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On the Ionic Species Formed in Reactions of Sulfur Dioxide with Cyclic Ethers and Propylene Sulfide

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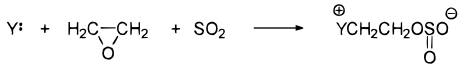
ABSTRACT: The reactions of SO_2 with various oxiranes, propylene sulfide, and oxetane have been studied. It was found that SO_2 activates these monomers toward ring opening polymerization. The spontaneous reactions lead to the formation of cationic active centers, on which the heterocyclic monomer homopropagation and various cyclization processes mainly proceed. Anionic alternating copolymerization of SO_2 with ethylene oxide or propylene oxide was observed after the spontaneous termination of cationic active species. Zwitterions with active anionic sites are formed in the presence of pyridine. They can initiate the alternating copolymerization of SO_2 and oxiranes. The relative reactivity of the oxiranes in the addition to anionic species increases in the following order: epichlorohydrin < glycidyl acetate < propylene oxide < butyl glycidyl ether < ethylene oxide < 1,2-cyclohexene oxide. Styrene oxide, oxetane, and propylene sulfide undergo spontaneous reactions also in the presence of pyridine. In systems with the former two monomers the alternating copolymerization proceeds simultaneously with the processes initiated by cationic centers; propylene sulfide, however, does not form copolymers with SO_2. Monomers of low ring strain like THF or trioxane do not undergo ring opening in the presence of SO_2 and pyridine.

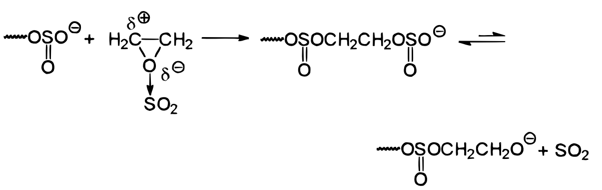
Introduction

Numerous papers have been devoted to the free radical copolymerization of sulfur dioxide with various monomers comprising an unsaturated carbon−carbon bond. In these reactions SO_2 behaves like a monomer of high general reactivity and strong electrophilic properties. Its Q and e parameters are 0.93 and 3.3, respectively.[1] The ionic copolymerization of SO_2 has not been hitherto systematically studied. There are only scarce reports on the copolymerization of SO_2 with certain oxiranes in the presence of an initiator characterized by nucleophilic or electrophilic properties, but in a majority of systems the reaction mechanism has not been explained.[2−12] The SO_2 copolymerization with ethylene oxide (EO) initiated by strong organic Lewis bases[8,10−12] such as amines, phosphines, alkyl sulfides, or salts of various inorganic or organic acids is relatively best known.

It has been shown by us[10,12] that the reactions of monomers with Lewis bases lead to the formation of zwitterions of an onium−sulfite structure.


(1)

The isolated zwitterions do not react with EO alone, but initiate the copolymerization in the presence of SO_2. Therefore, it can be assumed that the oxirane molecule addition to sulfite ions is activated due to the formation of a complex with SO_2.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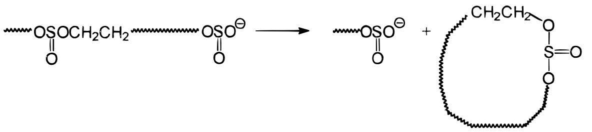
Sulfite active species are very stable and do not disappear during standard polymer isolation and drying procedures, and the copolymerization products are active initiators.[12] Attempts to transform sulfite species into alcoholate ones by prolonged heating of copolymers under vacuum at 50 °C were not successful. We did not observe either the evolution of SO_2 or the occurrence of any of the reactions recognized in the model reactions between the copolymer and alcoholates [chain scission *via* a nucleophilic attack on the carbon (~80%) or sulfur atom (~20%)].[12] Thus, it seems that the equilibrium in eq 2 is shifted almost completely toward the sulfite ion formation. The SO_2 copolymerization with EO is accompanied by back-biting reactions leading to the formation of cyclic products of different sizes.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The M_n of a freshly isolated mixture of linear and cyclic poly(ethylene sulfite)s obtained in bulk in the presence of 0.1−1 wt % of Lewis bases is in the (9−15) × 10^3 range.[12] These products decompose very rapidly to the five-membered cyclic sulfite (1,3,2-dioxathiolane 2-oxide) above 140 °C,[2,8] under UV radiation,[3] or in the presence of various types of catalysts, especially those characterized by electrophilic properties, such as, e.g., BF_3 or chlorotrimethylsilane.[12]

The present work is devoted to studies on the reactions of SO_2 with various oxiranes, propylene sulfide (PS), oxetane, and THF. The main purpose of it was to obtain answers to the following three questions.

1. Is SO_2 a sufficiently strong acid to initiate cationic polymerization in the systems studied?

2. Do the studied heterocyclic monomers complexed with SO_2 undergo ring opening under the influence of a strong nucleophilic agent, such as pyridine?

3. Is the anionic copolymerization of SO_2 with the comonomers studied possible, and what is the relative

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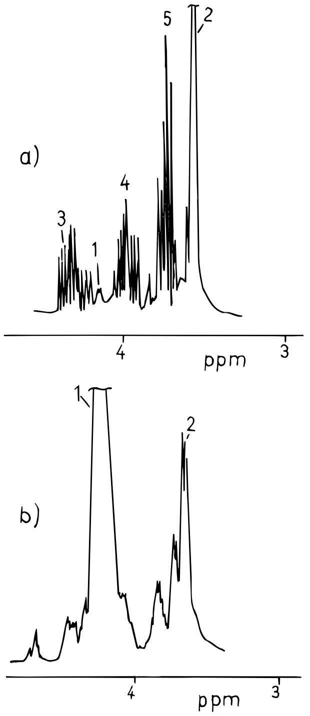
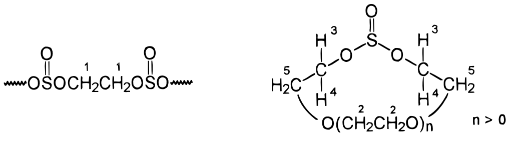


