1111. *The Condensed Phases of Sulphur Trioxide. Part III.*[1] *The Formation and Growth of Solid Polymer.*

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Vapour pressures are reported for polymeric (β) sulphur trioxide and are represented by $\log_{10} p$ (mm.) = 12·1831 − 2923·7/T (°K). The calculated ceiling temperature for polymerisation and the heat of polymerisation from the liquid phase are 30·4° and 3·04 kcal. (mole SO_3)$^{-1}$. Vapour-pressure values are identical whether the polymer is grown from the liquid or from the vapour at 20°, but the rates of establishing solid–vapour equilibrium may vary. The rate of growth from the liquid of crystalline polymer has been measured in the range 20—25° and shown to decrease with rise in temperature and with addition of polymerisation inhibitors. Addition of sulphuric acid also reduces the rate of growth of individual solid nuclei but markedly accelerates multiple nucleation. Viscosity measurements are reported for liquid sulphur trioxide containing small amounts of added sulphuric acid. There is no evidence of a slow polymerisation in the liquid phase but a relatively rapid formation of some molecules larger than disulphuric acid is indicated.

It is concluded that the rate of polymerisation is controlled by the slow nucleation of low concentrations of polysulphuric acid molecules, which are present in sulphur trioxide containing traces of water, this stage being followed by a slow increase in degree of polymerisation in the solid state. It is suggested that conversion of the β-polymer into the high-melting (α) polymer may occur by a condensation of the end hydroxyl groups of solid polyacid chains, thereby increasing the resistance to depolymerisation. The mode of action of inhibitors of polymerisation is discussed.

The states of molecular aggregation of sulphur trioxide have been summarised by Hyne and Tiley[2] and further experimental work has been recently reported.[3] It is well established that traces of water are necessary for polymerisation and the simplest interpretation, originally suggested by Gerding and Gerdings-Kroon,[4] is that the polymers are effectively solid polysulphuric acids of high molecular weight and of general structure, $HO\cdot(SO_2\cdot O)_n\cdot SO_2\cdot OH$. X-Ray diffraction patterns of the polymer[5] have confirmed the chain structure but cannot reveal the nature of the end-groups.

Since rapid melting of the solid polymer often requires temperatures above the normal boiling point of liquid sulphur trioxide (44·5°), the inhibition of polymerisation is important in use of the liquid, and since 1939 over thirty patents have appeared on the use of additives as inhibitors. Bevington and Pegler[6] reviewed the patent literature up to 1958, and reported experimental results on the screening of many inorganic compounds for inhibitor action; since 1958 a diversity of organic additives have been patented, *e.g.*, esters, amides, and chlorides of sulphonic acids;[7a] aromatic amines, amides, and nitro-compounds;[7b] nitriles;[7c] and aliphatic ethers.[7d] Testing of inhibitor action has been entirely of an *ad hoc* nature, generally involving cooling of liquid sulphur trioxide below room temperature, rewarming, and observing visually the amount of unmelted solid. Such observations yield only qualitative information on the rate of formation of solid polymer; in one case[7a] the technique was varied in order to allow observation of the growth of a seed crystal of polymer, and we have found this method suitable for quantitative studies.

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[1] Part II, Abercromby and Tiley, *J.*, 1963, 4902.

[2] Part I, Hyne and Tiley, *J.*, 1961, 2348.

[3] (*a*) Lovejoy, Colwell, Eggers, and Halsey, *J. Chem. Phys.*, 1962, **36**, 612; (*b*) Colwell and Halsey, *J. Phys. Chem.*, 1962, **66**, 2179, 2182.

[4] Gerding and Gerdings-Kroon, *Rec. Trav. chim.*, 1937, **56**, 800.

[5] Westrik and MacGillavry, *Acta Cryst.*, 1954, **7**, 764.

[6] Bevington and Pegler, *Chem. Soc. Special Publ.*, 1958, No. 12, 283.

[7] (*a*) U.S.P. 2,868,624/1959; (*b*) U.S.P. 2,986,450/1961; (*c*) G.P. 1,085,862/1960; (*d*) B.P. 874,344/1961.

EXPERIMENTAL

Liquid sulphur trioxide was prepared by a double distillation from oleum after addition of potassium permanganate to remove sulphur dioxide. No further purification was used except for the vapour-pressure measurements.

