

Kinetics of retardation in persulphate- Fe^{3+} -bisulphite initiated polymerization of acrylamide

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The kinetics of persulphate- Fe^{3+} -bisulphite initiated polymerization has been studied at $30 \pm 0.2^\circ\text{C}$ in oxygen atmosphere. It has been found that the polymerization kinetics is significantly altered by Fe^{3+} concentration. At lower concentration ($2.0 \times 10^{-4} \text{ mol dm}^{-3}$) of Fe^{3+} the rate of polymerization follows the rate equation $R_p \propto [\text{monomer}] [\text{S}_2\text{O}_8^{2-}]$ while at higher concentration ($8.0 \times 10^{-4} \text{ mol dm}^{-3}$) the rate equation becomes $R_p \propto [\text{M}][\text{HSO}_3^-]$. Besides affecting the polymerization kinetics Fe^{3+} also decreases the molecular weight of the resulting polymers. The effects of added salts and temperature on the polymerization process have also been investigated and energy of activation is calculated to be 42.6 kJ mol^{-1} . Retarding effect of various aliphatic alcohols, nitro compounds and nitrophenols has been studied in terms of retardation constants.

The decomposition of persulphate and its activation by reductants and metal ions have been extensively studied in the recent past^{1,2}. The introduction of metal ions to persulphate coupled redox systems has facilitated its decomposition in most of the polymerization studies. However, a retarding behaviour of the added metal ion has also been noticed in a few cases. In the present paper the retarding role of Fe^{3+} has been reported kinetically and the retarding influence of several alcohols, nitro compounds and nitrophenols on the polymerization kinetics has been discussed.

The monomer chosen is acrylamide since its low and high molecular weight polymers have major industrial applications. The superiority of the redox system selected for the study lies in the fact that Fe^{3+} will act both as an activator and a terminator in free radical polymerization and yields relatively lower molecular weight polymer.

Materials and Methods

Acrylamide (Robert Johnson, India) was crystallized twice from hot methanol (G R grade) and dried *in vacuo* over anhydrous silica gel for a week. Ferric chloride (Sarabhai Chemicals, India) was used as received and its aqueous solution was prepared as described elsewhere³. Potassium peroxydisulphate (BDH, England) was used without any pre-treatment and its freshly prepared aqueous solution was used for every run.

The techniques adopted for polymerization and

molecular weight determination were similar to those described in our earlier communication⁴.

Results and Discussion

[Monomer] dependence

The effect of increasing [acrylamide] on the rate of polymerization has been studied by varying the concentration of monomer in the range 5.0 to $25.0 \times 10^{-2} \text{ mol dm}^{-3}$. It has been observed that on increasing [monomer] both the initial rate of polymerization and percentage conversion increase as shown in Fig. 1.

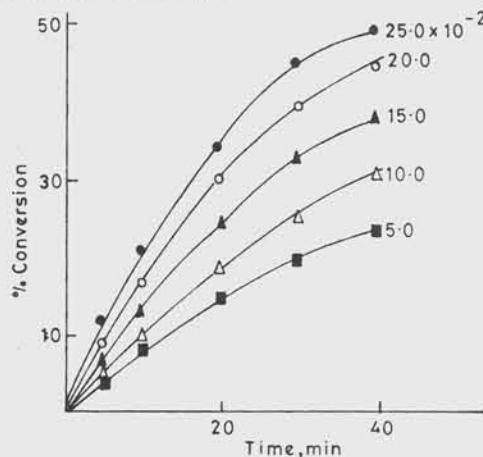


Fig. 1—Time versus percentage conversion curves for the polymerization of acrylamide with varying initial [monomer] at fixed [persulphate] = $4.0 \times 10^{-3} \text{ mol dm}^{-3}$, [bisulphite] = $3.4 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Fe}^{3+}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, temp. = $30 \pm 0.2^\circ\text{C}$

The first power dependence of the rate of polymerization on [monomer] has been confirmed by the double logarithmic plot and has been widely reported in redox initiated polymerization systems⁵. This also reveals from the observed first order that the possibility of primary termination is ruled out as evident from the mechanism also.

