A Kinetic Study of the Reaction between Sulfite Ion and Propylene Oxide[1a]

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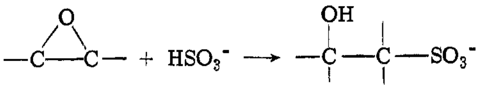
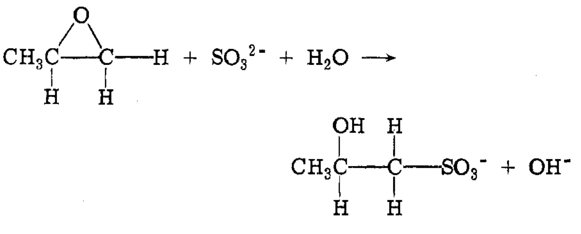
The reactive sulfur species in the sulfur(IV)–propylene oxide reaction is sulfite ion. The reaction is first order in sulfite and also first order in propylene oxide under conditions of dilute base in nearly pure water. The reaction order with respect to propylene oxide becomes less than one as the propylene oxide concentration is increased. These observations are consistent with simple nucleophilic attack by the sulfite ion, and with strongly concentration-dependent activity coefficients for propylene oxide.

Reactions between epoxides and sulfur(IV) generally result in ring opening[2] as illustrated by eq 1. If the ring carbon atoms in the reactant are substituted unsymmetrically, then nonequivalent sites for sulfur(IV) attack exist and either or both of the isomeric products may be obtained.[2] If one of the ring carbon atoms is bound to more bulky substituents than the other, as in propylene oxide, then the major product is usually predicted to have the sulfonate group in the terminal position owing to smaller steric resistance to attack at the terminal carbon atom.[2] However, this generalization is not valid for every reaction. For example, the reactions of sulfite with styrene oxide and with 1,2-epoxyoctane have been reported to give only the corresponding 2-sulfonic acids.[3] The product of the sulfite reaction with propylene oxide, the epoxide of principal interest in the present report, has been reported to give only the terminal sulfonate[4,5] but may give a mixture.[6] Even greater disagreement exists about the product of the sulfur(IV)–epichlorohydrin reaction. A product with a normal terminal sulfonate group has been reported,[7] but the reaction has also been reported[8] to give under some conditions terminal sulfonate by replacement of the chloride, without disturbing the ring. However, this last report has been questioned.[9]


(1)

Some very early observations of epoxide reactions with sulfite were made,[10] but not much work has been done recently.[9] One moderately recent study[3] was a stoichiometric and kinetic investigation of the reaction between sulfite and styrene oxide in two phases. It was concluded that sulfite ion is the reactive sulfur(IV) species and that the reactions are first order in sulfite ion; however, an attempt to study the reaction between propylene oxide and sulfite in a single aqueous phase was not successful because the reaction was too fast to study by methods then available.

Owing to our interest in reactions of sulfur(IV)[11] and to the absence of detailed kinetic data for reactions of the class shown in eq 1, we have studied the sulfur(IV)–propylene oxide reaction indicated by eq 2 and have made a few observations of some related reactions.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Experimental Section

Reagents. Oxygen-free aqueous sodium sulfite solutions and sodium perchlorate solutions were prepared as described earlier.[12] Reagent grade sodium carbonate, sodium hydroxide, perchloric acid, ethylene oxide, propylene oxide, propylene sulfide, epichlorohydrin, epibromohydrin, and deuterium oxide were used without purification. The water used for preparation of each solution was redistilled from laboratory distilled water and was stored in a polyethylene tank.

Rate and Nmr Measurements. Rates of reaction 2 were measured at 4.0, 14.1, and 25.0° in aqueous alkaline solutions of 0.25 *M* ionic strength maintained with $NaClO_4$. The reactant solutions were contained in 5- or 10-cm spectrophotometer cells positioned in a Beckman ACTA V recording spectrophotometer. The progress of each reaction was observed by measuring the absorbance decrease at 270 nm, where SO_3^{2-} is the principal absorbing species. Propylene oxide was in large excess in each experiment. Each individual experiment was first order in sulfite and the pseudo-first-order rate constant was obtained from a plot of ln $(A - A_\infty)$, *vs.* time, where A and A_∞ are the absorbances at 270 nm at a particular time and at completion of the reaction, respectively.