Equilibrium between Solid Polymer and Vapour.—The apparatus was similar to that described previously,[2] involving a glass high-vacuum system and a helical pressure gauge, with no oxidisable material present. Solid polymer was formed in a bulb connected to the gauge, by first condensing liquid, freezing at 0°, and rewarming to 20°, and then removing by distillation all the remaining liquid and some of the solid. The bulb finally contained about 2 g. of needle-like crystals, and the bulb and gauge were sealed from the vacuum line and immersed in a thermostat-bath. Equilibrium vapour pressures (Table 1) were measured, as previously,[2] and fitted the following equation, with a mean deviation of $\pm 0{\cdot}5\%$, $\log_{10} p$ (mm.) $= 12{\cdot}1831 - 2923{\cdot}7/T$ (°K).

TABLE 1.

Equilibrium vapour pressures of solid polymer.

Temp. (°c)	0·0°	10·0°	15·0°	19·5°	22·9°	25·0°	27·0°
p (mm.)	30·6	72·1	107·3	156	203	240	279

The calculated heat of sublimation is 13·37 kcal. (mole SO_3)$^{-1}$ which, combined with the heat of evaporation of the liquid,[2] gives a heat of fusion at 25° of 3·04 kcal. The vapour-pressure curve of the solid intersects that of the liquid at 30·4°, and a temperature around this value is generally claimed as the melting point of the β-polymer. In fact, we have never observed a rapid and complete melting at, or just above, this temperature; some liquid is formed slowly if the needle-like crystals are maintained at 31—32° for several hours, but much longer periods and higher temperatures are required for complete melting of most samples. This supports the idea that the process occurring at this temperature is not a physical melting but a depolymerisation, and the heat values above are the enthalpies of depolymerisation.

The equilibrium vapour pressure of the above sample was not established instantaneously. On lowering the temperature of the solid by 5—10°, 4—6 hr. were necessary for equilibrium to be reached and, on raising the temperature, up to 48 hr. were required. However, in a separate experiment with similar apparatus, except that the glass bulb had not been heated during evacuation, a small quantity (about 0·3 g.) of needle-like crystals was formed at 20° directly from the vapour. The equilibrium vapour-pressure values agreed with the above equation but in this case equilibrium was established rapidly. It is noteworthy that Smits and Moerman[8] observed instantaneous equilibrium with their sample of the β-form, but Colwell and Halsey[3b] report that periods of 30 min. were required for equilibration; our equilibrium values are in reasonable agreement with the results of both of the above groups of workers.

Rate of Growth of Solid Polymer from the Liquid.—Glass tubes (3 mm. bore × 20 cm.) were cleaned with chromic acid, washed, dried at 250°, and stored over phosphorus pentoxide until use. The tubes were partially filled with liquid sulphur trioxide and sealed, and the bottom tip of the tube was placed in a bath at −78° for a few seconds, thereby forming a macro-nucleus of solid. On immersion of the tube in a thermostat-bath at 20—25°, crystallisation of polymer proceeded steadily up the tube. The solid–liquid interface remained sharp in most cases, and the rate of growth was readily followed with a vernier microscope and found to be linear with time (Table 2). The period of observation (2—6 hr.) was generally limited by the fact that other solid nuclei were formed on the walls of the tube and eventually amalgamated with the original moving boundary. The presence of other nuclei had no apparent effect on the rate of growth of the original nucleus before amalgamation.

TABLE 2.

Rate of growth of solid polymer from liquid sulphur trioxide.

Temp. (°c)	20°	22·5°	25°	25°	25°	25°	20°	20°	20°	20°
Additive	None	None	None	H_2SO_4	H_2SO_4	H_2SO_4	CCl_4	CCl_4	CCl_4	CCl_4
Wt.-%	—	—	—	0·04	0·28	0·82	0·08	0·23	0·29	0·43
Rate (cm./hr.)	2·39	2·22	1·25	1·05	0·88	0·65	2·38	1·50	1·32	0·36

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[8] Smits and Moerman, *Z. phys. Chem.*, 1937, **35**, 60.

The rate of growth of polymer from samples of liquid sulphur trioxide, without additives, was reproducible within ±3%, and above 25°, the rate decreased sharply, whilst below 20°, rapid multiple nucleation tended to occur.