Fe^{3+} dependence

Incorporation of Fe^{3+}/Fe^{2+} to the redox systems has been proved to be a powerful tool for enhancing the polymerization rate and percentage conversion⁶. However, retarding role of Fe^{3+} and Cu^{2+} (as $FeCl_3$ and $CuCl_2$) has also been noticed by several workers⁷. In the present case we have found very interesting results that the polymerization kinetics is directly controlled by $[Fe^{3+}]$. The dependence of rate of polymerization on redox components varies with $[Fe^{3+}]$ in the system. At lower concentration (2.0×10^{-4} mol dm⁻³) the rate varies with the first power of [persulphate] and [bisulphite] while at the higher value (8.0×10^{-4} mol dm⁻³) the rate varies with the first power of [bisulphite] only. In both the cases an order of unity with respect to monomer is always retained.

The overall rate of polymerization does not change appreciably with increase in $[Fe^{3+}]$ in the studied range. This zero order dependence of rate of polymerization on $[Fe^{3+}]$ may be explained by the fact that a balance always exists between Eqs. (1), (2) and (7) in such a way that whereas Eqs. (1) and (2) tend to rise the rate of polymerization, Eq. (7), retards it in the whole studied range of $[Fe^{3+}]$. Due to these opposing reactions the rate of polymerization is negligibly affected by increase in $[Fe^{3+}]$. However, due to Eq. (7) a significant drop in the molecular weight of polyacrylamide has been observed as shown in Table 1. This clearly explains the retarding role of $FeCl_3$ in the polymerization reaction.

Moreover, if the radical concentration is increased by increasing $[Fe^{3+}]$ (Eq. 1) then an increase in $[Fe^{3+}]$ must bring a decrease in MW since the rates of termination steps (6) and (7) are

proportional to $[RM_n]$ and

$$DP = \frac{\text{Rate of polymerization}}{\text{Rate of termination}} \\ = \frac{k_p [RM_n][M]}{k_t [RM_n] + k_t' [RM_n][Fe^{3+}]}$$

(assuming that termination is first order)

$$\frac{1}{DP} = \frac{k_t}{k_p [M]} + \frac{k_t' [Fe^{3+}]}{k_p [M]}$$

i.e. a plot of $1/DP$ versus $[Fe^{3+}]$ should be linear. In Fig. 2 the plot has been drawn and found to be linear.

[Persulphate] dependence

The effect of [persulphate] on the rate of polymerization has been studied by varying its concentration in the range 2.0×10^{-3} to 10.0×10^{-3} mol dm⁻³. The results clearly indicate that the effect of persulphate on the polymerization kinetics is dependent on $[Fe^{3+}]$. At lower $[Fe^{3+}]$ (2.0×10^{-4} mol dm⁻³) a simple first order dependence is exhibited by persulphate while at higher $[Fe^{3+}]$ (8.0×10^{-4} mol dm⁻³) a zero order dependence of rate of polymerization on [persulphate] is observed.

The results may be interpreted as follows:

(i) At lower $[Fe^{3+}]$ an increase in the initial rate and percentage conversion is observed with increase in [persulphate]. This observation is quite obvious as on increasing [persulphate] greater number of primary free radicals will be generated (Eq. 2), and, therefore, the initial rate of polymerization increases. Also, from the double logarithmic plot a first order dependence of rate on [persulphate] has been confirmed.

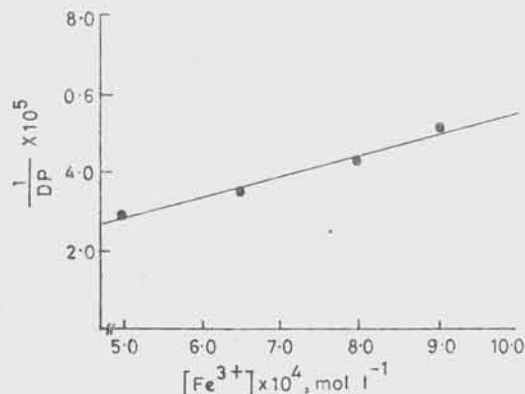


Fig. 2—Variation of $1/DP$ with $[Fe^{3+}]$ ion at fixed, [monomer] = 10×10^{-2} mol dm⁻³, [persulphate] = 4.0×10^{-3} mol dm⁻³, [bisulphite] = 3.4×10^{-2} mol dm⁻³, temp. $30 \pm 0.2^\circ\text{C}$