Figure 1. ^{1}H-NMR ($CDCl_3$) spectra of products of the spontaneous SO_2 and ethylene oxide reaction carried out at 50 °C for (a) 6 h and (b) 24 h. Signal assignments:



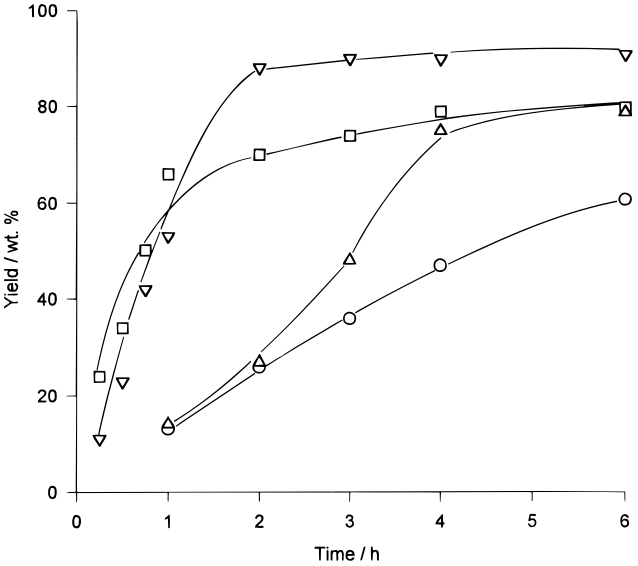


Figure 2. Dependence of polysulfite yield on time in reactions carried out at an equimolar amount of comonomers at 50 °C (1 mol % of initiator with respect to SO_2): (□) poly(ethylene sulfite), initiator pyridine; (△) poly(ethylene sulfite), initiator KI; (▽) poly(propylene sulfite), initiator pyridine; (○) poly(propylene sulfite), initiator KI.

reactivity of these monomers in the addition to anionic active species?

Experimental Section

Measurements. The NMR spectra were recorded using a Varian VXR-300 MHz spectrometer in DMSO-d_6 or $CDCl_3$. The UV spectra were measured at room temperature on a Perkin-Elmer UV/vis Lambda 2 spectrometer using the solvent mixture as a blank. Number-average molecular weights were determined by means of a Hewlett Packard 302 VPO vapor pressure osmometer or cryoscopically in benzene. GC–MS analyses were run on a 30 m long capillary column DB5, by using a HP 5890 II gas chromatograph equipped with a MS 5971 ion trap detector. GPC experiments were conducted in THF solutions at 35 °C using a Spectra Physics 8800 gel permeation chromatograph. The composition of the product was determined on the basis of elemental analysis and sequence analysis by means of ^{1}H-NMR spectroscopy.

Monomers. Glycidyl acetate and butyl glycidyl fumarate were obtained according to the procedures described in refs 13 and 14, respectively. Other commercial monomers were distilled twice in an atmosphere of dry nitrogen prior to use.

Polymerization and Preparation of Zwitterions. The reactions of SO_2 with heterocyclic monomers were carried out in glass pressure ampules equipped with a rubber septum, seal, and steel cap, according to a procedure described elsewhere.[10] The yield of the products obtained was determined on the basis of ^{1}H-NMR spectra of the postreaction mixtures upon distilling off the unreacted monomers under reduced pressure. The signal assignments are given in Figures 1 and 2, Tables 1 and 2, refs 10–12, and the next section of the paper. The reactions of pyridine (Py), SO_2, and heterocyclic monomers at a 1:1:1 initial monomer feed were carried out in diethyl ether (50 wt %) at room temperature. The zwitterions isolated in the form of a white precipitate were purified by dissolution in methanol and precipitation with diethyl ether. Other reactions were carried out in bulk. The copolymers, poly(PS), and oligomers formed in reactions with 1,2-cyclohexene oxide (CHO) and styrene oxide were precipitated with methanol, washed several times, dried under reduced pressure, and characterized by elemental analysis, VPO, and cryoscopic techniques. The fractions soluble in methanol were concentrated and analyzed using ^{1}H-NMR and GC–MS or GPC techniques. In some experiments the reaction products were treated with a 0.5 M NaOH solution in a methanol/water mixture and heated under reflux for 8 h, neutralized with hydrochloric acid, concentrated, and analyzed by the GC–MS method.

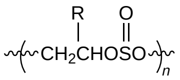
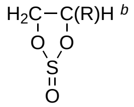
The low molecular weight compounds formed in the reactions studied were identified mainly on the basis of ^{1}H-NMR and MS spectra, and in some systems also by the GC method using corresponding standards. In the case of cyclic oligomers of SO_2 and EO, containing more than one EO monomeric unit (m.u.), the parent ions are usually very weak or nonexistent. The bands M − 30 and M − 60 are characteristic of the fragmentation of these compounds, and the most intense bands appear at $m/e = 92$ ($C_4H_4SO_2$) and $m/e = 43$ (C_3H_3O).

Results

Spontaneous Reactions. From among the heterocyclic monomers studied only styrene oxide and propylene sulfide react spontaneously with SO_2 at room temperature, forming products which can be isolated after evaporation of SO_2. In UV spectra of diluted SO_2 solutions in oxiranes and THF ($\sim 10^{-4}$ mol L^{-1}) characteristic absorption bands occur with a maximum at 275–280 nm. Similar bands were observed in mixtures of SO_2 with trimethylamine and other strong Lewis bases and were attributed to the formation of charge transfer complexes stabilized by the partial transfer of an electron from the lone pair orbital of the donor to a lowest unoccupied orbital of SO_2.[15,16] Unfortunately, in the case of the cyclic ethers studied the differences between the absorbance of the complex and that of SO_2 in an inert solvent (n-hexane, ϵ max at 290 nm) were not large enough to obtain reliable values of the complexes equilibrium constant.