Additions of sulphuric acid resulted in a solid–liquid interface of a more diffuse nature and markedly accelerated multiple nucleation. Measurements were therefore more difficult, but nevertheless, several clear-cut observations showed that the presence of sulphuric acid reduced the rate of growth of the original polymer nucleus. However, the excessive nucleation which occurred resulted in complete polymerisation of the sample in a much shorter time.

Carbon tetrachloride [9a] additions reduced the rate of growth proportionately to the amount added; and, with quantities over 0·5%, no observable growth occurred, the solid formed by cooling generally remelting at 20°. The experiment was performed of adding the equivalent of about 0·5% carbon tetrachloride to a tube in which some polymer had been grown at 20° from pure sulphur trioxide. The tube was resealed and maintained at 20°, but no further growth occurred.

Experiments were attempted with a sample of liquid sulphur trioxide which had been stabilised by addition of 0·3% of antimony pentachloride,[9b] this sample being heated at 70—80°. It was impossible with this sample to form a nucleus which would grow at 20°. It required additions of sulphuric acid of over 1% (~0·2% of water) to produce an observable phenomenon within the normal period of observation, and the result was always a multiple nucleation along the tube, giving a rapid complete polymerisation.

Some qualitative observations were made of the influence of low temperatures on the overall rate of polymerisation. Samples of liquid sulphur trioxide, from the same original bulk sample, were sealed in glass tubes of 5-mm. bore and given the following treatments, each sample being duplicated. Sample A was cooled from 25° to 0° and rewarmed to 25°, the whole cycle occupying 6 hr. with approximately uniform rate of change in temperature. Sample B was cooled rapidly and maintained at −30° for 6 hr., then rewarmed rapidly to 25°. Sample C was treated as for sample B except that the lower temperature was −78°.

All tubes contained some unmelted polymer. Whereas the amounts in B and C were approximately the same, the amount of solid in sample A was appreciably greater, indicating that temperatures below 0° do not accelerate polymerisation as is sometimes claimed.

Viscosity of Liquid Sulphur Trioxide containing Added Sulphuric Acid.—Viscosity measurements were made by using an Oswald viscometer, calibrated with water, and modified in such a way that the liquid was exposed only to an atmosphere of dry nitrogen. Glass stopcocks greased with silicon grease controlled the nitrogen flow and, whilst the liquid was never in contact with the grease, the diffusion of vapour caused a very slow attack on the grease over a period of days.

The procedure involved filling the viscometer with liquid sulphur trioxide and adding known volumes of 100% sulphuric acid from a calibrated micropipette. Efficient mixing required 5—10 min. before a flow measurement was recorded, and it was then found that there was no indication of the increase of viscosity with time which is characteristic of many liquid-phase polymerisations. The viscosity values were calculated from the density figure for pure sulphur trioxide; [2] the estimated maximum error caused by change in density is ±0·5%. Whilst the main series of measurements were performed at 30° (Table 3), flow times at 25° were recorded for one sample and were constant for several hours and then became irregular; a close inspection of the viscometer revealed a nucleus of solid polymer in the capillary.

TABLE 3.

Viscosity of sulphur trioxide at 30°.

H_2SO_4 added (wt.-%)	0	0·55	0·95	2·09	3·74
H_2O equivalent (wt.-%)	0	0·086	0·173	0·377	0·669
Viscosity (cp.)	1·54	1·71	1·84	2·18	2·81

The viscosity of rigorously purified sulphur trioxide [2] is 1·524 cp. at 30°. If this value is taken as reference (our original sample would contain traces of moisture), the above results fit the equation, η (cp.) = 1·524 + 1·84 w, where w is % H_2O. On this basis, the water content of our original sample is estimated as 0·01% before any additions were made.

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[9] (*a*) B.P. 780,627/1957; (*b*) B.P. 669,214/1952.

Whilst it is assumed that the sulphuric acid added is converted, first, into disulphuric acid, $H_2S_2O_7$, it is not immediately apparent whether these relatively large increases in viscosity are caused by the further conversion into larger polysulphuric acid molecules; disulphuric acid itself has a high viscosity[10] (about 45 cp.) and no theory is available for reliable prediction of the viscosities of liquid mixtures.[11] Measurements were therefore made of viscosities of dilute solutions of ethylene glycol in two organic solvents, in order to assess the effect of 1 mole % of a hydrogen-bonded viscous solute of low molecular weight on the viscosity of a mobile solvent. The comparison is shown in Table 4, together with the recorded data[12] on the viscosity of aqueous glycerol.