Table 1—Effect of increasing $[Fe^{3+}]$ and [persulphate] on the molecular weight of resulting polyacrylamide

$[Fe^{3+}] \times 10^4$ (mol dm ⁻³)	$Mv \times 10^{-4}$	[Persulphate] $\times 10^3$ (mol dm ⁻³)	$Mv \times 10^{-4}$
5.0	2.4	2.0	2.3
6.5	2.0	4.0	2.0
8.0	1.6	6.0	1.8
9.0	1.3	8.0	1.6
10.0	1.0	10.0	1.3

(ii) When [persulphate] is increased at higher $[\text{Fe}^{3+}]$ then almost no change in the initial rate of polymerization and percentage conversion is observed which indicates a zero order dependence of rate on [persulphate]. The results may be explained by the fact that at higher $[\text{Fe}^{3+}]$ the following two reactions become significant viz. (i) with increase in [persulphate] the production of primary free radicals increase (Eq. 2), and (ii) the termination of growing chains by Fe^{3+} (Eq. 7) increases. It may lead to a zero order dependence of polymerization rate on [persulphate]. To justify our interpretation the molecular weight of resulting polymers were determined (Table 1). It is clearly shown by data in Table 1 that with increase in [persulphate] the molecular weight decreases which support the idea of predominating termination step (Eq. 7).

[Bisulphite] dependence

When the concentration of bisulphite is raised in the range 2.0 to $8.0 \times 10^{-2} \text{ mol dm}^{-3}$ at the lower ($2.0 \times 10^{-4} \text{ mol dm}^{-3}$) and the higher ($8.0 \times 10^{-4} \text{ mol dm}^{-3}$) concentrations of Fe^{3+} , in both the cases the initial rate and percentage conversion are found to increase and a first order dependence of rate on [bisulphite] is observed.

When the polymerization system at lower $[\text{Fe}^{3+}]$ is considered, it can be seen that with increase in [bisulphite] more and more number of primary free radicals will be generated by Eq. (1) and consequently the initial rate and percentage conversion will increase.

When $[\text{Fe}^{3+}]$ is fixed at $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ the initial rate and percentage conversion increase with increase in [bisulphite]. This may be attributed to the fact that at higher $[\text{Fe}^{3+}]$ the balance between the generation of free radicals (Eq. 1) and termination of growing macroradicals (Eq. 7) does not exist. This unbalance is due to the reason that in Eq. (1) Fe^{3+} are directly involved in free radical production and there is no competing step which could use Fe^{3+} for yielding free radicals. While in Eq. (7) macroradicals $\text{RM}_n^\cdot$ have to compete with Eq. (6) for termination and, therefore, in comparison to Eq. (1) less Fe^{3+} would be involved in Eq. (6). This discussion reveals that under the existing experimental conditions Eq. (1) may be considered as a dominating reaction over Eq. (6) which implies that the initial rate and percentage conversion should increase with increase in [bisulphite]. Our results are in complete agreement with the mechanistic predictions.

Temperature dependence

The effect of increase in temperature of the po-

lymerization medium on the initial rate and percentage conversion has been investigated by varying the temperature in the range 25° to 45°C . The results reveal that with the rise in temperature both the initial rate and percentage conversion increase.

The activation energy of overall rate of polymerization has been calculated with the help of Arrhenius plot to be 42.6 kJ mol^{-1} .

Effect of added inorganic salts

The effect of addition of equimolar amount of salts on the initial rate of polymerization has been investigated by adding various salts of sodium and chlorides of various cations to the polymerization medium. The results clearly indicate that in the case of addition of anions both the initial rate and percentage conversion fall. The increasing order of depression by the added anions follow the sequence: $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$.

Likewise in the case of effect of cations both the initial rate and percentage conversion decrease in the order, $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Ca}^{2+} < \text{Cu}^{2+}$.

The reasons for the observed depression of the initial rate and percentage conversion have been discussed elsewhere⁸.

Solvent effect

The presence of organic solvents in free radical polymerization is important not only because of their retarding property but also due to their impact on the stereoregularity of the resulting polymer. In the present study various organic solvents have been added to the reaction medium in 5% (v/v) and their effect on the rate of polymerization has been investigated. The results are shown in Fig. 3 which clearly imply that on addition of organic solvents the initial rate and percentage conversion decrease in the following order: $\text{MeOH} < \text{EtOH} < \text{iso-PrOH} < \text{nBuOH}$.

