Studies of the Reactions of Anhydrosulphites of α-Hydroxycarboxylic Acids. Part VIII.[1] Polymerisation of Anhydrosulphites of α-Hydroxycycloalkanecarboxylic Acids

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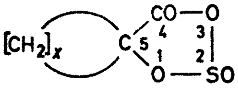
The anhydrosulphites of α-hydroxy-cyclobutane-, -cyclopentane-, -cyclohexane-, and -cycloheptane-carboxylic acids have been prepared in order to examine the effect of ring strain on polymerisation rates. Of this series only the spirocyclobutane derivative was not obtainable substantially pure. This compound is also abnormal in that the major product of thermal decomposition in non-hydroxylic solvents is glycollide rather than the expected poly-α-ester. The less strained spirocyclopentane and spirocyclohexane derivatives eliminate sulphur dioxide smoothly by a first-order process in the well-established manner of the open-chain analogues. The effect of increased ring strain in α-hydroxycycloheptanecarboxylic acid is reflected in its greater rate of thermal decomposition. The relative magnitudes of the kinetic parameters are discussed and the tendency of the anhydrosulphites to undergo direct bimolecular reaction with attacking hydroxylic species assessed. Although the spiro-cyclopentane, -cyclohexane, and -cycloheptane derivatives yield the appropriate poly-α-esters, these, in contrast to the symmetrical open-chain analogues, are non crystalline.

In previous Parts we have discussed various aspects of the stability of α-hydroxycarboxylic acid anhydrosulphites, with particular reference to their ability to undergo ring-opening polymerisations, in terms of both steric and electronic properties of the C(5) substituents. An additional feature, that of imposed ring strain, can in principle be deduced by studying the polymerisation of the anhydrosulphites of α-hydroxycycloalkanecarboxylic acids [cycloalkanespiro-5′-(1,3,2-dioxathiolan-4-one 2-oxides) (I)]. The only example of this type of spiro-compound previously studied is cyclohexanespiro-5′-(1,3,2-dioxathiolan-4-one 2-oxide) (I; $x = 5$) which has been shown to decompose thermally to form non-crystalline poly-α-esters.[2]

In the few cases of ring-opening polymerisation of other types of spiro-compound that are reported the effect of the conjoined cycloalkane ring varies considerably. The best documented examples are the *N*-carboxy-α-amino-acid anhydrides,[3] oxetans,[4] and propiolactones.[5] We now report the synthesis and polymerisation of the series (I) where x = 3, 4, 5, and 6, hereinafter referred to as C′butAS, C′pentAS, C′hexAS, and C′heptAS.



(I)

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[1] Part VII, G. P. Blackburn and B. J. Tighe, *J. Chem. Soc.* (*B*), 1971, 1384.

[2] G. P. Blackbourn and B. J. Tighe, *J. Polymer Sci.*, *Part A*-1, 1972, **10**, 295.

[3] M. Frankel and M. D. Bachi, *Biopolymers*, 1965, **3**, 15.

[4] T. W. Campbell and V. Foldi, *J. Org. Chem.*, 1961, **26**, 4654; S. Penczek and A. A. Vansheidt, *J. Polymer Sic. U.S.S.R.*, 1965, **4**, 927.

[5] H. K. Hall, J. B. Dence, and D. R. Wilson, *Macromolecules*, 1969, **2**, 475.

EXPERIMENTAL

α-Hydroxy-acids.—1-Hydroxycyclohexanecarboxylic acid and 1-hydroxycyclopentanecarboxylic acid were commercial (Newton–Maine Ltd.). 1-Hydroxycycloheptanecarboxylic acid (yield 40%) was prepared from cycloheptanone *via* the bisulphite compound and cyanohydrin by Tchoubar's method.[6] Ring-contraction and oxidation of cyclopentanone to cyclobutanecarboxylic acid[7] and subsequent α-bromination followed by hydrolysis was found to be the best route to 1-hydroxycyclobutanecarboxylic acid (yield 7% on cyclopentanone). All the acids were recrystallised to constant m.p. from benzene–light petroleum the exception (1-hydroxycyclobutanecarboxylic acid) being obtained as a viscous colourless oil contaminated with the derivative glycollide.

