MECHANISM OF Ru(III) CATALYSIS IN ACID BROMATE OXIDATION OF SOME GLYCOLS: A KINETIC STUDY

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ABSTRACT

Ru(III)-catalysed oxidation of methyldiethyleneglycol and ethyldiethyleneglycol by acidic solution of potassium bromate shows zero-order dependence on bromate and H^+ ions and first-order dependence on Ru(III) and each glycol. The corresponding aldehyde is the reaction product. The proposed mechanism involves slow and rate-controlling disproportionation of a transient complex formed between reactive species of Ru(III) and glycol. Various activation parameters have been computed.

INTRODUCTION

POTASSIUM bromate, being a powerful oxidant with a redox potential of 1.44 V in acidic media, has been widely used in the oxidation of alcohols[1], cyclanols[2,3], phenols[4], α-hydroxy acids[5], aldehydes[6-8], tartaric acid[9] and some labile substrates[10]. The literature on the role of Ru(III) chloride as catalyst in acid bromate oxidations is scanty. Only oxidative kinetics of a few ketones with bromate as oxidant and Ru(III) as catalyst have been reported[11] and mechanistic interpretations of the results are obscure. This prompted us to undertake the present investigation of the kinetics and mechanism of Ru(III)-catalysed oxidation of methyldiethyleneglycol (MDG) and ethyldiethyleneglycol (EDG) by acidic solution of potassium bromate in the presence of mercuric acetate as bromide ion scavenger.

EXPERIMENTAL

Materials and procedures

Potassium bromate (BDH, AR) was used as such. E. Merck samples of sodium perchlorate, perchloric acid (60%) and mercuric acetate were used. The other reagents used were of the highest purity available. Solutions of the glycols (BDH, LR) were prepared by weighing the samples. Ru(III) chloride (Johnson Matthey) solution was prepared by dissolving the sample in hydrochloric acid of known strength. All the solutions were prepared in triple-distilled water.

The reaction stills were blackened from the outside to avoid any photochemical reactions. All reactants except glycol were allowed to mix and the reaction was initiated by the rapid addition of an appropriate amount of glycol to the already equilibrated mixture of reactants. The progress of the reaction was monitored by estimating the amount of remaining bromate iodometrically. All the observations were taken at constant temperature ($\pm 0.1°C$).

RESULTS AND DISCUSSION

Stoichiometric data indicated consumption of one mole of bromate in the oxidation of each mole of glycol. The corresponding aldehydes were confirmed as end products by TLC and also by preparation of the dinitrophenylhydrazine (DNP) derivative[12]. Mercury(II) acetate[13] was used as bromide ion scavenger and it did not interfere with the reaction in any way. Zero-order dependence on bromate and first-order on each glycol were obvious from the data (table 1). Zero-order rate constants ($-dc/dt$ or k_0) were calculated from slopes of plots of unconsumed bromate versus time for different initial concentrations of bromate. First-order kinetics in Ru(III) and zero-order dependence on H^+ are also obvious from the results (table 2) Successive addition of mercuric acetate, chloride ions and sodium perchlorate (ionic strength variation) had insignificant effect. Successive addition of acetic acid increased the reaction rate, showing a negative dielectric effect on the rate (table 2). The values of activation parameters, computed from the rate at 30, 35, 40 and 45°C, are given in table 3.

Table 1 *Effect of concentration of reactants on reaction rate in acid bromate oxidation of glycols*

[Ru(III)] = 1.92×10^{-5} M (unless otherwise stated), [HClO$_4$] = 1.00×10^{-3} M, [Hg(OAc)$_2$] = 3.34×10^{-3} M at 35°C.