The observed depression by the organic solvents is a common observation in redox polymerization and has been widely discussed in the recent past^{9,10}.

Retardation by organic compounds

The phenomenon of retardation in vinyl polymerization has largely been employed in producing antioxidants and stabilizers for various uses^{11,12}. In the present paper we are quantitatively evaluating the retarding behaviour of several organic compounds in terms of retardation constant which is calculated using the equation.

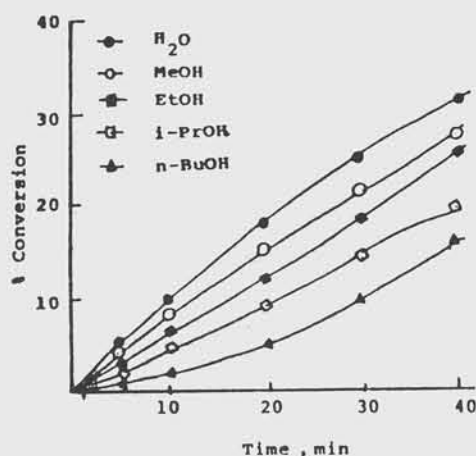


Fig. 3—Effect of addition of water miscible aliphatic alcohols (5% v/v) on the rate of polymerization of acrylamide at fixed [monomer] = 10×10^{-2} mol dm $^{-3}$, [perusulphate] = 4.0×10^{-3} mol dm $^{-3}$, [bisulphite] = 3.5×10^{-2} mol dm $^{-3}$, [Fe $^{3+}$] = 2.0×10^{-4} mol dm $^{-3}$, temp. = $30 \pm 0.2^\circ$

Table 2—Retardation constants (I) of various organic compounds as retarders

Retarder (Z)	Retarder concentration [Z]	$I \times 10^4$
<i>Aliphatic alcohols</i>		
Methanol	5% (v/v)	1.4
Ethanol	5% (v/v)	3.4
Iso-propanol	5% (v/v)	5.7
n-butanol	5% (v/v)	7.0
<i>Dinitrobenzenes</i>		
<i>o</i> -	1×10^{-4} mol dm $^{-3}$	3.5
<i>m</i> -	1×10^{-4} mol dm $^{-3}$	5.7
<i>p</i> -	1×10^{-4} mol dm $^{-3}$	9.1
<i>Nitrophenols</i>		
<i>o</i> -	1×10^{-4} mol dm $^{-3}$	5.7
<i>m</i> -	1×10^{-4} mol dm $^{-3}$	4.1
<i>p</i> -	1×10^{-4} mol dm $^{-3}$	2.0

$$[M]_0 = I \frac{[W]_0}{\frac{1}{(DP)'} - \frac{R_p}{R_p'}}$$

Here different terms have their usual significance as described elsewhere¹³.

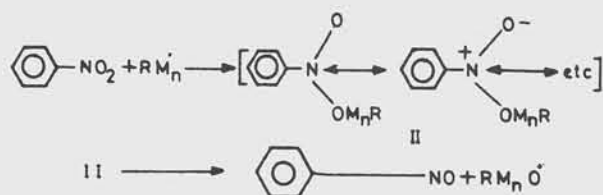
Now we will discuss the retarding behaviour of various organic compounds in light of the above parameters.

(i) *Aliphatic alcohols*—The retardation constant (I) of aliphatic alcohols have been calculated and summarized in Table 2 which confirms the following retarding sequence order MeOH < EtOH < iso-PrOH < nBuOH.

The cause of retardation is mainly attributed to the chain transfer reaction⁹.

(ii) *Nitro compounds*—In the present study the retarding effect of nitro compounds on the course of polymerization has been investigated taking *o*-, *m*- and *p*-dinitrobenzenes as retarders. When their equimolar concentrations (1×10^{-4} mol dm $^{-3}$) are added to the reaction medium both the initial rate and percentage conversion fall with the following order of increasing effectiveness *o*- < *m*- < *p*-.