Several cyclic ethers undergo various types of ring opening reactions in the presence of SO_2 at about 50 °C. The heterocyclic monomers conversion in spontane-

Table 1. Chemical Shifts (DMSO-d_6) of Protons in Linear and Cyclic Sulfites[a]

	 $\sim\!\!\left(CH_2\overset{R}{\overset{|}{C}}HOS\overset{O}{\overset{\|}{}}O\right)_n\!\!\sim$			 H$_2$C−C(R)H[b]		
R	δ(CH_2)	δ(CH)	δ(R)	δ(CH_2)	δ(CH)	δ(R)
CH_3	3.9	4.8	1.3	3.87 (dd)		
	4.1			4.71 (dd)	5.11 (m)	1.43 (d)
				4.29 (dd)		
				4.50 (dd)	4.63 (m)	1.61 (d)
C_6H_5	3.8−4.3	5.2−5.5	7.0−7.4	4.21 (dd)		
					5.94 (t)	
	(3.4−4.3[c])			4.95 (dd)		
						7.3−7.6
				4.49 (dd)		
					5.42 (dd)	
				4.76 (dd)		
CH_2Cl	4.1−4.4	4.6−5.0	3.5−3.7		5.27 (m)	3.81 (m)
				4.3, 4.73		
					4.88 (m)	3.96 (m)
$CH_2OC_4H_9$	3.9−4.2	4.6−4.7	0.5−1.5	3.72 (dd)		
			(C_3H_9)		4.96 (m)	
				4.61 (dd)		
			3.3−3.5			
			(CH_2OCH_2)	4.20 (dd)		
					4.54 (m)	
				4.44 (dd)		
$CH_2O\overset{O}{\overset{\|}{C}}CH_3$	3.8−4.2	4.8−4.9	1.99−2.02		5.22 (m)	2.03 (s)
	(and OCH_2)		(CH_3)	4.2−4.7		
					4.85 (m)	2.04 (s)
						(CH_3)
$\begin{array}{l} CH_2OC(O)CH \\ \quad\quad\quad\quad\| \\ H_9C_4OC(O)CH \end{array}$					5.10 (m)	
				4.0−4.6		
				(and OCH_2)	4.70 (m)	
−$(CH_2)_4$−		4.3−4.5	1.2−2.1			
		(3.2−3.6[c])				

[a] In ppm. [b] Two stereoisomers, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets. [c] In etheral sequences.

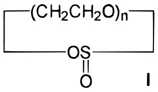
Table 2. Results of Spontaneous SO_2 Reactions with Heterocyclic Monomers (M)[a]

M		reacn time h	conversion of M %	SO_2 m.u. in products mol %	main products
ethylene oxide (EO)		3	4	21	cyclic sulfites
		6	9	22	cyclic sulfites
		15	16	28	cyclic sulfites
		24	44	40	alternating copolymer
	b	48	51	34	cyclic sulfites
propylene oxide		24	87	40	alternating copolymer
1,2-cyclohexene oxide		2	79	16	cyclic sulfites
		82	100	16	cyclic sulfites
styrene oxide (SO)		24	100	19	SO oligomer and 4-phenyl-1,3,2-dioxathiolane 2-oxide
	c	24	91	20	
SO/EO	*c*	24	40	24	SO and EO oligomers[d] and 4-phenyl-1,3,2-dioxathiolane 2-oxide
glycidyl acetate		24	83	49	4-(acetoxymethyl)-1,3,2-dioxathiolane 2-oxide
oxetane		24	48	8	oligomer
propylene sulfide		1	70	0	poly(propylene sulfide)
	b, e	24	85	0	poly(propylene sulfide)

[a] SO_2, 5 g; SO_2/M mole ratio in monomer feed = 1; temperature, 50 °C. [b] SO_2/M mole ratio in monomer feed = 10. [c] Temperature: 20 °C. [d] SO m.u./EO m.u. mole ratio in oligomer ≈ 1.1. [e] Temperature: 0 °C.

ous reactions and SO_2 m.u. content in the product mixture are presented in Table 2. The structure of the main reaction products depends very much on the kind of heterocyclic monomer used.

Ethylene Oxide. In reactions with EO the composition of the products changes with time. Cyclic sulfites **I** containing three or four EO m.u. and one SO_2 m.u. are the main reaction products at low conversion.

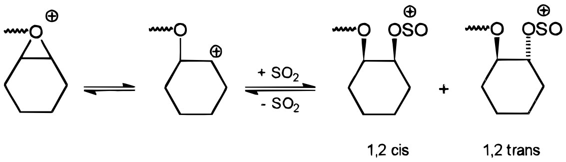


I

It can be estimated on the basis of the analysis of ^1H-NMR spectra of the reaction mixture (Figure 1a) and chromatographic analysis of poly(ethylene glycol)s obtained after the hydrolysis of ester bonds that a sulfite of $n = 3$ constitutes 60−80 mol % of the mixture of products and the sulfite of $n = 4$ that of 15−30 mol %. Besides these, sulfites of $n = 1$, 2, and 5, 1,4-dioxane, and 12-crown-4 are formed in small quantities. In the ^1H-NMR spectrum a very weak signal is visible, characteristic of the alternating SO_2EOSO_2 sequences in poly(ethylene sulfite) (at δ 4.20 ppm). The intensity of this signal increases within time and at about 40%

conversion poly(ethylene sulfite) is the main reaction product (Figure 1b). The cyclic sulfites of $n = 3$ and 4 can be obtained in high yield when the reaction is carried out using a large excess of SO_2 in the monomer feed (Table 2). Slow polymerization of these compounds, accompanied by SO_2 evolution is observed in these systems. This process is accelerated by electrophilic agents, like BF_3 or $(CH_3)_3SiCl$. However, it is not initiated by compounds of nucleophilic properties, such as Py, phosphines, or ammonium salts.