Anhydrosulphites.—Synthesis, purification, and characterisation were described.[8] C'pentAS, C'hexAS, and C'heptAS were prepared by the direct action of thionyl chloride on the parent hydroxy-acid, but C'butAS gave less glycollide impurity when prepared *via* the copper(II) salt of the acid. The methods and degree of purification were varied throughout the series to suit the characteristics of each individual member. Thus C'pentAS and C'hexAS were subjected to the previously described purification procedures of flash distillation, treatment with silver oxide, fractional distillation, and prepolymerisation;[8] but because of the tendency of C'heptAS to decompose into cycloheptanone at high temperatures, the product was vacuum-sublimed rather than distilled following silver oxide treatment. C'butAS was extremely reactive and therefore could only be subjected to silver oxide treatment. As a result the material was contaminated with its derivative glycollide.[9] The effectiveness of these methods is reflected in the purity of the product, here expressed in terms of α-chloro-acid chloride impurity per mole of product: C'butAS ($1{\cdot}6 \times 10^{-1}$); C'pentAS ($1{\cdot}4 \times 10^{-3}$); C'hexAS ($1{\cdot}0 \times 10^{-3}$); and C'heptAS ($5{\cdot}0 \times 10^{-2}$).

Kinetic Measurements.—These were carried out by constant-volume gas evolution and gravimetric and i.r. techniques as described previously.[2,10] Solutions for kinetic study were manipulated in a dry-box.

Solvents.—These were dried by prescribed methods[10] and distilled just before use, the middle fraction only being used.

Physical Measurements. Differential thermal analysis traces (d.t.a.), and i.r. and mass spectra were obtained with the instruments described previously.[10] Molecular weights ($\bar{M}_n$) were determined by a hot micro-titration technique[10] and vapour-pressure osmometry.[11,12]

RESULTS

Kinetic Studies of Decomposition.—Rates of decomposition were measured by following gas evolution and compared with the rate of polymer formation by the use of i.r.[2] and gravimetric[9] techniques. Velocity coefficients were measured in nitrobenzene over a range of temperature and found to be of the first order, with no indication of sulphur dioxide catalysis or inhibition. Rates of decomposition in nitrobenzene at 90 °C are shown in Figure 1; Figure 2 compares the Arrhenius plot for each anhydrosulphite in the same solvent. Velocity constants which are described by the rate curves in Figure 1 together with kinetic parameters derived from Figure 2 are summarised in Table 1.

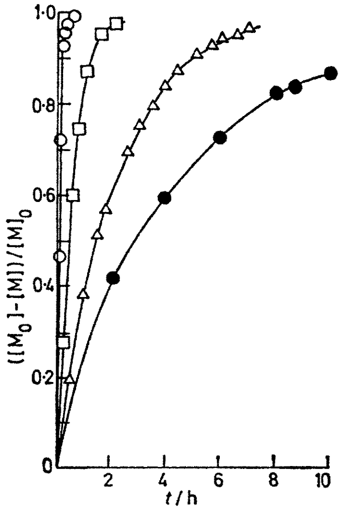

FIGURE 1 Decomposition of anhydrosulphites of α-hydroxycycloalkanecarboxylic acids in nitrobenzene at 90 °C; ○, C'butAS; □, C'heptAS; △, C'pentAS; ●, C'hexAS

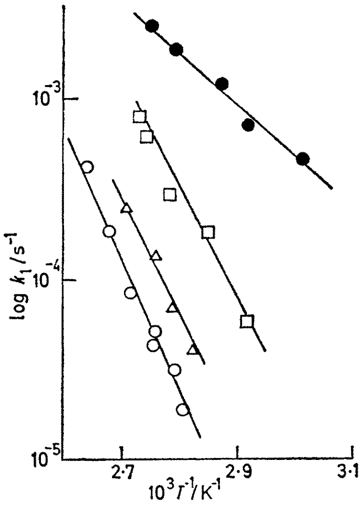

FIGURE 2 Effect of temperature of the rate of decomposition of anhydrosulphites of α-hydroxycycloalkanecarboxylic acids in nitrobenzene; ●, C'butAS; □, C'heptAS; △, C'pentAS; ○, C'hexAS

In all cases the rate of product (typically polymer) formation was found to be identical with the rate of monomer decomposition, *i.e.*, equation (1).

$$d[SO_2]/dt = -d[M]/dt = d[P]/dt = k_1[M] \qquad (1)$$

The change of rate with solvent polarity was studied, the effect being similar to that observed with di-n-alkyl substituted anhydrosulphites.[1,2,12] The observed rates of

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[6] B. Tchoubar, *Bull. Soc. chim. France*, 1947, 680; 1949, 160.