[Bromate] (10^{-3} M)	[Substrate] (10^{-2} M)	$\left(-\dfrac{dc}{dt}\right) \times 10^7$ (mol l^{-1} s^{-1})	
		MDG	EDG
0.67	3.34	3.16	3.16[a]
0.83	3.34	3.00	2.86[a]
1.00	3.34	3.36	2.66[a]
1.33	3.34	3.33	2.76[a]
2.22	3.34	2.83	2.85[a]
3.33	3.34	3.50	3.16[a]
1.00	1.00	0.53[b]	1.16[c]
1.00	1.66	0.88[b]	—
1.00	2.22	1.03[b]	2.58[c]
1.00	3.34	2.00[b]	4.00[c]
1.00	5.00	2.75[b]	5.83[c]
1.00	10.00	5.33[b]	12.08[c]
1.00	20.00	—	23.34[c]

[a]At [EDG] = 5.00×10^{-2} M; [b]at 30°C; [c]at [Ru(III)] = 3.84×10^{-5} M.

Table 2 *Effect of variation of concentration of Ru(III) and perchloric acid on reaction rate at 35°C*

[BROMATE] = 1.00×10^{-3} M, [MDG] = 5.00×10^{-2} M, [EDG] = 5.00×10^{-2} M (unless otherwise stated), and [Hg(OAc)$_2$] = 1.25×10^{-3} M.

[Ru(III)] 10^6 M	[HClO$_4$] 10^3 M	$\left(-\dfrac{dc}{dt}\right) \times 10^7$ (mol l^{-1} s^{-1})			
		MDG		EDG	
3.84	1.00	—		0.58	
5.76	1.00	—		0.81	
7.68	1.00	1.64	4.30[a]	0.15	6.00[e]
13.44	1.00	2.85	6.29[b]	—	7.83[f]
15.36	1.00	3.27	8.80[c]	2.32	13.83[g]
19.20	1.00	4.10	21.66[d]	2.92	23.33[h]
28.80	1.00	6.13		—	
38.40	1.00	8.00		5.83	
19.20	0.40	4.86		2.88	
19.20	0.50	4.72		2.90	
19.20	0.67	4.10		2.96	
19.20	1.00	4.66		2.89	
19.20	1.25	4.70		2.86	
19.20	2.00	4.86		2.92	
19.20	4.00	4.83		2.90	

[Acetic acid] = 5 (a, e), 10 (b, f), 20 (c, g) and 30% (d, h) at [Ru(III)] = 19.20×10^{-6} M and (e, f, g, h) [EDG] = 2.22×10^{-2} M.

The number of possible chloro species of Ru(III) present in solution is given by [Ru(III) $(6-n)(H_2O)$ Cl$_n$]$^{3-n}$, where $n = 1-6$. All these species are pH-