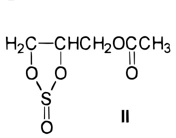
Cyclohexene Oxide. In the spontaneous reaction of SO_2 and CHO cyclic oligomers are formed in a high yield with an average molecular weight ~560, containing about 16 mol % of SO_2 m.u., which corresponds to an average CHO homosequence length of 5.2. After basic hydrolysis of the sulfite bonds a solid product was isolated with an average molecular weight ~470, which corresponds to a CHO oligomer terminated with OH groups of an average sequence length ~4.8. Besides this, also a mixture of *cis* and *trans* isomers of 1,2-cyclohexanediols in a 1:2 ratio is formed. These compounds result from the hydrolysis of an alternating SO_2CHOSO_2 triad, the content of which in the products (estimated on the basis of ^1H-NMR spectra) is ~7%. The basic hydrolysis of organic sulfites proceeds involving a S−O bond rather than C−O cleavage.[17] Therefore, the configuration of the diol resulting from the alternating triad hydrolysis is the same as that of the CHO m.u. The formation of 1,2 *cis* isomers in the products of spontaneous reactions suggests the possibility of SO_2 addition to carbocations formed in ring opening reactions according to the S_N1 mechanism.



(4)

It should be noticed that after hydrolysis of the alternating copolymer of CHO and SO_2 obtained in the presence of pyridine (see Table 4) the diol of the 1,2 trans structure is formed exclusively. This indicates an inversion of configuration that is characteristic for S_N2 ring opening reactions.

Glycidyl Acetate. In the reactions with glycidyl acetate a mixture of stereoisomers of the five-membered cyclic sulfite (4-(acetoxymethyl)-1,3,2-dioxathiolane 2-oxide) (**II**) is the main product. At an equimolar amount of reactants these compounds constitute about 90% of the products. Besides them, oligomers are also formed, in which the GA m.u./SO_2 m.u. mole ratio is ~2. The yield of these latter products increases when GA is used in excess with respect to SO_2.



II

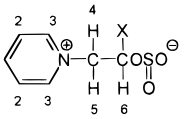
Styrene Oxide. Styrene oxide reacts with SO_2 at room temperature forming cyclic five-membered sulfite 4-phenyl-1,3,2-dioxathiolane 2-oxide in a ~50% yield. The other part consists of oligomers containing 7−10 mol % of SO_2 of an average molecular weight ~650. These oligomers undergo decomposition at room temperature with SO_2 evolution, which is accompanied by a decrease in the average molecular weight to about 300. 2,5-Diphenyl-1,4-dioxane (cyclic styrene oxide dimer) was found to be the main component of the mixture formed. A rise of the reaction temperature to 50 °C causes a decrease in the yield of five-membered cyclic sulfite to ~38% and a decrease in the SO_2 m.u. content in the other products.

Propylene Sulfide. PS undergoes homopolymerization in the presence of SO_2. Oligomers of PS (fraction soluble in methanol) are formed besides the polymer. The average molecular weight of the oligomers was found to be ~270, which is close to the average number of PS m.u. equal to 4 ($M_w = 284$). The reaction proceeds even at −78 °C. The use of a considerable excess of SO_2 in the reaction mixture does not lead to the products containing the SO_2 m.u.

Oxetane. A mixture of products containing about 8 mol % of SO_2 m.u. is formed in the reactions of SO_2 and oxetane at 50 °C at an equimolar amount of reactants. GPC chromatograms show that the bimodal molecular mass distribution, M_n, for the fraction of the higher molecular weight is ~540 (according to the polystyrene scale) and the polydispersity index is equal to 1.55. At a 10-fold excess of SO_2 in the monomer feed the m.u. content of this compound in the final products increases to about 12%.

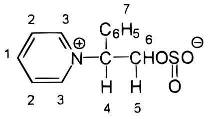
Other Monomers. Epichlorohydrin, THF, and trioxane did not undergo reaction at 50 °C in the presence of SO_2. We found, however, that THF undergoes terpolymerization with SO_2 and EO. At an equimolar amount of reactants a polymer is formed containing 42 mol % of EO m.u., 34 mol % of THF m.u., and 24 mol % of SO_2 m.u. (in the ^1H-NMR spectrum the signals characteristic for the THF m.u. appear at ~1.65 and 3.45 ppm). Besides this polymer, cyclic ethylene sulfite is formed in the system.

Reactions with Pyridine. Oxiranes. We showed previously that zwitterions of a pyridinium sulfite structure are formed in the reactions of SO_2 with an equimolar amount of Py and EO.[10] Presently, in order to obtain information on the regioselectivity in ring opening processes we determined the structure of products formed in reactions of asymmetric oxiranes such as PO, epichlorohydrin, and styrene oxide. On the basis of ^1H-NMR spectra (see Table 3) we found that in systems with the first two oxiranes zwitterions of the structure **III** are exclusively formed, in which the nitrogen atom is bonded with a CH_2 group. When the reaction is carried out at room temperature in a diethyl ether solution, the yield of ions of the structures **IIIA** and **IIIB** is nearly 100%. In the reactions with styrene oxide carried out under analogous conditions a zwitterion in which the nitrogen atom forms a bond with the more substituted carbon atom in the oxirane m.u. (**IV**) is the main product. The yield of this compound is about 48% (Table 3). A compound of the structure **III** is also obtained in about 24% yield, as well as the products of spontaneous reactions of styrene oxide and SO_2.