[7] G. B. Payne and C. W. Smith, *J. Org. Chem.*, 1957, **22**, 1680.

[8] G. P. Blackbourn and B. J. Tighe, *J. Chem. Soc.* (*C*), 1971, 257.

[9] J. Boeskin, *Rec. Trav. chim.*, 1937, **56**, 1211.

[10] G. P. Blackbourn and B. J. Tighe, *J. Polymer Sci.*, *Part A*-1, 1970, **8**, 3591.

[11] D. G. H. Ballard and B. J. Tighe, *J. Chem. Soc.*, (*B*) 1967, 976.

[12] D. G. H. Ballard and B. J. Tighe, *J. Chem. Soc.* (*B*), 1967, 702.

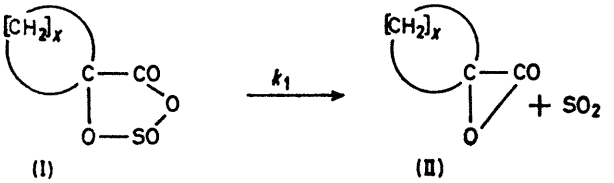
decomposition of C'pentAS, C'hexAS, and C'heptAS in decalin at 90 °C are shown in Table 1.

TABLE 1

The decomposition of C'butAS, C'pentAS, C'hexAS, and C'heptAS in various solvents at 90 °C. Values of frequency factor and energy and entropy of activation are derived from the first-order rate constants in nitrobenzene, $[AS]_0 = 0{\cdot}4\text{M}$

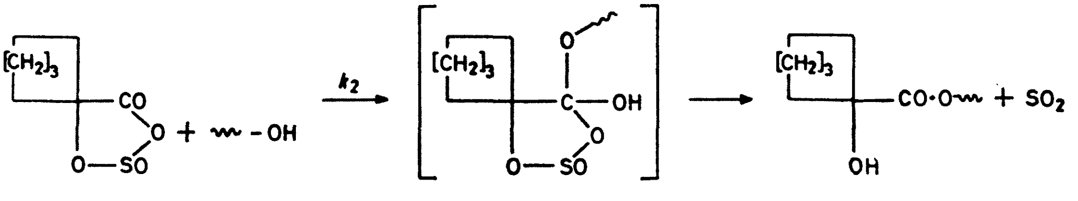
	C'butAS	C'pentAS	C'hexAS	C'heptAS
Nitrobenzene				
$10^5k_1/s^{-1}$	240·0	11·8	5·6	64·0
E/kcal mol^{-1}	17 ± 2·5	28·5	32·6	28·5
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	−26	0	+9·5	+3·2
A/s^{-1}	$4{\cdot}5 \times 10^7$	$1{\cdot}9 \times 10^{13}$	$3{\cdot}4 \times 10^{14}$	$1{\cdot}0 \times 10^{14}$
Decalin				
$10^5k_1/s^{-1}$		1·7	0·94	6·9
Benzyl alcohol				
$10^5k_b/s^{-1}$	1100	1·65	1·22	5·7
k_b/k_n	5·2	0·1	0·2	0·1

The kinetic behaviour of C'pentAS, C'hexAS, and C'heptAS in these reactions is typical of the established unimolecular thermal scission process [1] which results in the synchronous extrusion of sulphur dioxide and formation of a highly reactive intermediate (II) formally depicted as an α-lactone [equation (2)]. Further evidence for this intermediate is found in mass spectra of anhydrosulphites.[2,8,13] A similar pattern was displayed by all of the spiran series, in that the primary electron-induced fragment consisted of of a strong peak corresponding in mass number to the α-lactone.



