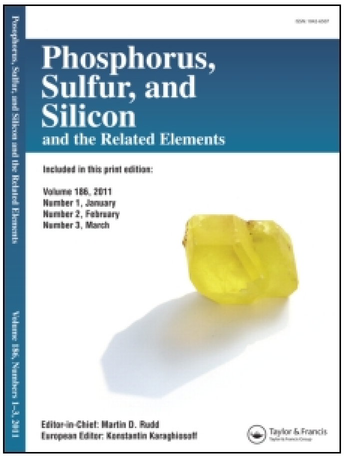

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PRIMARY AND SECONDARY PRODUCTS IN THE LIQUID PHASE SO_3-SULFONATION OF 1-ALKENES

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PRIMARY AND SECONDARY PRODUCTS IN THE LIQUID PHASE SO_3-SULFONATION OF 1-ALKENES

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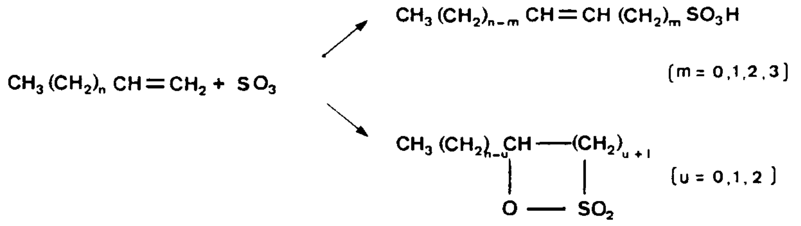
A number of linear (C_5–C_{14}) and branched (C_5–C_8) 1-alkenes were sulfonated by SO_3 free or as its dioxane adduct in liquid phase. The composition of the mixtures just after SO_3-consumption and several days later was investigated. In addition a thermochemical approach, by means of contributed bond energies, and a kinetic study of the evolution of the sulfonation mixtures show, at least with linear substrates, that a β-sultone is the product under kinetic control and slowly isomerizes into more stable alkenesulfonic acids, then γ- and δ-sultones. However alkenesulfonic acids, originating from the same zwitterionic intermediate as β-sultone, are already present in small amount at the very beginning of the sulfonation.

INTRODUCTION

Our previous article dealt with the spectrometric identification of the main products formed in the reaction of free SO_3 or its dioxane adduct on 1-alkenes (from C_5 to C_{14}).[1] It supported the generally accepted scheme,[2–4] recalled below in the case of linear compounds:



It is believed that the time of consumption of SO_3 (at least when used in stoichiometric amount) is very short;[5] however all these sulfonated products do not appear at the same rate and some of them possibly do not issue at first from the reactants through the transition state. In fact and despite some controversy[6] it is usually claimed that the main intermediate occurring during the addition of sulfur trioxide to a 1-alkene is a β-sultone.[5,7,8] Though this type of compound is thought to be rather unstable, one such sultone was isolated and its isomerization was observed.[8]

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The purpose of the present paper is to identify the intermediate rapidly obtained during the first step of the sulfonation and to study its transformation into the final products in order to discuss some mechanistic hypotheses.

The compounds present in the reaction medium just after the consumption of sulfur trioxide at low temperature are called "primary" products, those found after a few days at room temperature or after several hours of heating are called "secondary products".

RESULTS

Sulfonation of Linear 1-Alkenes

Linear 1-alkenes from C_5 to C_{14} were sulfonated by free SO_3 or its dioxane adduct. Typical chromatograms of primary and secondary mixtures resulting from the sulfonation of 1-hexene are shown on Figure 1. The components of these mixtures were identified and their structure evidenced by NMR[1,9,10] and mass spectrometry.[1,9] The following features can be pointed out: a β-sultone (analysed as the corresponding methyl 2-methoxyalkanesulfonate) is observed among the primary products but not among the secondary ones; the ratios of both alkenesulfonic acids and larger ring sultones are much higher in secondary mixtures than in primary ones. Therefore β-sultone isomerizes into alkenesulfonic acids, γ- and δ-sultones. Moreover the ratios of primary or secondary products strongly differ according to the sulfonating agent: it can be seen on Figure 1 (and in Table I) that SO_3-dioxane gives much less primary as well as secondary γ- and δ-sultones and about half less primary alkenesulfonic acids than does free SO_3.

Alkenesulfonic acids appear as complex mixtures including double bond position isomers as well as (E)- and (Z)-isomers. At least four double bond position isomers can be detected from the sulfonation of long chain 1-alkenes followed by degradative oxidation,[1,8,11,12] 2-alkenesulfonic acid always being the major one (ca 80%). Again free SO_3 and SO_3–dioxane give different ratios of secondary alkenesulfonic acids as shown in Table II in the case of 1-tridecene. Therefore using SO_3–dioxane as a sulfonating agent increases the selectivity of the reaction whether compounds with different functionalities (sulfonic acids and sultones) or isomers are concerned; in fact, SO_3–dioxane gives a larger amount of β-sultone in primary products and more 2-alkenesulfonic acid in secondary products than does free SO_3.