The results have been summarized in Table 2 in terms of retardation constants. The observed order of retardation may be explained by the mechanism of Bartlett¹⁴ according to which the growing macroradical attacks the oxygen atom of nitro group forming radical II which is also resonance stabilized and may further break as follows:



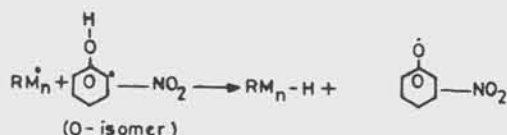
Now the reactivities of the three isomers may be compared on the basis of resonance stabilization of the intermediate radical species. It is quite clear that the contribution from resonance structures involving the two nitro groups will play an important role in stabilizing the radical intermediate in the three dinitrobenzenes. In the case of *para* isomers, since the free (unattacked) nitro group can readily assume the required coplanar configuration¹⁵ with respect to benzene ring and other nitro group, this isomer would be the most effective towards the macroradical attack. In the case of *meta* isomer, the two nitro groups are inclined at about 11° to the plane of benzene ring with a result that its contribution will be less than *para* isomer¹⁶ which makes this retarder weaker than *para* one. In *ortho* isomer, due to large steric hindrance, the two nitro groups will be non planar with the benzene ring and its contribution towards resonance structures will be least. This explains the observed order of effectiveness of the three isomers. Similar type of sequence has also been observed earlier¹⁷.

(iii) *Phenolic compounds*—In the present work we have studied the retardation of polymerization rate in the presence of *o*-, *m*- and *p*-nitrophenols. It is found that with all the three isomers both the initial rate and percentage conversion decrease. On the basis of the retarded initial rates the re-

tarding efficiency of the three isomers may be written as $o > m > p$.

The retardation constants as summarized in Table 2 have also been evaluated.

The mechanism of retardation may involve hydrogen abstraction followed by the coupling of the phenoxy radical with the growing macroradicals as shown below:



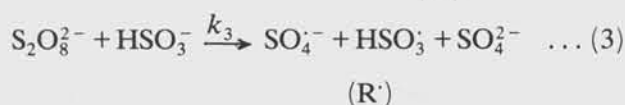
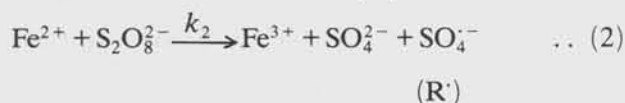
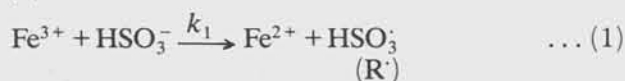
It also reveals from the above mechanism that the increasing order of stability of the three isomers' phenoxy radicals will be $o > m > p$.

Obviously the retarding efficiency of the three isomers follow the same order. Similar type of results have also been obtained by other workers¹⁸.

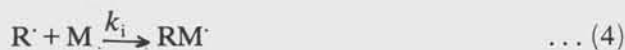
Mechanism

A stepwise plausible mechanism for the polymerization of acrylamide by the persulphate-Fe³⁺-bisulphite redox couple may be outlined as below:

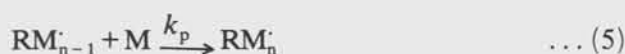
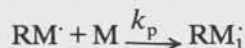
(a) Formation of free radicals



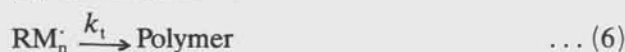
(b) Initiation



(c) Propagation



(d) Termination

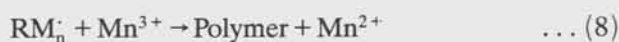


The unimolecular termination, as shown above, commonly takes place in metal ion containing re-

dox systems and may follow any of the suggested mechanisms as given below:

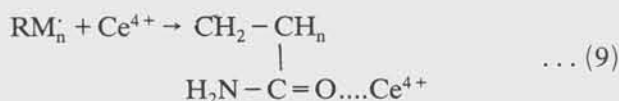
(i) By electron transfer

In this type of termination the growing macroradical transfer its electron to the metal ion¹⁹



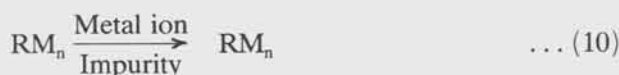
(ii) By coordination

Metal ion may also form a π complex with the growing macroradical as follows²⁰



(iii) By dissolved impurity

Dissolved metal ion impurities²¹ may also cause the termination of growing macroradicals,



In the present case termination by Fe³⁺ (Eq. 7) has been experimentally confirmed elsewhere²².

