Electron transfer reaction between triethylene glycol and bromate in acid medium: Mechanism of the rate processes

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Abstract: The electron transfer reaction between triethylene glycol (TEG) and potassium bromate was studied in acidic medium. The kinetics of the oxidation reaction was investigated under pseudo-first order condition over the temperature range 298-313 K. The reaction exhibits first order dependence each in $[BrO_3^-]$, [TEG] and $[H^+]$. The influence of mercuric acetate concentration and ionic strength on the reaction rate is insignificant. The reaction product has been identified as formaldehyde. The enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) for the overall reaction were evaluated. A tentative reaction mechanism involving two-electron transfer rate determining step in the oxidation process has been proposed.
Keywords: Triethylene glycol (TEG); Bromate; Electron transfer reaction; Mechanism; Rate process.

Introduction

Triethylene glycol, $HO(C_2H_4O)_3H$, is a straight chain organic compound with two hydroxyl groups along with two ether linkages, which account for its high water solubility and reactivity towards other reactants. TEG is an important non-volatile organic solvent used as a vinyl plasticizer and as an intermediate in the manufacture of polyester resin. It is also used in the dehydration of gases and in the production of insecticides, air sanitizer products, powdered ceramics, glue, cork, plastics etc. TEG is a component in the synthesis of printing dyes and inks. TEG exhibits antimicrobial activity and used as a mild disinfectant towards virus, bacteria and fungi[1]. The dihydroxy ether compounds readily undergo oxidation with different oxidants in acid medium and the relative kinetics and mechanisms have been reported[2-5]. Among the various dihydroxy ether compounds, TEG is especially importance owing to its use in industrial and pharmaceutical fields. Despite its enormous application, only a little kinetic studies of the oxidation of TEG have been reported[3-6]. Bromate is a powerful oxidizing agent in acid medium with a redox potential of 1.52 volts at 298 K[7]. Potassium bromate has been used in the oxidation of Fe(II)[8], Mn(II)[9] and Ir(III)[10] in presence of inorganic reductants. The kinetics and mechanism of the oxidation of many organic compounds by acid bromate has been investigated[7,11-14]. According to current position, no literature study has been cited involving the oxidation of triethylene glycol in particular with acid bromate. The present paper deals with the studies of the bromate ion oxidation of TEG with some interesting kinetic and mechanistic aspects and elucidation of the activation parameters.

Experimental

Reagents:

Triethylene glycol (Fluka) was used without further purification. Potassium bromate (BDH) solution was prepared by dissolving appropriate weighed amount of the salt in double distilled water and the solution

was standardized iodometrically against standard thiosulphate solution using starch solution as an indicator. Copper sulphate (S.D. fine Chem. Ltd.), sodium perchlorate (BDH), sodium thiosulphate (S.D. fine Chem. Ltd.), sodium chloride (SRL), mercuric acetate (E. Merck) and other inorganic compounds used were of analytical grade. All the solutions were made in double distilled water.

Kinetic measurements:

The kinetics of oxidation of triethylene glycol by bromate in acid medium was followed titrimetrically under pseudo-first order conditions keeping the concentration of TEG large excess compared to BrO_3^- concentration at a constant $[H^+]$. Before the kinetic run, solution of BrO_3^- and the mixture containing TEG, HCl and $Hg(OAc)_2$ were separately thermostatted. This is to be mentioned that the interference of the liberated Br_2 was prevented[7] by adding calculated amount of $Hg(OAc)_2$. The reaction was started by adding BrO_3^- to the mixture containing TEG and was followed by transferring aliquots of the mixture at different time intervals into an excess of potassium iodide solution. The liberated iodine was estimated against a standard thiosulphate solution in presence of starch indicator[15]. The pseudo-first order rate constant (k_{obs}) was evaluated. The pseudo-first order rate constant values were reproducible to within ± 5%.