III

X = CH_3, CH_2Cl, (C_6H_5)
A B C



IV

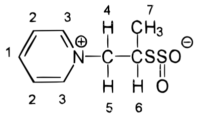
Propylene Sulfite. In systems with propylene sulfite the zwitterion **V** (Table 3) was isolated, the structure

Table 3. Chemical Shifts (DMSO-d_6) of Protons in Zwitterions[a]

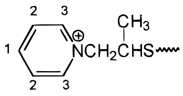
zwitterion	δ/ppm	coupling constant/Hz
IIIA[b]	H1, 8.58 (t); H2, 8.09 (t); H3, 8.92 (d); H4, 4.73 (dd); H5, 4.36 (dd); H6, 4.12 (m); H7 (CH_3), 1.27 (d)	$J_{4,6} = 2.76$, $J_{5,6} = 8.85$, $J_{4,5} = 13.02$, $J_{6,7} = 6.30$
IIB	H1, 8.61 (t); H2, 8.13 (t); H3, 9.01 (d); H4, 4.90 (dd); H5, 4.61 (dd); H6, 5.09 (dd); H7 (CH_2Cl), 3.74	$J_{4,6} = 2.91$, $J_{5,6} = 9.05$, $J_{4,5} = -13.23$
IIIC	H1, 8.65 (t); H2, 8.15 (t); H3, 9.02 (d); H4, 4.97 (dd); H5, 4.65 (dd); H6, 4.27 (dd); H7 (C_6H_5), 7.55	$J_{4,6} = 3.28$, $J_{5,6} = 8.85$, $J_{4,5} = -12.85$
IV	H1, 8.62 (t); H2, 8.17 (t); H3, 9.19 (d); H4, 6.14 (dd); H5, 4.46 (dd); H6, 4.20 (dd); H7 (C_6H_5), 7.44	$J_{4,6} = 4.20$, $J_{4,5} = 9.13$, $J_{5,6} = -12.40$
V[c]	H1, 8.52 (5); H2, 8.08 (5); H3, 8.93 (d); H4, 4.81 (dd); H5, 4.36 (dd); H6, 3.32 (m); H7 (CH_3), 1.32	$J_{4,6} = 3.92$, $J_{5,6} = 8.98$, $J_{4,5} = -12.42$, $J_{6,7} = 7.05$
VI	H1, 8.65 (t); H2, 8.10 (t); H3, 9.10 (d)	
VII	H1, 8.58 (t); H2, 8.12 (t); H3, 9.09 (d); H4, 4.67 (t); H5, 2.07 (m); H6, 3.43 (t)	$J_{4,5} = 7.00$, $J_{5,6} = 5.80$

[a] d = doublet, t = triplet, m = multiplet, dd = doublet of doublets. [b] Anal. Calcd for $C_8H_{11}NSO_3$ (**IIIA**): C, 47.76; H, 5.47; N, 6.96; S, 15.92. Found: C, 46.79; H, 6.70; N, 6.73; S, 15.64. [c] Anal. Calcd for $C_8H_{11}NS_2O_2$ (**V**): C, 44.24; H, 5.07; N, 6.45; S, 29.49. Found: C, 43.54; H, 5.17; N, 5.12; S, 29.52.

of which is analogous to that of **III**. The yield of this compound is not high since simultaneously PS homopolymerization proceeds and part of Py occurs as pyridinium cation **VI** at the ends of the chains.



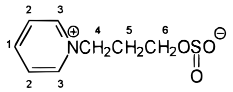
V



VI

For example, with an equimolar amount of Py with respect to PS and SO_2 at 0 °C after 24 h, the yield of **V** is 20% and about 7% of Py occurs as the end group in poly(PS), the yield of which is 51%. At a Py/PS mole ratio of 1.2 the yield of **V** increases to 55% and that of the polymer decreases to 24%.

Oxetane. Oxetane forms the zwitterion **VII** (Table 3) in about 90% yield under conditions as in reactions with oxiranes. Alternating oxetane and SO_2 oligomers are also formed in small quantities.



VII

Other Monomers. Attempts to obtain zwitterions in analogous reactions with THF, trioxane, and some other six- and seven-membered ring monomers (e.g. hexamethylcyclotrisiloxane, ϵ-caprolactone) carried out at up to 50 °C were not successful.

Copolymerization and Terpolymerization Initiated by Pyridine. Oxiranes. In Figure 2 is presented a relationship between conversion and time for the alternating copolymerization of SO_2 with EO and PO carried out at 50 °C in bulk with an equimolar monomer feed in the presence of Py or KI as initiator. When 1 mol % of Py is used, then after 1 h conversions in the 55−65% range are obtained, followed by a decrease in the reaction rate. The reactions in the presence of other active initiators such as phosphines, tertiary aliphatic amines, ammonium salts, or certain potassium salts complexed by crown ethers proceed in a similar way. In the absence of crown ethers the reactions initiated by potassium salts initially proceed slower, but after a certain time the reaction rate increases, probably as a result of the complexation of counterions by molecules of the polymer formed.

As can be seen from Table 4, CHO undergoes copolymerization with SO_2 much faster than EO and PO. However, the copolymer yields are generally small or no copolymer is formed at all in the reactions with the other oxiranes studied (epichlorohydrin, glycidyl acetate, maleic acid butyl glycidyl ester, and styrene oxide). In the case of these latter systems, five-membered cyclic sulfites are most often the main reaction products, which in the reactions with EO, PO, and CHO are formed in small yields or are not formed at all.

In the reactions with styrene oxide lowering the reaction temperature to 20 °C and increasing the Py concentration to 10 mol % caused the formation of a copolymer containing ∼42 mol % of SO_2 m.u. ^{1}H-NMR studies (Figure 3) show that this copolymer undergoes rapid degradation in solution to 4-phenyl-1,3,2-dioxathiolane 2-oxide and styrene oxide oligomers even at room temperature.

The diglycidyl ether of Bisphenol A in reaction with SO_2 forms a cross-linked copolymer, in which one oxirane m.u. falls per 0.6 SO_2 m.u.

Table 4. Yield and Composition of SO_2 Reaction Products with Various Cyclic Ethers, Initiated by Pyridine (Py)[a]

	reacn time	yield, mol %		
monomer (M)	h	polymer	cyclic sulfite	SO_2 m.u./mol % in copolymer
ethylene oxide	0.25	24		
	6	80	2	47
propylene oxide	0.25	11		
	6	91	2	49
1,2-cyclohexene oxide	0.25	89	0	50
epichlorohydrin	6	4	22	47
styrene oxide	6	5	90	∼0
c	3	50	44	42
butyl glycidyl ether	6	18	9	48
glycidyl acetate	6	22	49	
butyl glycidyl fumarate	24	0	80	
oxetane	6	46	0	36
Bisphenol A diglycidyl ether	6	77[d]		60

[a] SO_2, 5 g; feed mole ratios SO_2/M = 1, Py/M = 0.01. [b] Yield with respect to cyclic ether. [c] Py/M mole ratio in feed = 0.1; temperature, 20 °C. [d] Solvent: toluene.