(2)

In non-hydroxylic solvents the isolable products of anhydrosulphite decomposition are normally [10,12] sulphur dioxide and poly-α-ester although at high temperatures [1,10] or with highly polar C(5) substituents [14] a competing fragmentation to ketone, carbon monoxide, and sulphur dioxide is observed. At temperatures between 60 and 100 °C C'pentAS, C'hexAS, and C'heptAS decomposed smoothly in non-hydroxylic solvents to yield polymer. Under the same conditions however C'butAS produced mainly (*ca.* 70%) glycollide together with small amounts of oligomer. The products showed characteristic i.r. carbonyl absorption frequencies ($\nu_{C=O}$) at 1730 (glycollide) and 1765 cm^{-1} (polymer). With the exception of C'butAS therefore, the sequence of reactions leading to polymer formation is apparently in no way different from that established for dialkyl-substituted anhydrosulphites.[1,10,12]



(4)

Rates of anhydrosulphite decomposition were studied in hydroxylic solvents (*e.g.*, benzyl alcohol) because reaction with an alcoholic function has been shown to reflect the feasibility of bimolecular hydroxy-initiated anhydrosulphite polymerisation. With the exception of C'butAS the observed rate was considerably less than that in nitrobenzene, as would be predicted on grounds of reduced solvent polarity. C'butAS, however, decomposed more rapidly in benzyl alcohol indicating that direct bimolecular hydroxy-attack on the ring makes a significant contribution. The major product of these reactions was benzyl 1-hydroxycyclobutanecarboxylate. The overall first-order rate constants obtained in benzyl alcohol at 90 °C for the decomposition of the spiran series, together with the rate observed in nitrobenzene under the same conditions (k_b/k_n), are included in Table 1.

For the specific decomposition of C'butAS in benzyl alcohol the observed overall pseudo-first-order rate constant (k_b) can be resolved into first- and second-order components as in equation (3). Other members of the spiran series,

$$k_b = k_1 + k_2[\text{Ph·CH}_2\text{OH}] \qquad (3)$$

however, simplify to $k_b = k_1$ since the second-order components are negligible. The bimolecular rate constant (k_2) was estimated by substitution of the value obtained in nitrobenzene at the same temperature for k_1 in equation (3). The observed rate constants (k_b) together with the derived rate constants k_2 are in Table 2. Manipulation of k_2 data yields values of energy and entropy of activation (E, 14·9 kcal mol^{-1}; $\Delta S^{\ddagger}$, −35 cal mol^{-1} K^{-1}) together with frequency factor (A, 1×10^6 l mol^{-1} s^{-1}) which are typical of a bimolecular process involving a transition state more polar than the reactants. Decomposition rates in non-hydroxylic solvents such as nitrobenzene suggest that the unimolecular reaction contributes significantly in addition to the bimolecular decomposition route. A similar competition of reaction modes is to be expected in the propagation reaction during polymerisation. Thus propagation by interaction between the terminal hydroxy-group of a polymer chain and the α-lactone (II) occurs more readily than does direct bimolecular reaction with the anhydrosulphite ring [equation (4)]. Thus the overall

TABLE 2

First-order overall rate constants (k_b) and second-order rate constants (k_2) for the decomposition of C'butAS in benzyl alcohol at various temperatures

$[\text{C'butAS}]_0 = 0{\cdot}5$ mol l^{-1} $[\text{Ph·CH}_2\text{OH}]_0 = 8{\cdot}75$ mol l^{-1}

T/°C	$10^4k_b/s^{-1}$	10^5k_2/l mol^{-1} s^{-1}
49·4	9·3	7·4
59·5	19·3	16·6
71·0	38·2	32·8

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[13] B. W. Evans, D. J. Fenn, and B. J. Tighe, *J. Chem. Soc.* (*B*), 1970, 1049.

[14] A. J. Crowe and B. J. Tighe, *Chem. and Ind.*, 1969, 170.

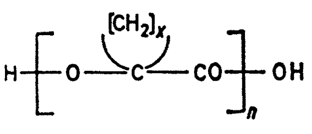
decomposition can be represented by equation (5) where [C'butAS] and [SO_2] refer to the molar concentrations of

$$-d[\text{C'butAS}]/dt = d[SO_2]/dt = (k_1 + k_2[\text{ROH}])[\text{C'butAS}] \quad (5)$$

C'butAS and sulphur dioxide and [ROH] to the total concentration of hydroxy-function. In this case, however, the overall decomposition rate does not coincide with the rate of polymer formation since the glycollide is formed as a competing product in thermal polymerisation.