The procedures used in the propylene oxide experiments were also used in attempts to measure the rate of reaction of sulfite ion with ethylene oxide and with propylene sulfide. These same procedures were also used in attempts to measure the rates of reaction with epichlorohydrin and epibromohydrin, except the solvent was 50% ethanol owing to the insolubility of these organic compounds in pure water.

A Varian XL-100 spectrometer was used to measure the proton nmr spectra of the reactants and products of reaction 2 and of the analogous epichlorohydrin reaction in D_2O solution.

Results

Reaction Product. We used proton nmr spectra to confirm that the sulfonate group in the reaction 2 product is indeed in the terminal position as expected[2] and as asserted by some earlier workers.[4,5] Our measurement of the spectrum of reactant propylene oxide gave an upfield doublet assigned to the methyl group. In addition to the upfield doublet, multiplets centered at 75 and 93 MHz downfield from the doublet and a poorly resolved multiplet centered at 108 MHz downfield from the doublet were observed. The spectrum had the same appearance as spectra reported earlier[13,14] for propylene oxide. In addition, our assignments are in agreement with the earlier ones;[13,14] the methyl group resonance is upfield, the resonances for the two hydrogen atoms on the other terminal carbon atom are at 75 and 93 MHz, and the resonance for the remaining hydrogen atom is at 108 MHz downfield.

Reaction 2 was allowed to occur in D_2O solution under conditions of excess sulfite so that all the propylene oxide was converted to product. The proton nmr spectrum of the resulting solution had the following downfield resonances (still referred to the upfield doublet for propylene oxide): a doublet centered at 8 MHz assigned to the methyl group, multiplets at 113 and 120 MHz assigned to the hydrogen atoms on the terminal carbon atom containing the sulfonate group, and a multiplet at 190 MHz assigned to the hydrogen atom on the central carbon atom. The assignment of the downfield multiplet is based on the low relative intensity and on the similarity in shape to the analogous mul-

Table I
Observed Pseudo-First-Order Rate Constants for Reaction 2 at 0.25 *M* Ionic Strength and 0.005–0.01 *M* NaOH

$[C_3H_6O]$,[a] mol %	$10^3k'$, sec^{-1}	$[C_3H_6O]$,[a] mol %	$10^3k'$, sec^{-1}
0.534	0.208[b]	0.192	0.218[c]
1.08	0.447	0.485	1.49
2.23	1.24	0.980	2.54
3.20	1.44	1.03	2.62
3.44	1.58	2.02	5.64
3.70	1.78	2.06[d]	5.83
4.74	1.35	2.06[e]	5.73
6.12	0.940	2.06[d,f]	5.77
7.58	0.759	4.28	9.90
7.89	0.645	5.75	12.6
0.520	0.510	9.78	15.4
1.05	0.672	17.1	14.2
2.16	2.31	27.3	12.6
4.61	3.08	36.8	11.1
5.95	3.22	41.1	10.6
7.37	2.25		

[a] Mole per cent solvent, considering only propylene oxide and water. [b] Each of the first ten rate constants listed in this column was measured at 4.0°. The remaining six were measured at 14.1°. [c] Each of the rate constants listed in this column was measured at 25.0°. [d] $[OH^-]$ was 0.0094 *M*. [e] $[OH^-]$ was 0.00504 *M*. [f] The reaction occurred in an oxygen-free solution.

Table II
Observed and Calculated Values for k^0 and Activation Parameters for k^0, Valid in the Limit as [PO] Approaches Zero

Rate constant k^{0}[a]			ΔS^*, eu	ΔH^*, kcal/mol
4°	14.1°	25°		
0.045	0.108	0.290	2.5_5	14.0

[a] The rate constants are defined by eq 4; the units are (mole fraction)$^{-1}$ sec^{-1}.

tiplet in propylene oxide. We conclude that the hydroxyl group in the reaction 2 product is indeed on the central carbon atom, rather than on the terminal one, because the resonance assigned to this hydrogen atom shifted farther downfield than any of the other peaks, in accord with the greater deshielding strength of OH relative to SO_3^- or SO_3H.

We were able to measure an nmr spectrum of epichlorohydrin that agrees with spectra already reported,[15] but the products of the reaction of epichlorohydrin with excess sulfite in D_2O solution apparently include at least two organic species. The nmr spectrum of the product mixture is complex and is not consistent with complete conversion to any one of the three expected products (1-chloro-2-hydroxy-3-sulfonic acid,[7] 1-chloro-3-hydroxy-2-sulfonic acid, or 1,2-epoxy-3-sulfonic acid[8]).