Table 3 *Activation parameters for bromate oxidation of glycols*

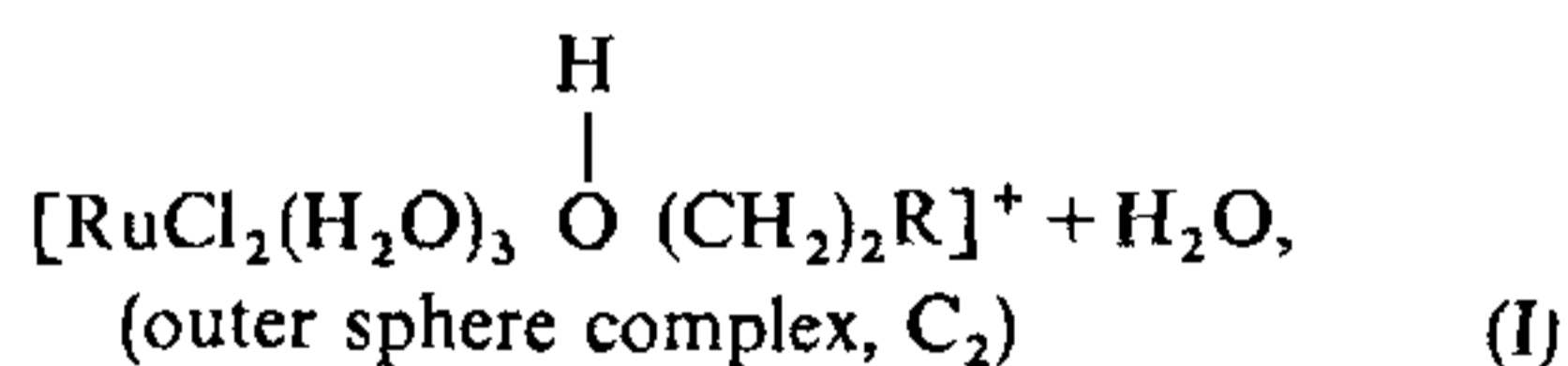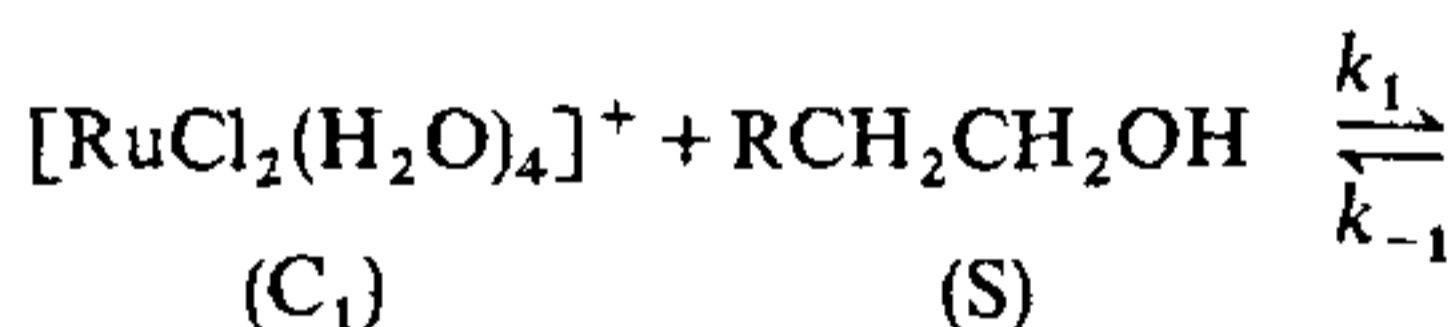| Parameter	MDG	EDG
10 kr (30°C) (mol^{-1} l s^{-1})	2.86	2.17
10 kr (35°C) (mol^{-1} l s^{-1})	4.29	3.04
10 kr (40°C) (mol^{-1} l s^{-1})	6.09	4.41
10 kr (45°C) (mol^{-1} l s^{-1})	9.00	7.50
ΔE^* (kJ mol^{-1})	63.84	69.60
log A	10.45	11.27
ΔS^* (JK^{-1} mol^{-1})	-48.84[a]	-33.13[a]
ΔF^* (kJ mol^{-1})	78.88[a]	79.80[a]

[a]At 35°C.