Investigations of ketone formation for C'hexAS has shown this to be due to a competing first-order fragmentation of high activation energy, but even at temperatures in the region of 180 °C only 5% of ketone was formed.[2] C'heptAS exhibited similar kinetic behaviour but with a more marked tendency to ketone formation and even when present as a 20% contaminant cycloheptanone did not significantly interfere with polymerisation rate or polymer formation.

Polymer Characterisation.—With the exception of poly-C'butAS which was only obtained as oligomer, all polymers precipitated from reaction solution on cooling, and were white powders when dry. N.m.r. and i.r. spectra together with elemental analysis showed the essential structures of the polymers to be given by (III). The polymers were



$$H{-}\left[O{-}C[(CH_2)_x]{-}CO\right]_n{-}OH$$

(III)

essentially amorphous in that no sharp line was obtained in the *X*-ray powder photographs and no crystalline m.p. (T_m) was observed by d.t.a. (heating rate 10 K min^{-1}). As a result of non-crystallinity, and in direct contrast with the dialkyl polymers, the spiro-polymers were soluble in chloroform. Molecular weights determined by carboxylic acid end-group titration of v.p.o. reflected the ease of monomer purification as shown in Table 3 which represents polymers under identical conditions of temperature, concentration, solvent, *etc.* The temperature at which degradation set in (T_d), as measured by thermogravimetry (nitrogen, 10 K min^{-1}) was found to decrease with increasing bulk of substituent (see Table 3). The identity of molecular weights determined by the two techniques suggests that each chain contains one carboxy-end group or its chemical equivalent (*e.g.*, COCl).

TABLE 3

Monomer purity (expressed as mol of chlorine containing impurity per mol of anhydrosulphite), molecular weight (M_n), and degradation onset temperature (T_d) of resultant polymers, for the spiran series

	Chlorine content/ mol	M_n	T_d/°C
C'butAS	$1{\cdot}6 \times 10^{-1}$	700	—
C'pentAS	$1{\cdot}4 \times 10^{-3}$	9260	274
C'hexAS	$1{\cdot}0 \times 10^{-3}$	12,240	256
C'heptAS	$5{\cdot}0 \times 10^{-2}$	2500	230

DISCUSSION

It was initially intended to include the spirocyclopropane derivative in this study but as the results indicate, synthesis and isolation of the spirocyclobutane derivative represents the effective limit of applicability of the techniques used. Of the series represented by (I; $x = 3$—6) only C'butAS ($x = 3$) was not isolated in a high state of purity. The two synthetic routes (*via* acid or copper salt) both lead to a product contaminated with a small quantity of the parent acid, together with the derived α-chloro-acid chloride and glycollide. Despite this, for various reasons, samples of different origin gave extremely consistent kinetic results. First, chloride-containing compounds are efficiently removed during purification[8] and do not, in any case, affect the primary decomposition step;[1,10,12] secondly only minimal quantities of acid are present and this species only affects the decomposition of sterically unhindered anhydrosulphites;[15] and thirdly glycollides have been shown to have no effect on the rate of anhydrosulphite decomposition.[12] These points were experimentally confirmed with the present system. With the exception of C'butAS therefore the series was no more difficult to prepare and manipulate than the corresponding dialkyl-substituted anhydrosulphites.

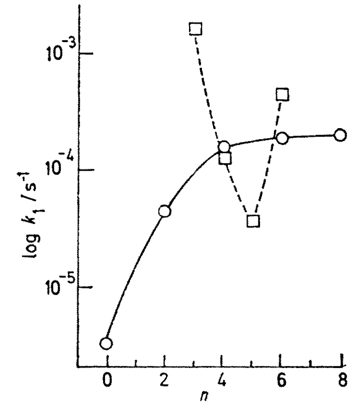


FIGURE 3 Effect of number of substituent carbon atoms on first-order rate constant for the thermal decomposition of anhydrosulphites in nitrobenzene at 90 °C; □, spirocycloalkane substituents; ○, symmetrical di-n-alkyl substituents

Thermal Decomposition.—In attempting to compare the contributions of ring strain and steric and electronic effects to the primary thermal decomposition process it is relevant to compare the symmetrically di-n-alkyl-substituted anhydrosulphites with the spirocycloalkyl series. The comparison is shown in Figure 3 and since electronic effects in the two series are similar, but weak,[16] differences between the two curves are primarily attributable to steric and ring strain effects.