Product analysis:

After the kinetic experiments, the reaction mixture was allowed to stand for ~ 2 h and the organic product of the reaction between TEG and bromate in acid medium was confirmed by the following tests. To a small portion of reaction mixture an equal volume of 12 N H_2SO_4 was added. The reaction mixture was then treated with a pinch of solid chromotropic acid and warmed on a water bath for a few minutes. An immediate appearance of pink violet color indicated the occurrence of formaldehyde as an oxidized product during the reaction[16-18]. Another part of the reaction mixture was acidified in 4N H_2SO_4 and excess 2,4-dinitrophenyl hydrazine solution was added when a yellow precipitate of 2,4-dinitrophenyl hydrazone derivatives of the product was obtained. The precipitate was filtered, washed, dried and analyzed. The melting point of the derivative of the product was recorded to be 168°C[19-21]. The C, H, N analysis result of the 2,4-dinitrophenyl hydrazone derivative are as follows[22]: found C = 40.07, H = 2.84, N = 25.7 %; calculated for for $C_7H_6N_4O_4$, C = 40.0, H = 2.85, N = 26.6 %. The mp as well as the C, H, N analysis results of the 2,4-DNP derivative confirm that formaldehyde is formed as the reaction product.

Results and Discussion

In all the kinetic runs TEG was present at least ten times in higher concentration than potassium bromate i.e., the kinetics was investigated under pseudo-first order conditions. The kinetics of oxidation of TEG by potassium bromate was studied at several initial concentrations of bromate ($(1.0 - 6.0) \times 10^{-3}$ mol dm^{-3}) but at fixed concentration of DEG (5×10^{-2} mol dm^{-3}) and H^+ ion (0.5 mol dm^{-3}). The pseudo-first order plots were found to be linear and parallel lines were obtained for different concentration of range of bromate at 298 K. The values of k_{obs} was found to be independent of the initial concentration of bromate (Table 1), indicating that the order in bromate concentration is unity.

Table 1. Effect of BrO_3^- concentration on the rate oxidation of TEG at 298 K.
[TEG] = 5×10^{-2} mol dm^{-3} and $[H^+]$ = 0.5 mol dm^{-3}.

10^3 [BrO_3^-] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.0	8.46
2.0	8.42
3.0	8.48
4.0	8.40
5.0	8.38
6.0	8.49

The dependence of the reaction rate on the concentration of triethylene glycol was studied by varying its concentration in the range ($(1.5 \text{ to } 25) \times 10^{-2}$ mol dm^{-3}) at constant [BrO_3^-] and [H^+] of 1.0×10^{-3} mol dm^{-3} and 0.5 mol dm^{-3}, respectively. The reaction was also carried out in the temperature range 298-313 K. Increasing TEG concentration at constant temperature accelerates the rate of reaction. The values of k_{obs} and

second-order rate constant ($k_2 = k_{obs}/[\text{TEG}]$) are presented in Table 2. The plot of pseudo-first order rate constant (k_{obs}) against [TEG] gave straight passing through the origin (Figure 1) at each temperature. The results indicate that the order of the reaction with respect to TEG is one. The reaction appeared to follow the rate law,

$$-\frac{1}{[\text{BrO}_3^-]}\frac{d[\text{BrO}_3^-]}{dt} = k_2\,[\text{TEG}] \tag{1}$$

Table 2. Variation of TEG concentrationon the pseudo-first order rate constant at different temperatures. $[\text{BrO}_3^-] = 1.0 \times 10^{-3}$ mol dm^{-3} and $[\text{H}^+] = 0.5$ mol dm^{-3}. Figures in the parentheses are the values of second-order rate constant (dm^3 mol^{-1} s^{-1}).

10^2 [TEG] (mol dm^{-3})	$10^3\,k_{obs}$ (s^{-1})			
	298 K	**303 K**	**308 K**	**313 K**
1.5	0.254 (0.0169)	0.369 (0.0246)	0.535 (0.0357)	0.742 (0.0495)
2.5	0.427 (0.0171)	0.624 (0.0249)	0.887 (0.0355)	1.30 (0.0520)
5	0.845 (0.0169)	1.25 (0.0250)	1.85 (0.0370)	2.47 (0.0494)
10	1.63 (0.0163)	2.52 (0.0252)	3.56 (0.0356)	4.84 (0.0484)
15	2.42 (0.0161)	3.67 (0.0245)	5.41 (0.0361)	7.44 (0.0496)
20	3.32 (0.0166)	5.02 (0.0251)	7.01 (0.0351)	10.1 (0.0505)
25	4.25 (0.0170)	6.17 (0.0247)	8.98 (0.0359)	12.4 (0.0496)