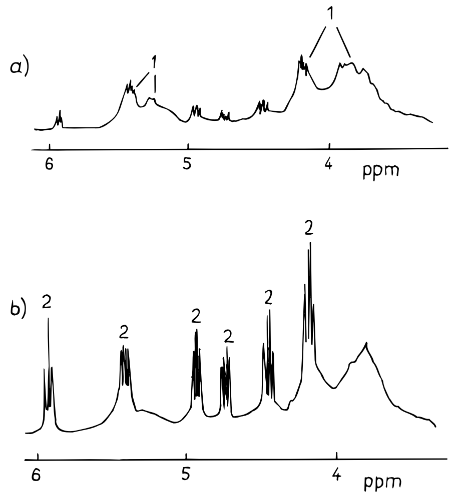
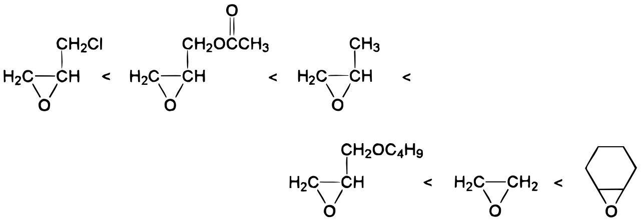


Figure 3. ^{1}H-NMR ($CDCl_3$) spectrum of a SO_2 and styrene oxide copolymer solution: (a) 0.5 h after dissolution; (b) 12 h later at 25 °C; (1) signals characteristic for the copolymer protons; (2) signals characteristic for styrene sulfite protons (two isomers) (signal assignments are presented in Table 1).

The relative reactivity of oxiranes in competitive addition to sulfite anions was compared on the basis of the product composition formed in ternary systems comprising SO_2 and two oxiranes (Table 5). EO was chosen as a reference monomer and reactions were carried out in a considerable excess of oxirane with respect to SO_2 in the presence of Py as initiator. In a majority of the systems studied terpolymers containing nearly 50 mol % of SO_2 m.u. and cyclic sulfites resulting from the terpolymer degradation are the only reaction products and thus oxirane homopropagation can be exluded.

The oxirane reactivity order determined in this case is as follows:



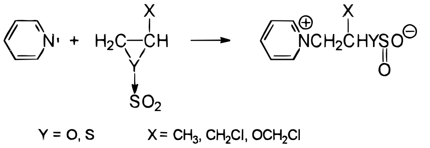
In ternary systems containing styrene oxide, also other reactions proceed besides aternating propagation, which makes the comparison of the reactivity of oxiranes in anionic copolymerization difficult. However, it can be stated that styrene oxide is clearly less reactive than EO in reactions initiated by Py (Table 5), whereas in the absence of Py (Table 2) the styrene oxide conversion is about twice as high as that of EO. Styrene sulfite and oligomers containing an approximately equimolar amount of monomeric units of both oxiranes are formed as a result of a spontaneous reaction. Ethylene sulfite or alternating SO_2EOSO_2 sequences are not formed, which indicates that in the absence of Py the sulfite ion is not the active center in these systems.

Oxetane. In the copolymerization of SO_2 with oxetane in the presence of 1 mol % of Py a copolymer is formed containing 36 mol % of SO_2 m.u. An analysis of ^{1}H-NMR of the copolymer and especially the intensities of three clearly separated groups of signals characteristic for protons of the central methylene group (CH_2CH_2-CH_2; δ 1.7–2.0 ppm) in oxetane m.u. (OX) permits an estimate of the m.u. sequences distribution in this product. About 40% of oxetane m.u. occur in SO_2OXSO_2 alternating sequences, ~48% in $SO_2(OX)_2SO_2$ sequences, and about 12% in $SO_2(OX)_nSO_2$ sequences ($n \geq 3$).

When EO is additionally present in the reaction system, then terpolymers are the reaction products, in which oxetane and EO are present both in the alternating sequences with SO_2 and in etheral sequences. On the basis of analysis of ^{1}H-NMR spectra of the products one can roughly estimate that oxetane is about 2.4 times less active than EO in the addition to sulfite anions (Table 5).

Discussion

Generation of Anionic and Cationic Species. Although sulfur oxide is regarded as a relatively weak Lewis acid,[18] it activates the monomer molecules of high ring strain like oxiranes, PS, and oxetane, in ring opening reactions. The structure of zwitterions obtained in the reactions of Py, SO_2, and unsymmetrical oxiranes or propylene sulfide indicates that in a majority of systems the ring opening reaction proceeds probably according to the S_N2 mechanism.



(5)

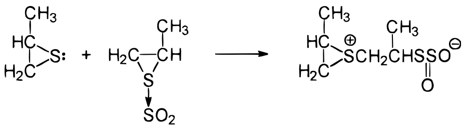
We suggest that the uncomplexed heterocyclic monomer can also play the role of a nucleophilic agent attacking the monomer−SO_2 complex.