Sulfonation of Branched 1-Alkenes by SO_3-Dioxane

The effect of the position of one or more methyl substituents on the nature of primary and secondary products was investigated. Our results, collected in Table III, show that the nature of the sulfonated products is strongly dependent on the position of the methyl group(s). Three main features may be underlined with respect to these products by and large confirming previous works:[2,4,13,14]

(i) the presence of a 2-methyl group precludes the formation of a β-sultone,
(ii) 3-branched 1-alkenes lead preferentially to γ-sultones,
(iii) 4- or 5-methyl 1-alkenes behave approximately like linear compounds.

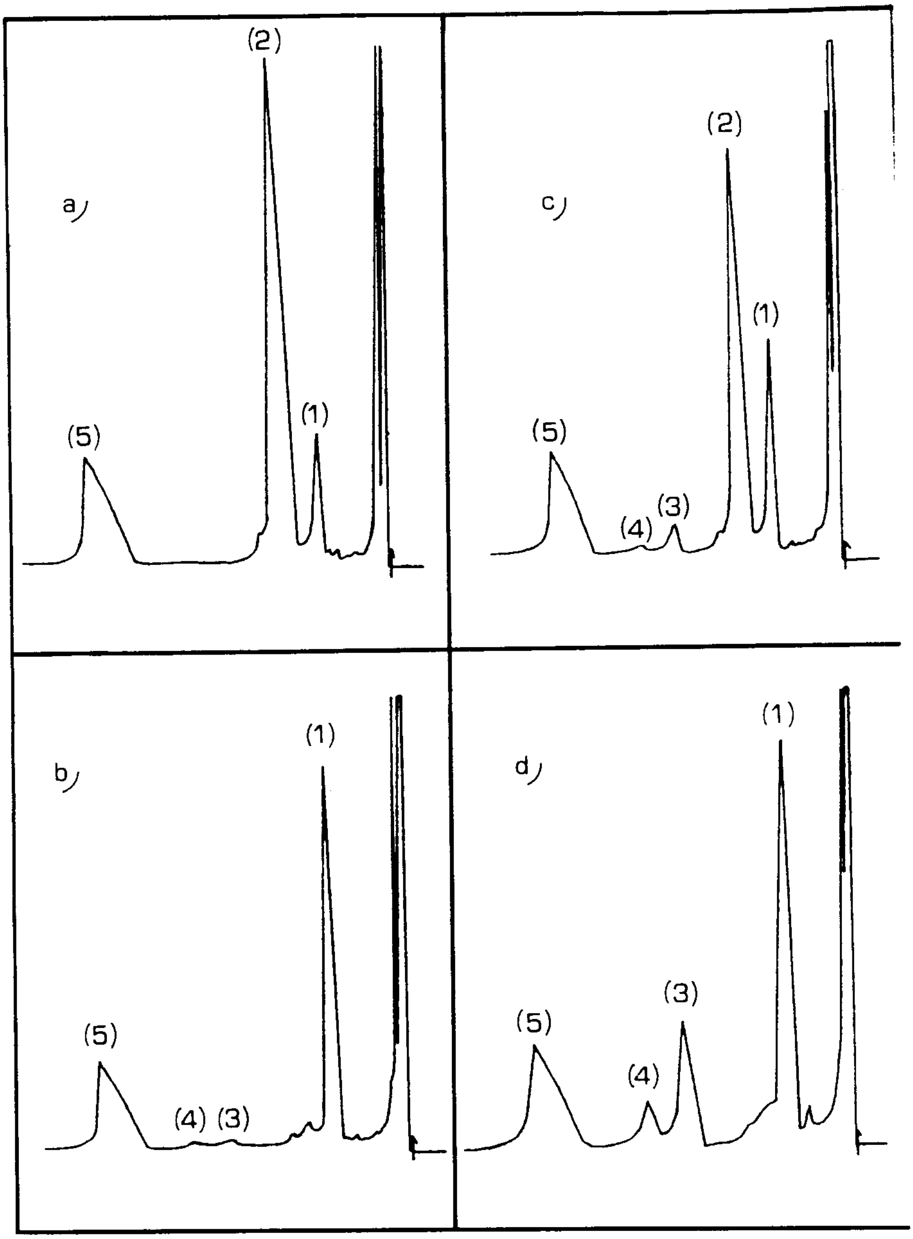


FIGURE 1 GLC analysis of the sulfonation products of 1-hexene. (a) dioxane–SO$_3$, primary products; (b) dioxane–SO$_3$, secondary products; (c) free SO$_3$, primary products; (d) free SO$_3$, secondary products; (1) hexenesulfonic acids (methyl esters); (2) 2-methoxyhexanesulfonic acid (methyl ester); (3) 4-ethyl-δ-sultone; (4) 3-*n*-propyl-γ-sultone; (5) internal standard.