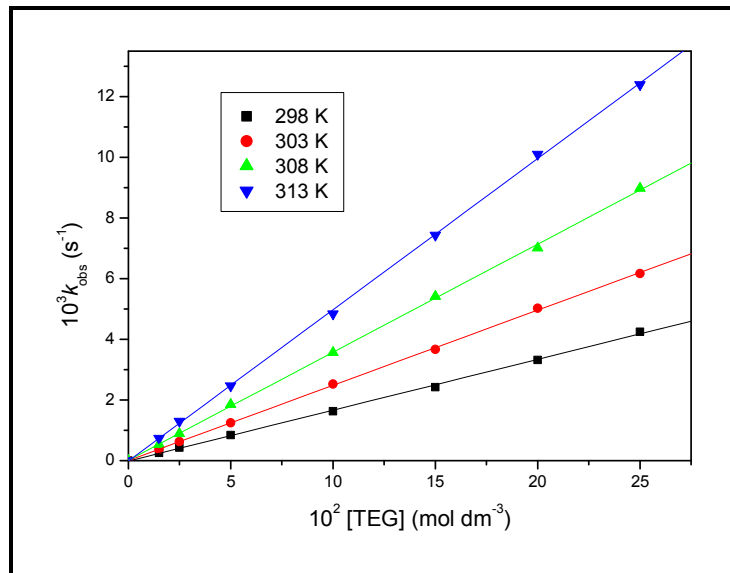
Figure 1. Variation of k_{obs} with TEG concentration. Plots of k_{obs} *versus* [TEG] in the temperature range 298-313K. $[\text{BrO}_3^-] = 1.0 \times 10^{-3}$ mol dm^{-3} and $[\text{H}^+] = 0.5$ mo dm^{-3}.

The dependence of reaction rate on the concentration of H$^+$ ion was performed by varying the concentration of hydrochloric acid in the range 0.1-1.0 mol dm^{-3} at constant ionic strength, $[\text{BrO}_3^-]$ and [TEG] of 0.9 mol dm^{-3}, 1.0×10^{-3} mol dm^{-3} and 10.0×10^{-2} mol dm^{-3} at 298 K. The rate of the reaction was found to increase with an increase in the H$^+$ concentration at constant temperature (Table 3). The plots of k_{obs} versus [H$^+$] were found to be linear passing through the origin (Figure 2), indicating that the order in H$^+$ concentration is unity.

Table 3. Variation of [H$^+$] on the rate of the oxidation of TEG at 298 K.
[BrO$_3^-$] = 1.0 × 10^{-3} mol dm^{-3} and [TEG] = 10.0 × 10^{-2} mol dm^{-3}.

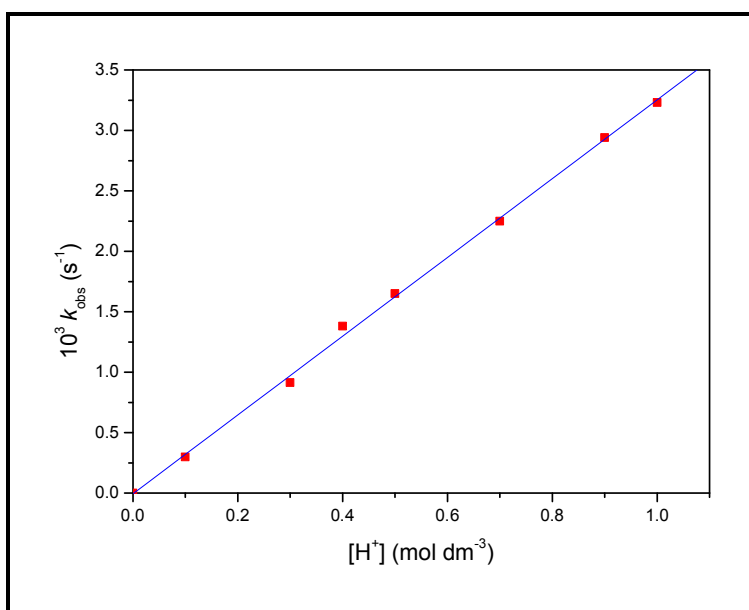| [H$^+$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^3 k_2 (dm^3 mol^{-1} s^{-1})
0.1	2.98	2.98
0.3	9.14	3.04
0.4	13.8	3.45
0.5	16.5	3.30
0.7	22.5	3.21
0.9	29.4	3.26
1.0	32.3	3.23