Phase Properties of the Water–Propylene Oxide System. The salt-free water–propylene oxide system is known[16] to form two liquid phases at mole fractions of propylene oxide ranging from about 0.17 to about 0.90. The two-phase region exists at all temperatures between the freezing and boiling points of the liquid. The solids that can exist in equilibrium with the liquid phases are pure propylene oxide, pure water, and a clathrate compound propylene oxide · 17 water.[17] Our visual observations of the system show that addition of 0.25 *M* $NaClO_4$ renders the solvents completely miscible at 25°, but two liquid phases remain at temperatures below about 20°.

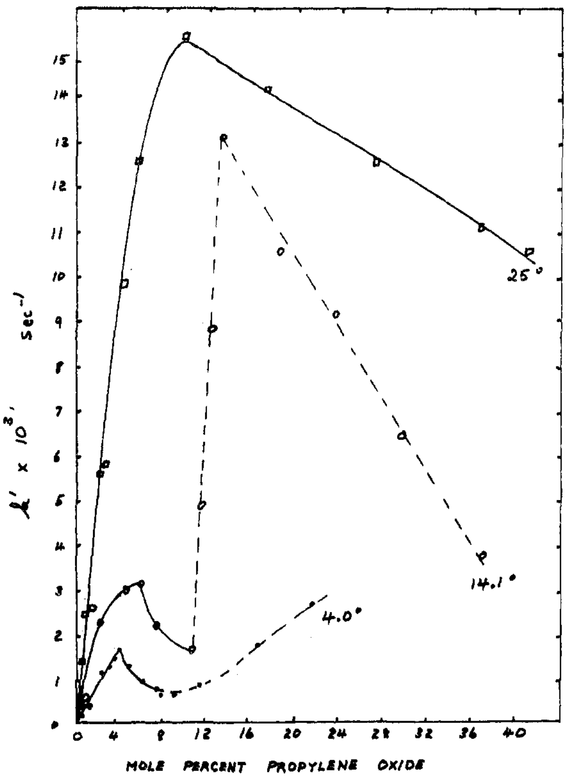


Figure 1. The relationship between observed rate constant for reaction 2, and mole per cent propylene oxide. The dashed lines connect points measured under two-phase conditions.

Rate Measurements. The numerical values of the pseudo-first-order rate constants measured for reaction 2 are listed in Table I. Each of the rate constants listed in the table occurred in a one-phase system and is defined by eq 3. These same rate constants are shown graphically in Figure 1, along with some apparent rate constants obtained from two-phase systems.

$$-\mathrm{d}\ln[SO_3^{2-}]/\mathrm{d}t = k' \qquad (3)$$

Experimental results listed in Table I show that small variations in $[OH^-]$ do not affect the value of k', although experiments in dilute acid solution showed an induction period; reaction was slow until the solution became basic due to production of OH^- by reaction 2. Similarly, Table I indicates that deoxygenation of the reaction mixture does not affect the value of k'. However, solvent phase separation does affect the apparent rate constant, as indicated in Figure 1.

Even the data obtained at 25°, all in a one-phase system, indicate a complex relation between the pseudo-first-order rate constant and the mole per cent[18] propylene oxide at high mole per cent propylene oxide. However, the data obtained at each of the temperatures conform to a first-order dependence on propylene oxide at low [PO].[19] The limiting slopes obtained from Figure 1 lead to the observed rate constants given in Table II, where the rate constant k^0 is defined according to eq 4. The values of k^0 are correlated

$$-\mathrm{d}\ln[SO_3^{2-}]/\mathrm{d}t = k^0[\mathrm{PO}] \qquad (4)$$

very well by the absolute rate theory equation, leading to the activiation enthalpy and entropy values of 14.0 kcal/mol and 2.5 eu, respectively, for k^0.

Some attempts were made to measure the rates of sulfite ion reaction with substrates other than propylene oxide.

Table III
Observed Pseudo-First-Order Rate Constants for Reaction of Sulfite Ion with Ethylene Oxide at 0° in Alkaline Aqueous Solution

$[C_2H_4O]$, M	$10^3 k'$, sec^{-1}
0.091	1.5
0.112	2.3
0.120	2.4
0.188	1.4
0.221	3.9
0.225	3.5
0.296	5.3

The sulfite reaction with propylene sulfide was rapid and yielded a polymeric solid that did not dissolve in any of the polar or nonpolar solvents we tested. Neither epichlorohydrin nor epibromohydrin was sufficiently soluble in water to permit rate measurements in water solution. In addition, both these substrates reacted quite rapidly with sulfite. However, a rate constant was measured for epichlorohydrin at 4° in 50 vol % water–ethanol solution; the rate was first order in sulfite, and based on the assumption that the rate is also first order in epichlorohydrin, the rate constant was about 0.02 M^{-1} sec^{-1} in a solution initially containing 4.88 $\times 10^{-3}$ M epichlorohydrin, 0.01 M NaOH, and about 2.30 $\times 10^{-3}$ M SO_3^{2-}.