The general form of the kinetic results (Table 1) demonstrates that the effect of the conjoined cycloalkyl ring on thermal decomposition is not substantially different (with the exception of the cyclobutane deriv-

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[15] D. J. Fenn, M. D. Thomas, and B. J. Tighe, *J. Chem. Soc.* (*B*), 1970, 1044.

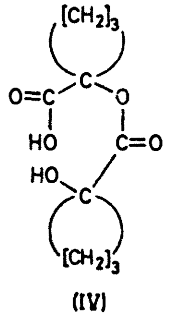
[16] R. C. Hahn, T. F. Corbin, and H. Schechter, *J. Amer. Chem. Soc.*, 1968, **90**, 3404.

ative) from that of simple alkyl substituents; there is similarly no abnormality in the stoicheiometry of the reaction. The behaviour of C'butAS in these respects is directly attributable to the unique geometry of the spirocyclobutane system. In contrast to the general kinetic behaviour the precise value of the rate constants provides an interesting contrast with the simple disubstituted anhydrosulphites (Figure 3). It is apparent that the ring has an effect in addition to the steric interaction attributable to the number of substituent carbon atoms and that (by analogy with alicyclic hydrocarbon chemistry) the predominant effect is one of ring strain.

When considered in isolation the thermal behaviour of C'hexAS was unexpected but the rate data are quite consistent with the rest of the spiran series. It is apparent that the cyclohexane ring imposes little tension on the anhydrosulphite ring during its conformational movements since its effect is similar to that of two methyl substituents (HBAS α-hydroxyisobutyric acid). Further, C'hexAS shows a limited sensitivity to change in solvent polarity in common with HBAS but in contrast to other members of both the dialkyl and cycloalkyl series. Less polarisation of bonds in the α-lactone and transitions leading to it are suggested to explain this phenomenon.

The cyclopentyl and diethyl derivatives are similar to each other both in rate and in their behaviour towards change in dielectric constant of the solvent medium. Pseudorotation of the cyclopentane envelope is able to occur with little imposed tension on the conjoined ring. Cyclobutyl and cycloheptyl derivatives, however, exhibit marked signs of ring strain since their rates are considerably greater than the plateau (maximum) value observed with the dialkyl series (Figure 3). Attempts to relate observed rate constants with the shift of a given absorption in the u.v. or i.r. spectrum of each anhydrosulphite, although qualitatively useful, defied quantitative correlation. The relative stabilities (cyclohexyl $>$ cyclopentyl $>$ cycloheptyl $>$ cyclobutyl) correspond with those recently observed in the thermal decomposition of the cycloalkyl chlorides.[17]

The behaviour of C'butAS is unusual not only because of the magnitude of the rate constant for thermal decomposition but also in the abnormality of the products. This is the only anhydrosulphite of those yet studied that shows any tendency to form the six-membered glycollide ring on decomposition. Two observations are relevant. First, Boeskin [9] has shown that of all the 1-hydroxycycloalkanecarboxylic acids the cyclobutane derivative is unique in having bond angles ideally constrained to favour conversion into glycollide. Dominy and Lawson [18] have observed, secondly, that 5-benzylidene-1,3-dioxolan-2,4-dione forms dibenzylideneglycollide as the predominant product of thermal decomposition whereas this type of product is unknown in the dialkyl-substituted analogues.[19] It seems evident, therefore, that tension imposed at C(5) which is a feature common to both these systems is responsible for this phenomenon. This could manifest itself in either of two ways (neither of which involves the rate-determining first-order sulphur dioxide elimination step). In the first of these, hydroxy-propagation involving the α-lactone proceeds to the dimer stage (IV) which is identical to the intermediate between acid and glycollide and which has a unique tendency to cyclise to glycollide.[9] In the second the Thorpe–Ingold effect is considered to promote the formation of an α-lactone with enhanced dipolar character. In such a species dimerisation to glycollide would be expected to compete favourably with the normal nucleophile-initiated lactone propagation step. Both suggestions are capable of accommodating the observation that C'butAS decomposition in the presence of a large molar excess of benzyl alcohol leads to ester rather than glycollide formation.