Figure 2. Effect of H$^+$ concentration on the pseudo-first order rate constants. Plots of k_{obs} *versus* [H$^+$] at 298 K. [BrO$_3^-$] = 1.0 × 10^{-3} mol dm^{-3} and [TEG] = 10.0 × 10^{-2} mol dm^{-3}.

The effect of ionic strength was studied keeping [BrO$_3^-$], [TEG], [H$^+$] and temperature constant at 1.0 × 10^{-3} mol dm^{-3}, 10.0 × 10^{-2} mol dm^{-3}, 0.2 mol dm^{-3} and 298 K, respectively. Sodium perchlorate, in the concentration range 0.05-0.5 mol dm^{-3}, was used to vary the ionic strength of the reaction mixture. The results indicate that there is no significant effect of ionic strength on the oxidation of triethylene glycol by potassium bromate.

To study the dependence of the reaction rate on the concentration of chloride ion, the reaction was varied by the addition of NaCl in the range 0.15- 0.85 mol dm^{-3} but at constant [BrO$_3^-$], [TEG], [H$^+$] and temperature of 1.0 × 10^{-3} mol dm^{-3}, 10.0 × 10^{-2} mol dm^{-3}, 0.1 mol dm^{-3} and 298 K, respectively. The rate of the oxidation reaction was found to be independent of NaCl concentration.

The effect of reaction rate on the concentration of mercuric acetate was examined by varying its concentration in the range (1.0-6.0) × 10^{-2} mol dm^{-3} at constant [BrO$_3^-$], [TEG], [H$^+$] and temperature of 1.0 × 10^{-3} mol dm^{-3}, 5.0 × 10^{-2} mol dm^{-3}, 0.5 mol dm^{-3} and 298 K, respectively. The pseudo-first order rate constant values are given in Table 4. The results indicate that the rate of the reaction remain unaffected due to the variation of Hg(OAc)$_2$.

Table 4. Variation of pseudo-first order rate constant with Hg(OAc)$_2$ concentration.
[BrO$_3^-$] = 1.0 × 10^{-3} mol dm^{-3}, [TEG] = 5 × 10^{-2} mol dm^{-3}, [H$^+$] = 0.5 mol dm^{-3} and temp = 298 K

10^2 [Hg(OAc)$_2$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.0	8.45
2.0	8.48
4.0	8.41
5.0	8.38
6.0	8.40

The intervention of free radicals was tested by the addition of acrylonitrile scavenger in the concentration range 4-25 % (v/v) to the reaction mixture containing constant concentrations of BrO$_3^-$, TEG and H$^+$ in an inert atmosphere of nitrogen. The reaction mixture was kept for an hour. No precipitate or suspension was observed, indicating the absence of free radical intervention in the oxidation of TEG by potassium bromate.

The effect of temperature on the reaction rate was studied with the change in TEG concentration at 298, 303, 308 and 313 K. The pseudo-first order rate constant values are recorded in Table 1. The values of third order rate constant, k_3 (=k_{obs}/[TEG][H$^+$]) were calculated at different temperatures. The enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) was calculated from the linear plot of log(k_3/T) *versus* 1/T (Figure 3) using the equation (2),

$$\log (k_3/T) = [\log(k_B/h) + \Delta S^{\neq} /2.303R] -\Delta H^{\neq} /2.303RT \qquad (2)$$