The reaction between sulfite ion and ethylene oxide was also quite fast and study of the reaction was further complicated by the inconvenient volatility of ethylene oxide. The ethylene oxide was added to the spectrophotometer cell by bubbling the gas into the water solution in the cell. The ethylene oxide concentration after completion of the reaction was determined by measuring the absorbance at 260 nm, using $\epsilon = 1.09$. The initial portions of the reactions had already occurred by the time rate measurements were started, and the data were only moderately reproducible. The data are listed in Table III, where k' is defined by eq 3. The k' data are approximately in accord with eq 5, where $k = 0.02$ M^{-1} sec^{-1}.

$$k' = k[C_2H_4O] \qquad (5)$$

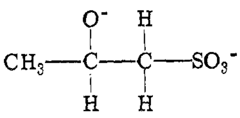
Discussion

The data at low [PO] are consistent with empirical eq 4. A possible minor contributor to the deviation from eq 4 at higher [PO] is a dependence on the activity of water; the activity of water would be expected to remain approximately constant with small changes in [PO] in nearly pure water, but would be expected to decrease slightly as [PO] becomes larger.[16] A probable major contributor to the deviation is the decreasing activity coefficient for propylene oxide with increasing [PO]. Activity coefficients for propylene oxide and water in the salt-free mixed solvent system have been determined at the normal boiling points of the system,[16] but have not been determined at any of the temperatures employed in the present study. The activity coefficient for propylene oxide at the mixed solvent boiling temperatures does decrease sharply in the [PO] range 0–0.4, however, and it appears reasonable to assume similar behavior at lower temperatures in the presence of dissolved salts. We think it is probable that either eq 6 or 7 accurately represents the rate behavior for reaction 2 in the one-phase reaction mixtures containing up to 0.41 mol fraction propylene oxide. The first-order dependence on sulfite ion concentration and the negligible importance of terms involving bisulfite concentration are well established by our work. Our conclusion that sulfite is the reactive sulfur(IV) species is in agreement with the conclusion reached from the earlier study,[3] although the earlier study did involve heterogeneous systems and the investigators apparently did not realize that SO_3^{2-} and HSO_3^- are in equilibrium in aqueous solutions.

$$-\mathrm{d} \ln [SO_3^{2-}]/st = ka_{PO}a_{H_2O} \qquad (6)$$

$$-\mathrm{d} \ln [SO_3^{2-}]/\mathrm{d}t = ka_{PO} \qquad (7)$$

The form of eq 4 is consistent with simple attack of the nucleophile sulfite ion upon the terminal ring carbon atom of propylene oxide to give



$$CH_3-\overset{O^-}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-SO_3^-$$

as the product of the rate-determining step if eq 7 is correct, or to give the final net reaction product if eq 6 is correct.

With respect to the reactions we studied more briefly than reaction 2, our results with ethylene oxide are not inconsistent with a mechanism analogous to that described just above for propylene oxide. The stoichiometric evidence for the epichlorohydrin reaction permits no generalization except that at least two competing pathways exist for reaction with sulfite. The sulfite-induced polymerization of propylene sulfide is not surprising; if the initial reaction is analogous to reaction 2, then a mercaptan is formed and the mercaptan could act as a nucleophile in attacking another propylene sulfide molecule to give a sulfur bridged dimer containing another mercaptan group capable of continuing the polymerization. A detailed description of an analogous process for the ethoxide-induced polymerization of propylene sulfide has already been presented.[20]

Registry No.—HSO_3^-, 15181-46-1; propylene oxide, 75-56-9; ethylene oxide, 75-21-8.

References and Notes

(1) (a) Supported by the Robert A. Welch Foundation; (b) Robert A. Welch Predoctoral Fellow, summer, 1973; (c) Robert A. Welch Undergraduate Scholar, 1972, 1973; (d) address correspondence to this author at R.R. 1, Box 115, Odessa, Missouri 64076.
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