dependent. The species present in the pH range[14,15] studied here is, however, [RuCl$_2$(H$_2$O)$_4$]$^+$. The absence of any effect on the reaction rate upon addition of chloride ions rules out the possibility of either dissociation or association of Cl$^-$ ions. Hence [RuCl$_2$(H$_2$O)$_4$]$^+$ is proposed as the reactive species of Ru(III) chloride in the employed pH range.
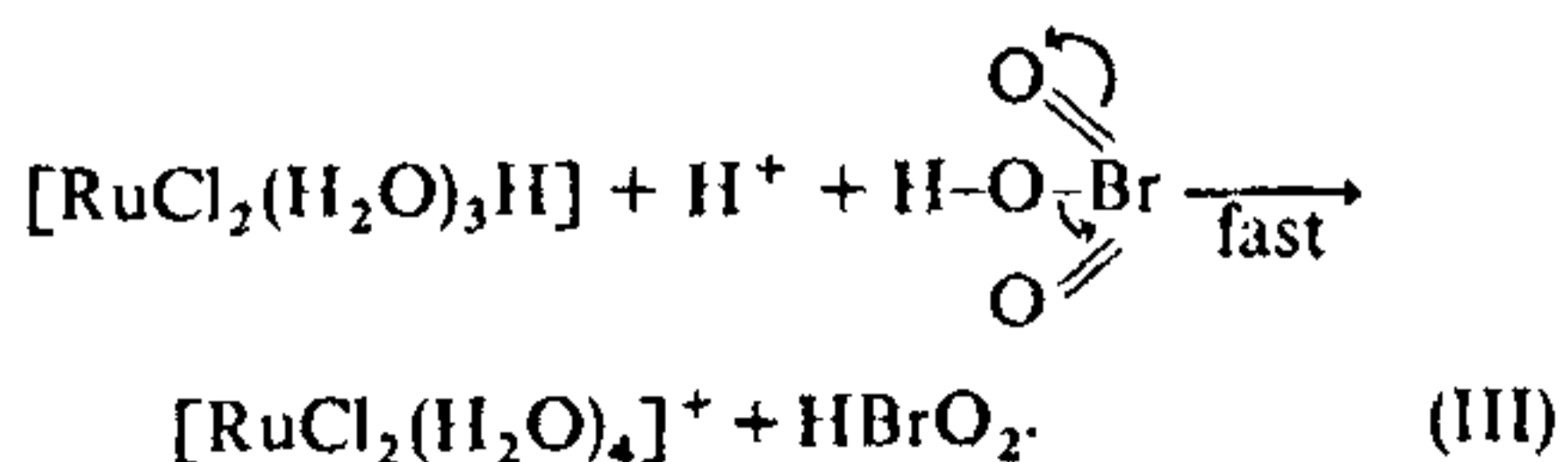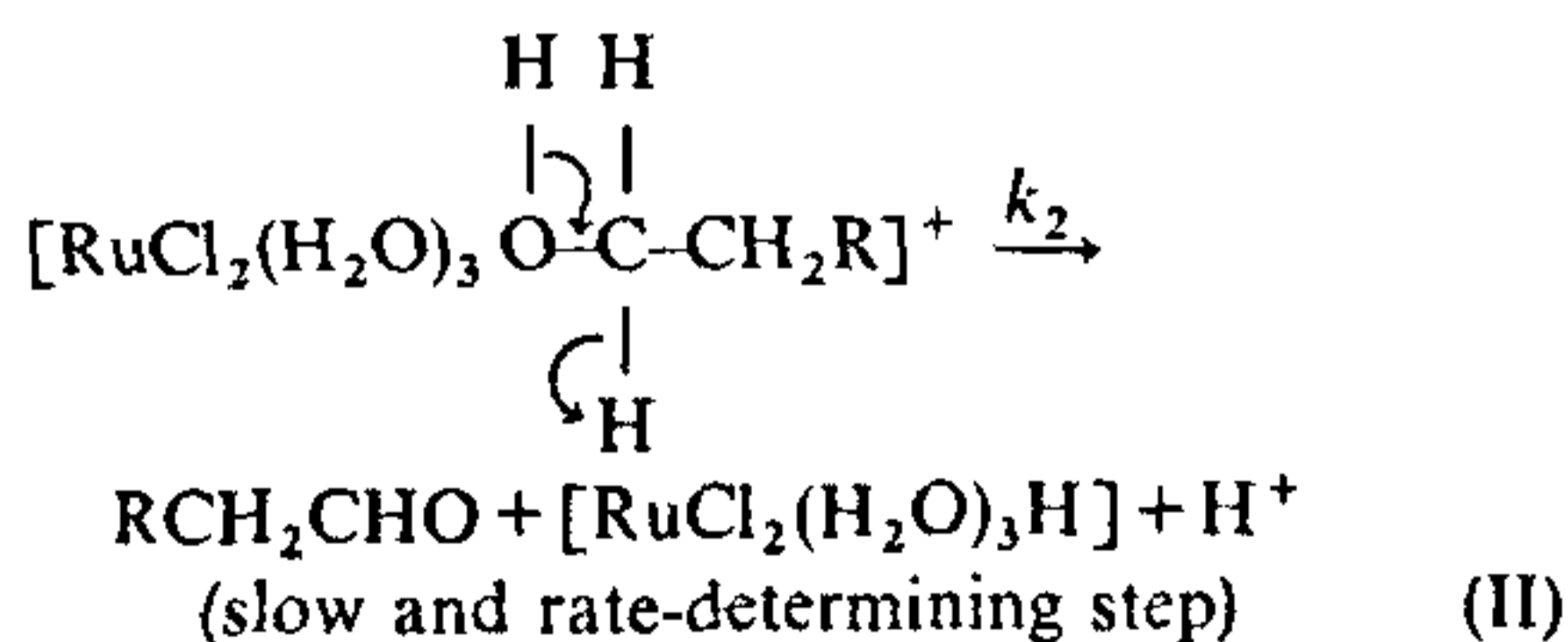
In acidic media bromate[9] ions form HBrO$_3$ according to equation (1):