The value of enthalpy of activation and entropy of activation are found to be 54 ± 4 kJ mol^{-1} and -92 ± 7 JK^{-1} mol^{-1}, respectively.
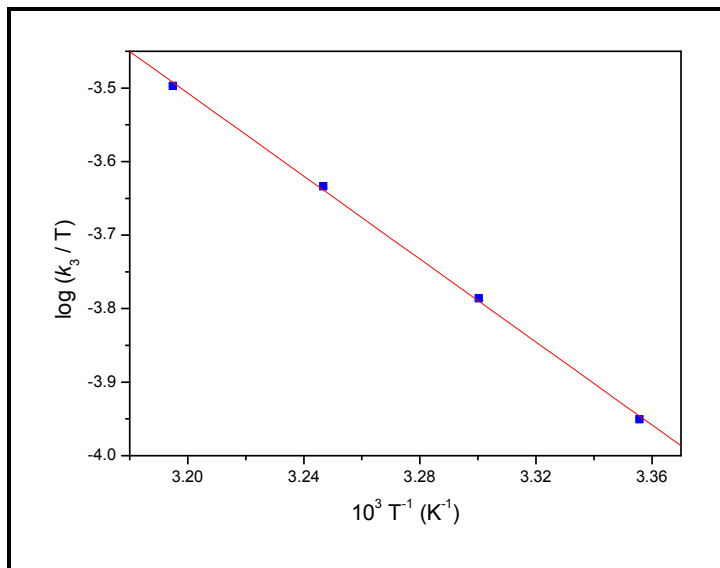

Figure 3. Temperature dependence of third-order rate constant (k_3).
Plot of log (k_3/T) *versus* 1/T.

The rate of the bromate oxidation of TEG increases with the first power of the concentration of bromate as well as of TEG. Again, the reaction rate increases linearly with an increase in H$^+$ concentration. The experimental results indicate that HBrO$_3$ is initially formed by the reaction between BrO$_3^-$ and H$^+$ and then reacts with the substrate in the rate determining step. The participation of such HBrO$_3$ species during oxidation reaction has already been reported in earlier investigations[11,13]. It is to be mentioned that the oxidation cannot be involved any reaction between ions because the rate of the reaction between TEG and bromate is independent of ionic strength. Under the present experimental conditions, the rate equation may be suggested as,

$$-d[BrO_3^-] / dt = k_3 [TEG] [BrO_3^-] [H^+] \qquad (3)$$

Triethylene glycol is a member of a homologous series of dihydroxy alcohols. It is a larger molecule than diethylene glycol and has two ether groups. Triethylene glycol is less hygroscopic than diethylene glycol, but has a higher boiling point, viscosity and other physical properties. The chemical properties of TEG resemble those of DEG and other glycols. Although, it is an ether alcohol derivative, but the ether group is relatively unreactive. The hydroxyl groups on triethylene glycol undergo the usual alcohol chemistry and it can be converted to aldehydes or other compounds in presence of suitable oxidant[5].

The absence of polymeric suspension in the reaction mixture due to addition of acrylonitrile indicates that there is no possibility of free radical mechanism in the oxidation of TEG by potassium bromate in acid medium. The kinetic results are reliable towards the reaction mechanism involving the reaction between triethylene glycol and $HBrO_3$ in the slow step. There has been earlier report of a similar type of reaction in the oxidation of α,β-unsaturated compounds by bromate[7] in acid medium under identical experimental conditions. A plausible sequence of reactions leading to the formation of unstable bromated ester (A)[11,13] in the rate determining step followed by its decomposition through neighboring group participation to give HCHO as well as ethylene glycol (C) via fast hydrolysis process[23]. The reactive ethylene glycol(C) undergoes oxidation with $HBrO_3$ to produce $HBrO_2$ along with formaldehyde as the reaction product[5].
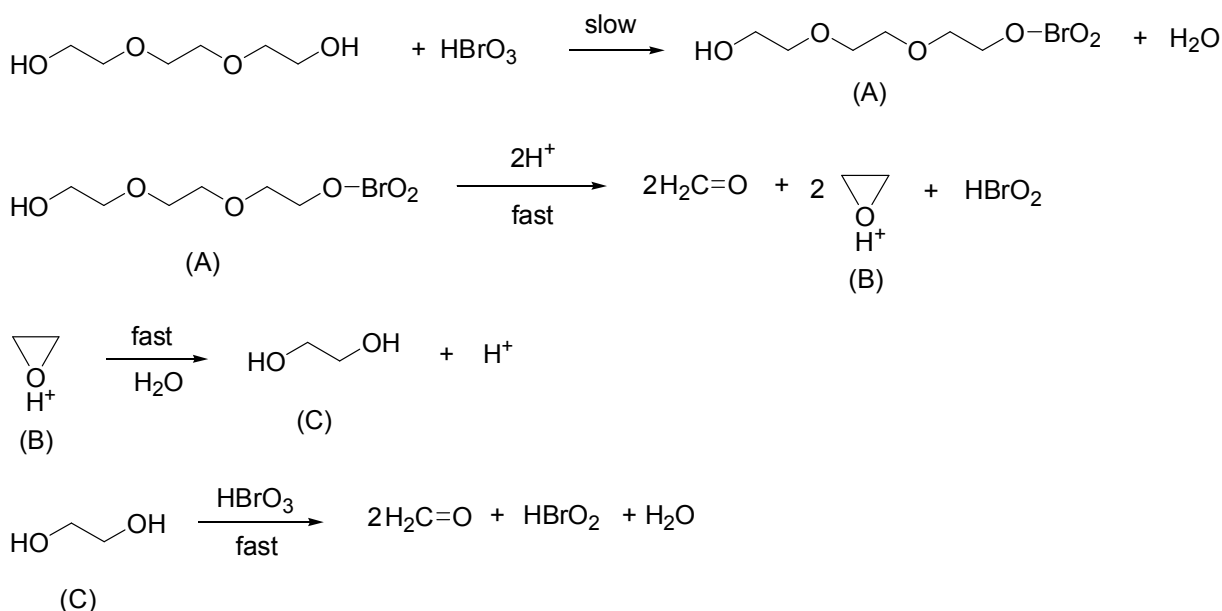
Scheme 1