It can be seen that the percentage increase in viscosity in the sulphur trioxide case is ten times greater than those for the two systems with similar solute–solvent viscosity ratios, and that the increase is significantly greater than that for the glycerol–water system which has an exceptionally high viscosity ratio. This anomaly would seem too great to be explained on the basis of differences in molecular interactions, and it is tentatively concluded that the viscosity of sulphur trioxide containing small amounts of water is greater than would be expected if disulphuric acid were the only solute species.

TABLE 4.

Increase in viscosity of solvent caused by 1 mole % of viscous solute.

Solvent (A)	Solute (B)	η_A (cp.)	η_B (cp.)	$\eta_{soln.}$ (cp.)	$\Delta\eta_A$ (%)	η_B/η_A
SO_3	$H_2S_2O_7$	1·524	45	1·943	27	30
$C_2H_4Cl_2$	$(CH_2{\cdot}OH)_2$	0·792	20	0·809	2·2	25
$CH_3{\cdot}OH$	,,	0·597	20	0·614	2·8	33
H_2O	Glycerol	1·005	1500	1·143	14	1500

Viscosity measurements were also made on sulphur trioxide containing polymerisation inhibitors (carbon tetrachloride and antimony pentachloride, as above), to which sulphuric acid was added. With two slight exceptions, the results were the same as those obtained in the absence of inhibitors. The exceptions were, first, that the presence of 1% of carbon tetrachloride resulted in slightly larger increases in viscosity on addition of sulphuric acid, and, secondly, that the viscosity of sulphur trioxide containing antimony pentachloride was slightly lower than that accepted for the rigorously purified sample. These differences were small, but outside the expected experimental error, and further studies are being made. However, the main experimental finding is not in doubt, namely, that the presence of these two polymerisation inhibitors does not prevent the increase in viscosity which occurs on addition of sulphuric acid at 30°.

The influence of ultraviolet radiation was briefly investigated for a rigorously purified sample of sulphur trioxide. The sample was exposed for 2 hr. at 20° to an ultraviolet source and the viscosity at 20° was remeasured. No change in viscosity was observed, though a separate experiment showed that the glass of the viscometer gave 50% transmission of 3000 Å radiation. It may be concluded that radiation of this wavelength effects no change in the structure of liquid sulphur trioxide.

DISCUSSION

Formation of Polysulphuric Acids.—The hypothesis that polymerisation of sulphur trioxide involves the formation of polysulphuric acids in the liquid phase, followed by nucleation of a solid phase, implies the following processes:

(*a*) Successive liquid-phase equilibria of the type,

$$H_2S_{n-1}O_{3n-2} + SO_3 \rightleftharpoons H_2S_nO_{3n+1}$$

(*b*) Solid nucleation, $xH_2S_nO_{3n+1}$ (liquid) $= xH_2S_nO_{3n+1}$ (solid)

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[10] Timmermans, " The Physicochemical Constants of Binary Systems in Concentrated Solutions," Interscience Publ., Inc., New York, 1960, Vol. IV, p. 540.

[11] McLaughlin, *Quart. Rev.*, 1960, **14**, 252.

[12] Hodgman, " Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland, 1962, p. 2273.

The cryoscopic measurements of Gillespie [13] for dilute oleums, and our viscosity measurements, indicate indirectly the existence of polysulphuric acids higher than $H_2S_2O_7$. Millen [14] claimed that certain lines in the Raman spectra of concentrated oleums were indicative of $H_2S_3O_{10}$ and $H_2S_4O_{13}$, but these lines are not apparent in the Raman spectra reported by Walrafen and Young.[15] Whilst further experimental evidence is necessary to establish clearly the amounts of higher acids under different conditions, it would be expected that the ratio of concentrations of polyacids to diacid would increase with increase of sulphur trioxide : sulphuric acid ratio, and that the solubility of the polyacids would decrease with increase of molecular weight. Lower temperatures would favour both the formation and precipitation of polyacids. Our viscosity measurements suggest that, above 25°, the formation of polyacids in solution is relatively rapid, implying that the rate of deposition of solid polyacids is controlled by the rate of nucleation from very dilute solution.