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3. \tag{1}$$
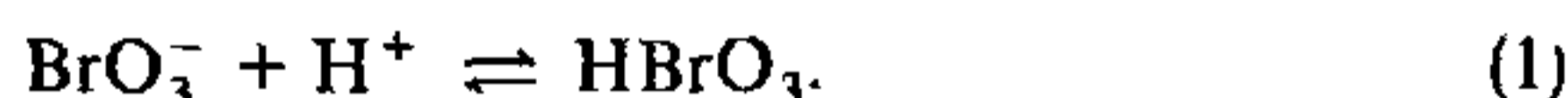
The zero-order dependence on both bromate and H$^+$ indicates that HBrO$_3$ formed in (1) acts as an oxidant and is involved in the fast step. On the basis of these statements and kinetic results the following reaction routes are suggested:

$$[RuCl_2(H_2O)_4]^+ + RCH_2CH_2OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$(C_1) \qquad\qquad (S)$$

$$\begin{array}{c} H \\ | \\ [RuCl_2(H_2O)_3 \; O \; (CH_2)_2R]^+ + H_2O, \end{array}$$

(outer sphere complex, C$_2$) (I)

where R stands for $-OCH_2CH_2OR'$ and R' for either $-CH_3$ or $-C_2H_5$ group in MDG or EDG.

$$[RuCl_2(H_2O)_3 \; O\text{-}C\text{-}CH_2R]^+ \xrightarrow{k_2}$$

RCH$_2$CHO + [RuCl$_2$(H$_2$O)$_3$H] + H$^+$
(slow and rate-determining step) (II)