Since $HBrO_2$ is highly reactive, it reacts further with excess substrate and ultimately reduced to HBr (eqn. 4 and 5) as mentioned in earlier investigations[11].
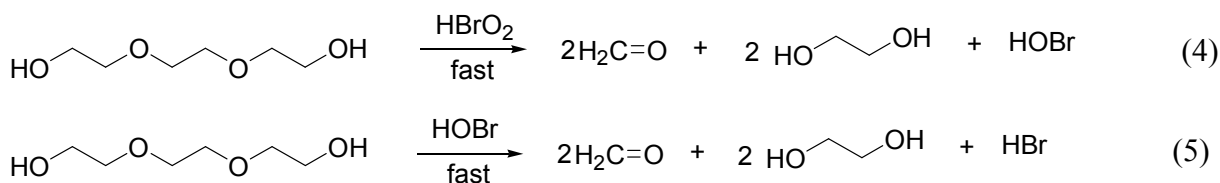
Scheme 2

The reactive oxidant species $HBrO_2$ and HOBr may also oxidizes intermediate ethylene glycol to give product of reaction in a fast step. In a secondary reaction, the bromide ion could have produced bromine molecule by reacting with bromate in acid medium. Thus, in order to evade the formation of Br_2 and further parallel oxidation reaction set by Br_2, mercuric acetate was used as bromide ion scavenger to remove Br^- by forming complex. As a result the presence of $Hg(OAc)_2$ in the reaction mixture avoided the unwanted complicacy that could have created by bromine molecule. Again, in the present investigation, the rate of the reaction is independent of the initial concentration of mercuric acetate which rule out the possibility of $Hg(OAc)_2$ acting as either oxidant or catalyst[24] during the reaction.

The cleavage of the carbon-carbon and carbon-oxygen bonds in the oxidation of triethylene glycol by bromate ion in acid medium has been shown to occur to give formaldehyde. Under the present experimental conditions, further oxidation of formaldehyde seems unlikely[25]. The mechanism is well consistent with the experimental results and also with the activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$). This is to be mentioned that triethylene glycol reacts at a faster rate than diethylene glycol due to the increase chain length and this is in agreement with the results obtained earlier[3].

Conclusion

The oxidation of triethylene glycol by acid bromate was found to follow first order kinetics with respect to substrate and oxidant. The reaction rate also depends on the first power of H^+ concentration. The reaction involves the formation of unstable intermediate bromate ester in the slow rate determining step. The fission of C-C and C-O bonds leads to the formation of formaldehyde, the main oxidation product of TEG with acid bromate.

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