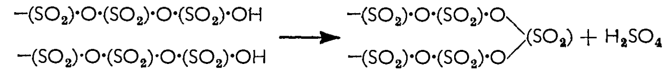
It has been shown [13,16] that ionisation occurs in oleums to an appreciable extent, but the dielectric constant of sulphur trioxide at 18° is only 3·11,[17] and whilst polyacid formation in solution may proceed by an ionic mechanism it seems unlikely that ionisation equilibria will be significant in the composition range close to pure sulphur trioxide. It is noteworthy that the dielectric constant increases rapidly with water content, and measurements of electrical capacitance have been used successfully for monitoring moisture content in liquid sulphur trioxide.[18]

Changes in the Solid Polymer.—Since there is a manifest equilibrium between β-polymer and vapour, there must be a reversible process involving a change in degree of polymerisation of the solid, thus:

$$\mathrm{H_2S}_n\mathrm{O}_{3n+1}\ \text{(solid)} + \mathrm{SO_3} \rightleftharpoons \mathrm{H_2S}_{n+1}\mathrm{O}_{3n+4}\ \text{(solid)}$$

The growth of polymer needles shows that this process takes place from the liquid with a decrease in free energy below 30·4°, in accordance with the relative vapour pressures. The temperature of 30·4° is analogous to the ceiling temperature for polymerisation discussed by Dainton and Ivin,[19] and this ceiling temperature will be lower for a liquid phase containing less sulphur trioxide, as in the oleums,[3b] though in considering solid deposition from oleums it must be remembered that the freezing point of disulphuric acid itself is around 30°.

The slowness of " melting " of the polymer at temperatures just above 30° suggests that depolymerisation occurs at these temperatures by step-wise degradation of chains rather than by general chain disintegration. However, some cross-linking of adjacent chain ends may be possible in the solid state by a condensation process, thus:



$$\begin{array}{l}-\mathrm{(SO_2)\cdot O\cdot (SO_2)\cdot O\cdot (SO_2)\cdot OH}\\ -\mathrm{(SO_2)\cdot O\cdot (SO_2)\cdot O\cdot (SO_2)\cdot OH}\end{array} \longrightarrow \left.\begin{array}{l}-\mathrm{(SO_2)\cdot O\cdot (SO_2)\cdot O}\\ -\mathrm{(SO_2)\cdot O\cdot (SO_2)\cdot O}\end{array}\right\rangle \mathrm{(SO_2)} + \mathrm{H_2SO_4}$$

Such cross-linking would not affect the general crystal structure but would produce molecules which could only depolymerise by chain-rupture and would thus be slower in melting and in equilibrating with vapour. This may well correspond to the so-called high-melting (α) polymer, the *X*-ray pattern of which is not clearly distinguishable from that of the β-form, and which is so slow in establishing solid–vapour equilibrium that the equilibrium vapour pressures are uncertain.[3b] It seems likely that samples of solid polymer can be formed with varying degrees of cross-linking of chain ends and, whilst such samples differ in ease of melting and in rate of establishment of vapour equilibrium, they are all

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[13] Gillespie, *J.*, 1950, 2518.

[14] Millen, *J.*, 1950, 2589.

[15] Walrafen and Young, *Trans. Faraday Soc.*, 1960, **56**, 1419.

[16] Arotsky and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1426.

[17] See ref. 12, p. 2613.

[18] T. F. Eden, personal communication (Research Department, Stanton and Staveley Limited).

[19] Dainton and Ivin, *Quart. Rev.*, 1958, **12**, 61.

essentially the same crystalline phase. This explains the universally accepted fact that solid polymer is never formed above 30°, despite the claims of Smits and his co-workers [8,20] (since disputed [3b]) that the α-form is thermodynamically stable at temperatures up to 60°.

Cross-linking in this way provides for a termination of the increase in degree of polymerisation of the solid. Berthoud [21] and others have observed that, with sulphur trioxide of very low water content, some solid polymer may be formed on the walls of the containing glass vessel, but that the solid does not grow in amount though solid and liquid may be in contact at 20—25° for a period of months. This solid must have a high degree of cross-linking so that further polymerisation cannot occur without further nucleation, and it is generally observed that such solid is difficult to melt. It is also observed,[6] with the crystalline needles of polymer, that initial melting at 32—35° often leaves an amorphous gelatinous residue which is very slow in melting; these residues would consist of chains with cross-linked ends.