The onium ions resulting from spontaneous reactions are reactive and easily undergo further transformations. These reactions proceed especially easily in systems with PS, which exhibits the strongest nucleophilic properties from among the monomers studied. Even

Table 5. Results of Terpolymerization of SO_2 and Ethylene Oxide (EO) with Cyclic Ethers Initiated by Pyridine (Py)[a]

		terpolymer composition/mol %			
monomer (M)	EO/M overall conversion ratio	SO_2	EO	M	EO m.u/ M m.u. ratio in terpolymer
propylene oxide	1.63	50	31	19	1.63
[b]	1.38	50	29	21	1.38
cyclohexene oxide	0.42	49	15	36	0.42
epichlorohydrin	4.8	50	43	7	6.14
styrene oxide	1.11	45	37	18	2.05
butyl glycidyl ether	1.23[c]				
glycidyl acetate	2.93[c]				
oxetane	2.91[c]	40	41	19	2.15
	(2.41[d])	(50)	(33)	(17)	(1.95)

[a] SO_2, 1 g; SO_2/EO/M mole ratio = 1:5:5; initiator, Py (1 mol % with respect to SO_2); temperature, 50 °C. [b] Initiator: KI (1 mol % with respect to SO_2). [c] Not separated mixture of cyclic sulfites and oligomers; monomer conversion ratio was determined on the basis of ^{1}H-NMR spectra. [d] Sulfite m.u. and cyclic sulfites.

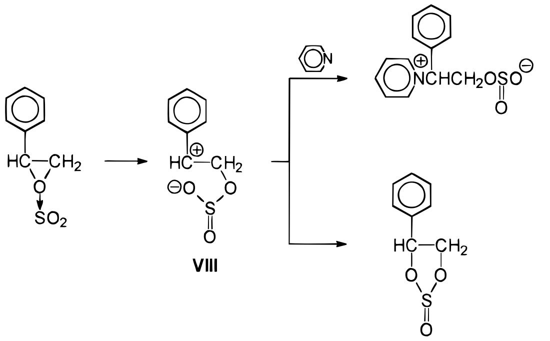


(6)

when Py is present in the system, a considerable amount of PS undergoes spontaneous reactions and the yield of the zwitterion formed in reaction 5 is small.

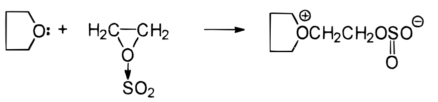
The rates of the reactions of oxiranes with the oxirane−SO_2 complex are usually much lower than that of reaction 5, and in the presence of a small amount of Py no products of spontaneous reactions are observed. The activity of these latter reactions decreases with a decrease in the nucleophilic properties of the oxirane. For example, EO reacts slower than CHO and PO, and epichlorohydrin, which contains an electron acceptor substituent in its molecule, does not undergo spontaneous reactions in the temperature range studied.

The formation of zwitterion **IV** indicates that heterolytic dissociation of the oxirane−SO_2 complex and addition of the nucleophile molecule according to the S_N1 mechanism are possible in the reactions with styrene oxide. The zwitterion **VIII** formed in the first stage may undergo intramolecular recombination, yielding a cyclic sulfite, and also initiate cationic polymerization. This type of ring opening mechanism probably results from the high resonance stabilization of the carbocation in zwitterion **VIII**. Since the ring opening occurs as a result of an intramolecular reaction, the cationic active species in reactions with styrene oxide are generated also at a high Py concentration in the reaction system. This leads, among others, to the occurrence of styrene oxide homosequences in the polymers obtained and also to rapid degradation of the alternating sequences to cyclic styrene sulfite (since this latter reaction is catalyzed by electrophiles).



(7)

SO_2 is too weak a Lewis acid to activate monomers of low ring strain like THF or trioxane in ring opening reactions. However, THF, as a relatively strong nucleophilic agent (pK_a = 2.1[19]), can react with the oxirane−SO_2 complex.



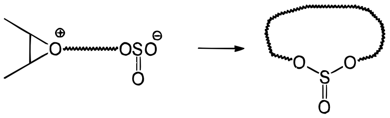
(8)

The carbon−oxygen bond in the tetrahydrofuranium (oxolanium) cation formed can be broken in S_N2 reactions with monomers or sulfite anions, and thus some THF m.u. are introduced into the polymer chain in ternary systems. The yield of these reactions is generally low, but they proceed even in the presence of a small amount of amines in the reaction system.

Reactions of Cationic Species. The onium ions generated in spontaneous reactions participate mainly in propagation and cyclization reactions. These latter ones may involve back-biting reactions and end to end closure *via* intramolecular conversion of zwitterions in covalent compounds.

In systems with PS the propagation of the heterocyclic monomer and back-biting reactions predominate, which results in the formation of poly(PS) and cyclic PS oligomers analogously as in the classic cationic polymerization of this monomer.[20] Therefore, it can be assumed that the sulfur atoms in the monomer and polymer chain are much stronger nucleophiles than oxygen atoms in SO_2 and the $-SS(O)O^-$ anion (see eq 6). As a result of this the SO_2 m.u. do not occur in the final reaction products but are only a part of the counterion.

On the contrary, the cationic propagation in systems with oxiranes is rapidly terminated as a result of intramolecular recombination of the ions. The products of back-biting type reactions (e.g. dioxane or 12-crown-4) are formed only in small quantities.

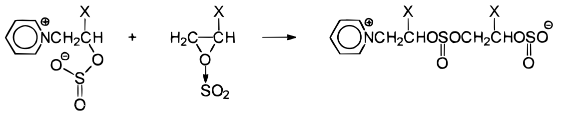


(9)

It is known that some oxiranes, e.g. PO or CHO, undergo cationic copolymerization with SO_2 in the presence of Lewis acids[1,6,7] forming poly(ether sulfites) of an average molecular weight M_n 1500−2000. They contain oxirane homosequences composed of 1−12 m.u. separated by a singular SO_2 m.u. From our observations it is shown that in systems containing equimolar amounts of SO_2 and EO in the presence of Lewis acids mainly dioxane and higher cyclic ethers are formed and the total content of SO_2 m.u. in the products does not exceed 2 mol %. In systems with PO and CHO, under analogous conditions, the average length of oxirane sequences in the polymeric products does not exceed ~5 and ~11, respectively. Hence it can be expected that in spontaneous reactions the SO_2 addition to onium ions is much less probable than the oxirane homopropagation and intramolecular recombination of the ions. Thus, most of the cyclic products formed contain only one SO_2 m.u.

