3^-}]}{dt} = \frac{K_1K_2\ [\mathrm{HBrO_3}]\ [\mathrm{Ru\ (III)}]_T[H^+]\ (K_{-1} + K_2)}{(K_{-1} + K_2)\ \{[H^+]\ (K_{-1} + K_2) + K_1\ [\mathrm{HBrO_3}]\}}$$

$$\text{or} \quad \frac{-\ d[\mathrm{BrO_3^-}]}{dt} = \frac{K_1K_2\ [\mathrm{HBrO_3}]\ [\mathrm{Ru\ (III)}]_T[H^+]}{[H^+]\ (K_{-1} + K_2) + K_1\ [\mathrm{HBrO_3}]} \quad \text{----------(8)}$$

On assuming $K_{-1} >> K_2$ as K_2 is small (step III is slow).
Hence,

$$\text{or} \quad \frac{-\ d[\mathrm{BrO_3^-}]}{dt} = \frac{K_1K_2\ [\mathrm{HBrO_3}]\ [\mathrm{Ru\ (III)}]_T[H^+]}{K_{-1}\ [H^+]\ K_1\ [\mathrm{HBrO_3}]} \quad \text{----------(9)}$$

Also on assuming K_{-1} [H+] >> K_1 [$HBrO_3$] we have

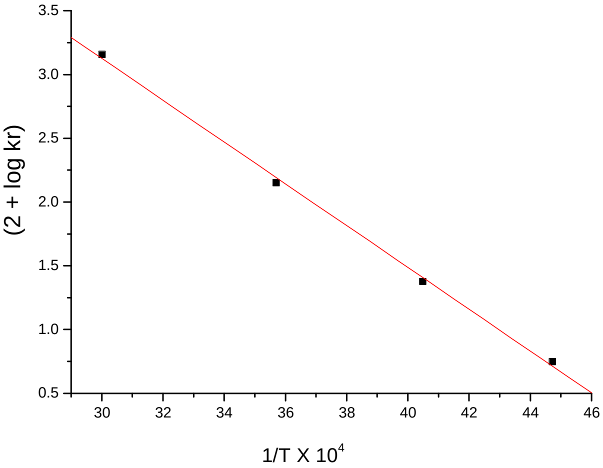
$$\text{or} \quad \frac{-\ d[\mathrm{BrO_3^-}]}{dt} = K_1K_2\ [\mathrm{Ru\ (III)}]_T[H^+]\,[\mathrm{HBrO_3}] \quad \text{----------(10)}$$

Since [$HBrO_3$] = [BrO_3]

Hence equation (10) becomes eq. (11)

$$\text{or} \qquad \frac{-\,d[BrO_3^-]}{dt} = K_1K_2\ [Ru\ (III)]_T\,[HBrO_3] \quad \text{----------}(11)$$

Thus at constant [H^+] the rate low (11) is fully in agreement with experimentally observed kinetic results. Hence the proposed mechanism is valid.



Activation Parameter	Temperature ^{0}C	DMDG
$K_1x10^4s^{-1}$	30	.72
$K_1x10^4s^{-1}$	35	1.10
$K_1x10^4s^{-1}$	40	1.80
$K_1x10^4s^{-1}$	45	3.16
$\Delta E^*(KJmol^{-1})$	35	66.61
log A	35	10.52
$\Delta S^*(K^{-1}Jmol^{-1})$	35	-47.50
$\Delta F^*(KJmol^{-1})$	35	81.24

CONCLUSION

Ru(III) catalyzed Oxidation of dimethyl diethylene glycol (DMDG) by potassium bromate in acidic media in the presence of mercuric acetate shows zero order dependence on dimethyl diethylene glycol [H^+] ions while it is first order for [bromate] and Ru(III). Addition of mercuric acetate has no effect on the reaction. It is concluded from the present investigation Bro_3^- and [$RuCl_2\ (H_2O)_4$]$^+$ are the reactive species of Potassium bromate and Ru (III) Chloride in an Acidic medium respectively.

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REFERENCES

[1] R Natarajan **,** N Venkatasubramanian**,** *Tetrahedron Lett* , **1969,** 57**,** 502**.**
[2] R Natarajan , N Venkatrasubramanian, *Indian J Chem* , **1979,** A17**,** 257.
[3] Vijayalakshmi , E.V Sundaram**,** *J Indian Chem Soc,* **1978,** 55**,** 567.
[4] Vijayalakshmi, E V Sundaram**,** *Indian J Chem,* **1977,** A 15**,** 612.
[5] R Natarajan , N Venkatrasubranian**,** *Int J Chem Kinet,* **1976,** 8**,** 205.
[6] V Avasthi, A C Chaterjee**,** *Z Phys. Chem (Leipzig),* **1970,** 245**,** 154.
[7] V Avasthi, A C Chaterjee**,** Z *Phys. Chem (Leipzig),* **1972,** 249**,** 17.
[8] S Anandan, R Gopalan**,** *J Indian Chem Soc,* **1985,** 62**,** 216.
[9] C S Reddy, E V Sundaram**,** *J Indian Chem Soc,* **1985,** 62**,** 209.
[10] R Natarajan , N Venkatrasubranian , *Tethedron***,** **1974,** 30**,** 2785.
[11] P S Radhakrishnamurti, D K Mahapatro, *Indian J Chem* ,**1979** A 18, 53.
[12] I Vogal**,** *Elementary Practical Organic Chemistry***,** *Part III***,** Longmans Green London **1958.**

[13] H H Cady, and R E Connic, *J Am Chem Soc,* **1958,** 80, 2646.
[14] M M Taqui Khan, R S Shukla, *J Mol Catal,* **1986,** 34, 39.