(IV)

Hydroxy-initiated Decomposition.—Rate-determining bimolecular propagation, involving an anhydrosulphite, can compete with the thermal elimination reaction when structural features are favourable. At the outset of this work it was thought that restricted freedom of movement in the cycloalkane ring of C'pentAS might just allow direct interaction between an approaching hydroxy-group and the C(4) carbonyl to take place. Results in Table 1 clearly demonstrate that this is not so. C'butAS, however, does decompose by both first- and second-order processes. The conformation of the cyclobutane ring pins back the α-methylene groups and thereby reduces their steric interaction with approaching nucleophiles. Kinetic parameters associated with the second-order process are very similar to those reported for unsubstituted and monosubstituted anhydrosulphites.[15] The fact that relatively high second-order constants are obtained with C'butAS may support the view that the anhydrosulphite ring is puckered, the carbonyl carbon atom being therefore exposed more effectively in the reaction path. Although the second-order constant is high, Table 1 (k_b/k_n ratio) illustrates that the molar hydroxy-group concentration must be appreciable, and at least equal to the anhydrosulphite

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[17] M. Dakabu and J. L. Holmes, *J. Chem. Soc.* (*B*), 1971, 1040; J. M. Sullivan and W. C. Herndon, *J. Phys. Chem.*, 1970, **74**, 995.

[18] B. W. Dominy and R. G. Lawson, *Chem. Comm.*, 1968, 1448.

[19] B. J. Tighe, *Chem. and Ind.*, 1969, 1837.

concentration before competition with thermal decomposition becomes effective. This is why contamination with traces of parent acid has no noticeable effect on decomposition rates in non-hydroxylic solvents.

Other spirans are usually polymerised by ionic routes, the effect of substituent depending on its proximity to the reaction site. Thus the polymerisation of spiro-β-propiolactones, initiated by the pivalate anion,[5] shows a marked decrease in rate as the size of the substituent increases, whilst boron trifluoride-initiated polymerisation of cyclopropane and cyclohexane spiro-oxetans occurs at approximately the same rate. In the former the effect is steric since the equivalent open-chain dialkyl analogues show similar behaviour, but in the latter the reactive centre is too far divorced from the substituent to feel any effect of ring strain or steric bulk.

Spiran derivatives of *N*-carboxy-α-amino-acid anhydrides[3] show enhanced thermal stability compared with open-chain analogues, which is in contrast to anhydrosulphite behaviour. The rate of methoxide anion-initiated polymerisation was found to depend upon the spiro-substituent, both in terms of ring-strain and steric obstruction. An additional feature, the formational difficulty in incorporating a repeat unit into the polymer chain, was required to explain the low rate of polymerisation of the spirocyclopropyl derivative. A similar phenomenon may be responsible for the low yield of polymer (relative to glycollide) observed in the decomposition of C'butAS, but this would not affect the observed rate constant since incorporation of additional units in the polymer chain occurs after the rate-determining step in thermal polymerisation.

Spiro-substituents in linear polymers require that the rings are rigidly attached to the chain like the blades of a fan. As the size of the ring increases so does the degree of puckering, such that the substituent is effectively thicker and more likely to interfere with its near neighbours. Poly-β-esters and poly-β-ethers are improved by this phenomenon, which effectively increases chain stiffness, since their m.p.s are increased considerably, but not at the expense of crystallinity. In contrast, all spiropoly-α-esters are amorphous, because the ability to undergo chain-folding and extent of interchain cohesion are both reduced. As with the dialkyl series, the limitations of anhydrosulphite polymerisation as a general method for preparing spiropoly-α-esters are predominantly controlled by the limitations of synthesis and purification.

We thank the S.R.C. for a studentship (to G. P. B.).

[1/2416 *Received*, 16*th December*, 1971]