In the reactions of SO_2 with EO the spontaneous termination of cationic processes occurs and with the elapse of time the anionic alternating copolymerization becomes the predominant reaction in these systems. This phenomenon indicates a transformation of active cationic species into unstrained onium ions, which become stable counterions, whereas sulfite ions start "to work" as active species. The transformation of onium ions can involve reactions with oxygen or sulfur atoms in the growing polymer chain or in the oligomeric products formed in the initial reaction period. The structure of the stable onium ions formed in these reactions is unknown. We found that they react neither with Py nor with phosphines, which are commonly used in the so-called ion trapping technique[21] to determine the structure of the cationic active species.

Reactions of Anionic Active Species. In systems in which active onium ions are formed, the anions terminated with a SO_2 m.u. usually play the role of counterions. They may become the active species when the spontaneous deactivation of onium centers occurs or when inactive cations are formed in the initiation reaction. In the copolymerization of SO_2 with oxiranes initiated by pyridine the first propagation step (eq 10)

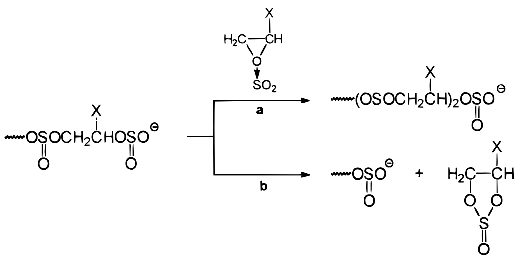

(10)

is probably significantly slower than the initiation one (eq 5). Due to this, in many systems zwitterions can be isolated in a nearly 100% yield. At a high content of the initiator in the reaction mixture a considerable amount of the initially formed zwitterions remains unreacted even at high monomer conversion. For example, in the copolymerization of SO_2 and PO at 20 °C in the presence of 10 mol % of Py, after 24 h the monomer conversion is about 60%, whereas the zwitterion conversion is only 28%. Therefore, it can be assumed that after the first propagation step (eq 10) the reactivity of sulfite ions increases, probably as a result of a decrease in the energy of their electrostatic interactions with the onium ion.

The reactivity of oxiranes in the addition to sulfite ions should depend mainly on the facility of complex formation with SO_2 and reactivity of the complex formed.

CHO appeared to be decisively most reactive in these reactions from among the monomers studied. This probably results from the positive substituent induction effect and the largest strain in the oxirane ring due to the presence of the second ring. Monosubstituted oxiranes are less reactive than EO. The lowest activity in the addition to sulfite ions is exhibited by oxiranes containing electron acceptor substituents (e.g. epichlorohydrin, glycidyl acetate), which indicates that the propagation rates depend more on the facility of the complex formation with SO_2 than on the electrophilic properties of oxirane.

In some systems the rate of propagation may be strongly reduced by steric repulsion between the penultimate monomeric unit and the oxirane$-SO_2$ complex. For example, butyl glycidyl ether readily undergoes terpolymerization with SO_2 and EO, but it is of little activity in the copolymerization, since both the penultimate monomeric unit and monomer complex contain large substituents. The slow propagation favors the back-biting reaction, and thus, in systems comprising oxiranes of low reactivity a considerable amount of five-membered cyclic sulfites is formed under the standard copolymerization conditions (Table 3).

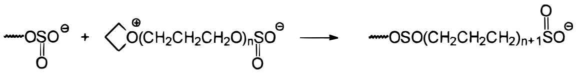


(11)

We found that five-membered cyclic sulfites added to the reaction system are not incorporated into the growing chain. Therefore, it can be assumed that reaction **11b** is practically irreversible.

The contribution of cyclic sulfites in the final reaction products usually increases considerably upon the addition of nucleophilic agents to the system, which form complexes with SO_2 easier than oxiranes (e.g. THF).

Oxetane exhibits a lower activity in reactions with the sulfite ion than EO, but is more reactive than oxiranes containing electron-withdrawing substituents. Ring strain in an oxetane molecule ($\sim$107 kJ mol^{-1} [22]) is smaller than that in EO ($\sim$114 kJ mol^{-1} [22]). Therefore, it can be assumed that oxetane complexes are less reactive in ring opening reactions than oxirane complexes. The nucleophilic properties of oxetane (pK_a = 2.02[18]) are, however, significantly stronger than that of oxiranes (e.g. pK_a for EO $\approx$ 3.7[23]). Due to this it should form complexes with SO_2 more readily and easier generate cationic species. The addition of a small amount of Py does not inhibit the spontaneous reactions of oxetane and SO_2. The addition of zwitterions formed in spontaneous reactions to sulfite ions may result in the formation of homosequences of oxetane m.u. (mainly dyads), besides the alternating sequences.


(12)

Conclusions

It has been found that sulfur dioxide may initiate the cationic polymerization of propylene sulfide, oxetane, and some oxiranes. However, in the case of the cyclic ethers studied, the chain growth is rapidly terminated due to the intramolecular recombination of oxonium and sulfite ions.

In the presence of pyridine the heterocyclic monomers mentioned and SO_2 form zwitterions of a pyridinium$-$sulfite structure. These ions initiate the anionic copolymerization of SO_2 with oxiranes and oxetane. The copolymerization proceeds most rapidly in systems with cyclohexene oxide, ethylene oxide, and propylene oxide. In systems with styrene oxide and oxiranes containing electron acceptor substituents, five-membered cyclic sulfites are generally the main product of reactions initiated by pyridine. They are probably formed in back-biting reactions and also as a result of the alternating copolymer degradation initiated by spontaneously generated cationic active species. In reactions with a strong nucleophile like propylene sulfide, pyridine does not inhibit the cationic polymerization of the heterocyclic monomer, and SO_2 is not incorporated into the growing chain.

The electron acceptor properties of SO_2 seem to be too weak to activate monomers of low ring strain like THF, trioxane, hexamethylcyclotrisiloxane, and ϵ-caprolactone in spontaneous or induced by pyridyne ring opening reactions.

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