Unpolymerised sulphur trioxide freezes at 16·8° to give the trimeric γ-form, which has a higher vapour pressure, and is therefore metastable with respect to the β-polymer. If a nucleus of polymer is present when complete solidification occurs, then polymerisation in the solid state will continue by diffusion of sulphur trioxide molecules through the vapour or solid phase. Whichever mechanism operates, the rate of solid interconversion is likely to decrease at low temperatures and the maximum rate of polymerisation will be around the freezing point of the γ-form. It is the coincidence of this temperature with normal ambient temperatures which creates the difficulty of handling liquid sulphur trioxide without polymerisation.

Inhibition of Polymerisation.—Inhibition of the nucleation and growth of solid polyacids must involve interaction of the additive with the end hydroxyl groups. With certain inorganic additives, heating of the sulphur trioxide with additive is necessary for effective inhibition, and it has been suggested [6] that the traces of sulphuric acids present are converted into complex molecules to which further sulphur trioxide cannot be bound; *e.g.*, boron compounds form complexes in oleums possibly of the form $H[B(HSO_4)_4]$ [22] or $B(HS_2O_7)_3$.[16] In view of the diversity of organic compounds which can inhibit polymerisation without heat treatment, it is unlikely that a chemical interaction of this kind operates in all cases.

The sulphur trioxide molecule is non-polar whereas organic inhibitors are either polar [7] or are rapidly oxidised by sulphur trioxide to polar molecules; *e.g.*, carbon tetrachloride [9a] is oxidised to carbonyl and sulphuryl chloride. The inorganic complexes suggested above will also be polar. It may be assumed that there will be a physical attachment of inhibitor molecules to the end hydroxyl groups of the polysulphuric acids due to hydrogen-bonding. This could have little influence on the equilibrium formation of polyacids in solution since the effect will be independent of size of the polyacid, but it may well inhibit solid nucleation. Additionally the adsorption of inhibitor molecules on the ends of solid polymer chains would reduce the rate of growth of solid nuclei. Such adsorption would also inhibit cross-linking of the chain ends and it is commonly observed that, if polymer forms in " stabilised " liquid sulphur trioxide, the solid is readily melted.

The influence of sulphuric acid on the rate of growth of solid nuclei may be explained similarly since mono- and di-sulphuric acid are capable of hydrogen bonding to the end-groups of polyacid chains. However, added sulphuric acid increases the concentration of polyacids present, which increases the rate of nucleation and gives an overall increase in the rate of polymerisation, polycrystalline polymer being formed rather than the oriented needles of asbestos-like polymer which grow from sulphur trioxide of low water content.

Nucleation and growth of polymer needles from the vapour phase is a common observation when the glass surfaces have not been thoroughly baked under a vacuum, which

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[20] Smits and Schoenmaker, *J.*, 1926, 1108.
[21] Berthoud, *Helv. Chim. Acta*, 1922, **5**, 513.
[22] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

shows that sulphur trioxide vapour reacts with chemisorbed water to form polyacid nuclei which subsequently grow quite rapidly. This surface nucleation is also apparent with the liquid of low water content, where polymerisation, if it occurs, often results in a firm attachment of polymer needles to the glass surface. Westrik and MacGillavry [23] observed a " conjunction " of the crystal to the wall of the capillary tube in their *X*-ray studies of solid sulphur trioxide. Polar molecules would be expected to inhibit surface nucleation by preferential adsorption on the hydroxyl groups in the glass surface, thereby giving an increased energy barrier for the formation of polymer nuclei.

In attributing inhibitor action to the existence of hydrogen-bonding energies of the order of 2—6 kcal. mole^{-1}, it must be emphasised that the enthalpy and free energy of polymerisation from the liquid are equally low, 3·04 and 0·06 kcal. mole^{-1}, respectively, at 25°. It also follows that complete inhibition of polymerisation is dependent on the relative molar concentrations of additive and water present. Small amounts ($<1\%$) of additive cannot prevent polymerisation if the sulphur trioxide absorbs much more than 0·1—0·2% of water.[6]

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[23] Westrik and MacGillavry, *Rec. Trav. chim.*, 1941, **60**, 794.