It is worth mentioning here that besides the usual unimolecular termination of growing macroradicals (Eq. 6) an additional termination will also be caused by Fe³⁺. Due to this extra retardation Fe³⁺ exhibits a retarding behaviour.

As an approximation the overall rate of polymerization may be expressed as,

$$R_p = k_p [\text{M}] [\text{RM}_n^\bullet] \quad \dots (11)$$

Now, from the steady state assumption we can write

$$\text{Rate of initiation} = \text{Rate of termination}$$

or

$$k_i [\text{R}'][\text{M}] = k_t [\text{RM}_n^\bullet] + k'_t [\text{Fe}^{3+}][\text{RM}_n^\bullet]$$

Therefore,

$$[\text{RM}_n^\bullet] = \frac{k_i [\text{R}'][\text{M}]}{(k_t + k'_t)[\text{Fe}^{3+}]} \quad \dots (12)$$

Substituting Eq. (12) in (11), we have

$$R_p = \frac{k_p k_i}{(k_t + k'_t)[\text{Fe}^{3+}]} [\text{M}]^2 [\text{R}] \quad \dots (13)$$

On applying steady state treatment to [R'], we get

$$\frac{d[R]}{dt} = 0 = k_1[Fe^{3+}][HSO_3^-] + k_2[Fe^{2+}][S_2O_8^{2-}]$$

$$+ k_3[HSO_3^-][S_2O_8^{2-}] = k_i[R][M]$$

$$\text{or } [R] = \frac{k_1[Fe^{3+}][HSO_3^-] + k_2[Fe^{2+}][S_2O_8^{2-}] + k_3[HSO_3^-][S_2O_8^{2-}]}{k_i[M]}$$

On substituting the above value of $[R]$ in Eq. (13) we get

$$R_p = \frac{k_p[M]k_1[Fe^{3+}][HSO_3^-] + k_2[Fe^{2+}][S_2O_8^{2-}] + k_3[HSO_3^-][S_2O_8^{2-}]}{(k_i + k'_i[Fe^{3+}])} \quad \dots (14)$$

On applying steady state condition to $[Fe^{2+}]$, we get,

$$k_1[Fe^{3+}][HSO_3^-] = k_2[Fe^{2+}][S_2O_8^{2-}]$$

or

$$[Fe^{2+}] = \frac{k_1[Fe^{3+}][HSO_3^-]}{k_2[S_2O_8^{2-}]} \quad \dots (15)$$

Substituting Eq. (15) in (14), we get

$$R_p = \frac{k_p[M]\{2k_1[Fe^{3+}][HSO_3^-] + k_3[HSO_3^-][S_2O_8^{2-}]\}}{(k_i + k'_i[Fe^{3+}])} \quad \dots (16)$$

or

$$R_p = \frac{k_p[M][HSO_3^-]\{2k_1[Fe^{3+}] + k_3[S_2O_8^{2-}]\}}{(k_i + k'_i[Fe^{3+}])} \quad \dots (17)$$

Now we analyze Eq. (17) in the light of $[Fe^{3+}]$,

(i) When $[Fe^{3+}]$ is of lower range, then we can assume that

$$k_3[S_2O_8^{2-}] \gg 2k_1[Fe^{3+}]$$

and

$$k_i \gg k'_i[Fe^{3+}]$$

Now Eq. (17) is reduced to,

$$R_p = \frac{k_p k_3 [M][HSO_3^-][S_2O_8^{2-}]}{k_i}$$

or

$$R_p \propto [M][HSO_3^-][S_2O_8^{2-}] \quad \dots (18)$$

(iii) At higher $[Fe^{3+}]$, we can suppose that

$$2k_1[Fe^{3+}] \gg k_3[S_2O_8^{2-}]$$

and

$$k'_i[Fe^{3+}] \gg k_i$$

Then Eq. (18) becomes

$$R_p = \left(\frac{2k_p k_1}{k'_i} \right) [M][HSO_3^-]$$

or

$$R_p \propto [M][HSO_3^-] \quad \dots (19)$$

Eqs (18) and (19) are in full agreement with our experimental findings.

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