$$[RuCl_2(H_2O)_3H] + H^+ + H\text{-}O\text{-}Br \xrightarrow{\text{fast}}$$

$$[RuCl_2(H_2O)_4]^+ + HBrO_2. \tag{III}$$

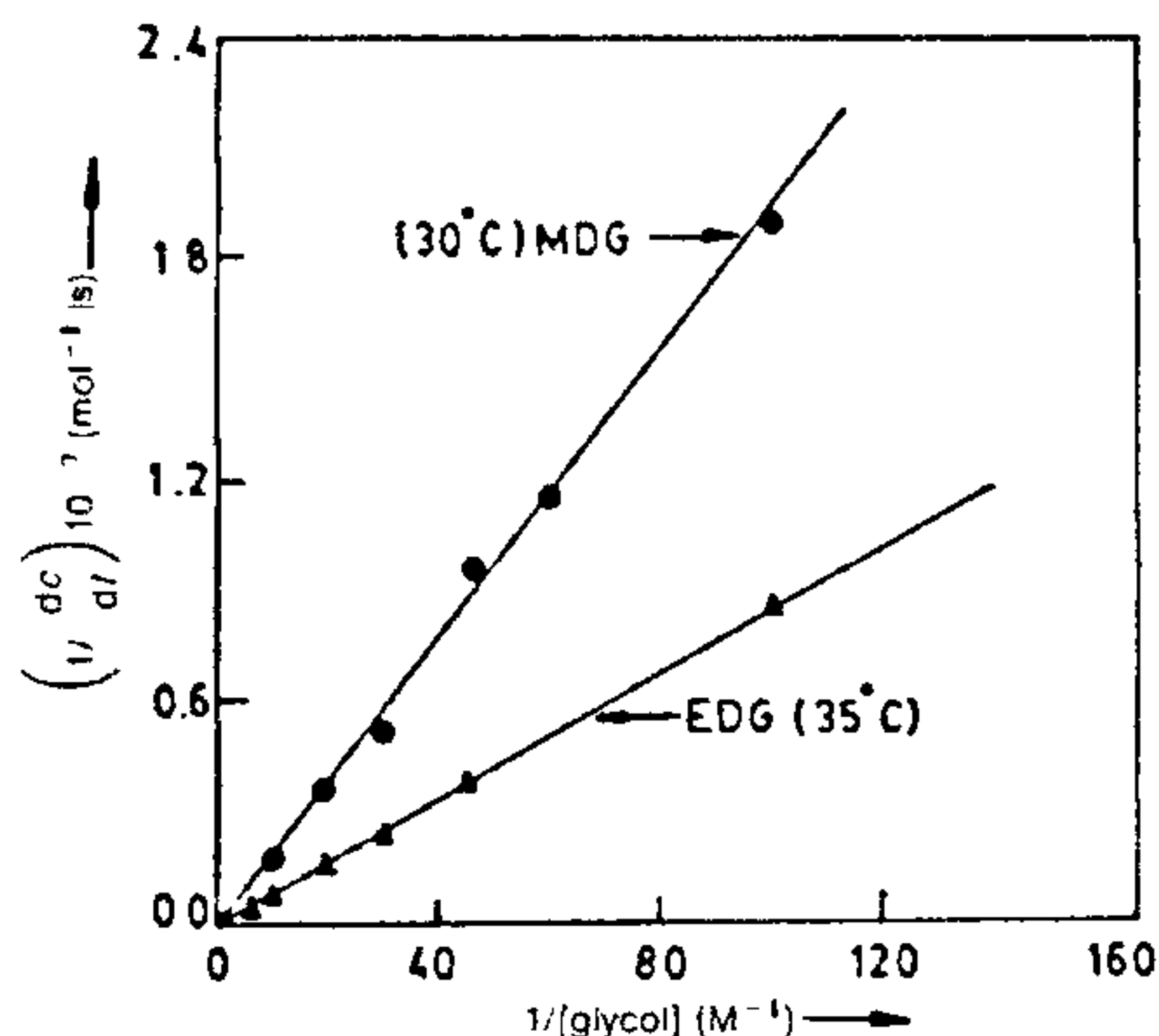**Figure 1.** $(1/\text{rate})$ vs $1/[\text{glycol}]$ plots for MDG and EDG. $[\text{Bromate}] = 1.00 \times 10^{-3}$ M, $[\text{HClO}_4] = 1.00 \times 10^{-3}$ M, $[\text{Ru(III)}] = 1.92 \times 10^{-5}$ M (MDG) 3.84×10^{-5} M (EDG), $[\text{Hg(OAc)}_2] = 3.34 \times 10^{-3}$ M.

Considering steps (I) and (II) and applying steady-state treatment to $[C_2]$, the rate of the reaction in terms of consumption of bromate may be expressed as equation (2) below, with limiting conditions $k_{-1} \gg k_2$ and $1 \gg K_1([\text{S}]/[\text{H}_2\text{O}])$, where K_1 is the complex formation constant and is equal to k_1/k_{-1}.

$$- \frac{d[\text{BrO}_3^-]}{dt} = k_0(\text{obs.}) = k_2 K_1 [\text{S}][\text{Ru(III)}]_T \quad (2)$$

The rate law (2) explains all the kinetic observations. The hydride ion transfer mechanism also finds support from Bailer *et al.*[16], and Ru(III)–alcohol complex formation is well established[17,18]. Plots of $1/(-dc/dt)$ vs $1/[\text{glycol}]$ are linear and pass through the origin, indicating that the complex has a low stability constant[19] (figure 1).

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