TABLE I

Ratios of primary and secondary sulfonated products from 1-hexene

	Primary products (area percentages)				Secondary products (area percentages)			
Sulfonating agent	(1)[a]	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Free SO_3	25	69	4	2	62	0	27	11
SO_3-dioxane	12	88	~ 0	~ 0	95	0	3	2

[a] Numerals in parentheses have the same meaning as in Figure 1.

TABLE II

Ratios of double bond position isomeric tridecenesulfonic acids (in secondary products)

	Area percentage of isomer with double bond in:			
Sulfonating agent	1-	2-	3-	4-
Free SO_3	12	74	12.5	1.5
SO_3-dioxane	9	87	4	< 1

TABLE III

Products of the sulfonation of branched 1-alkenes

	Primary products			Secondary products		
Alkene	(1)[a]	(2)	(3)	(1)	(3)	(4)
2-Methyl 1-pentene	+[b]			+[b]		
4-Methyl 1-pentene	+	+ +		+ +[c]	(+)	(+)
2,3-Dimethyl 1-butene	+			+		
3,3-Dimethyl 1-butene	+		+ +	+	+ +	
2,3,3-Trimethyl 1-butene			+ +		+ +	
2,4,4-Trimethyl 1-pentene	+[d]			+		
5-Methyl 1-hexene	+	+ +		+ +	(+)	(+)

[a] Numerals have the same meaning as in Figure 1.

[b] Mainly 2-pentenesulfonic acids: (E): 65%, (Z): 35%.

[c] Mainly 4-methyl 2-pentenesulfonic acids: (E): 90%, (Z): 10%.

[d] Mainly 2-methylene 4,4-dimethylpentanesulfonic acid and (E) 2,4,4-trimethyl 2-pentenesulfonic acid.

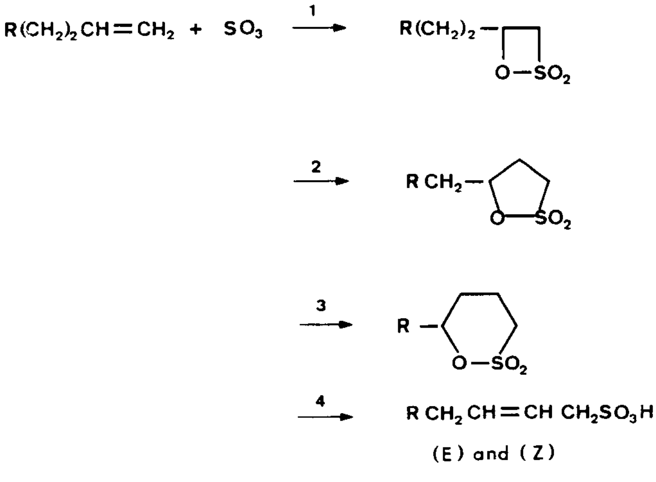
However some striking differences with published results have been found during this study. Firstly, contrary to Robbins *et al.*,[15] the sulfonation of 2,3-dimethyl 1-butene gave 2,3-dimethyl 2-butenesulfonic acid as the sole product. Secondly, we were able to isolate, purify and identify 2,3-dimethyl 2-butenesulfonic acid (as its methyl ester by ^{13}C NMR) from the sulfonated products of 3,3-dimethyl 1-butene, while these authors obtained only a γ-sultone (2,3,3-trimethyl 1,3-propanesultone) in slightly different conditions.[15] Thirdly, 4-methyl 1-pentene and 2,4,4-trimethyl 1-pentene led to predominant formation of 2-alkenesulfonic acids as did the greatest number of 1-alkenes, instead of 1-alkenesufonic acids as claimed by Bordwell.[13]

DISCUSSION

These results show the presence of a β-sultone in large amount among the primary products of the SO_3-sulfonation of linear 1-alkenes. The behavior of the branched 1-alkenes studied varies according to the substituted position(s), and remains consistent with that of the non-branched ones. Moreover, the β-sultone, when it occurs, does not seem to be the only primary product formed during the sulfonation of 1-alkenes, since just after the consumption of SO_3 alkenesulfonic acids are already present, as well as γ- and δ-sultones, yet in much smaller amounts. Now it is well known that β-sultone undergoes slow isomerization into alkenesulfonic acids.[8] Therefore it appears necessary to put forth thermodynamic and kinetic arguments to show whether or not the so-called primary alkenesulfonic acids actually form through the intermediacy of a β-sultone.

(a) Thermochemical Approach

In the literature some estimated values of the enthalpy of the SO_3 sulfonation of 1-alkenes can be found: they range from 40 to 50 kcal · mol^{-1}.[5,16,17] Nevertheless, to the best of our knowledge, precise thermochemical data are still lacking. Accounting only for initial and final states, the reactions of SO_3 with 1-alkenes may be written as follows:



A complete thermochemical study of these reactions should involve the knowledge of the dissociation energies (BDE) of all the bonds formed or broken during the process. However the paucity of thermochemical data with respect to these compounds compells us to have only an estimate of the corresponding reaction enthalpies.

The reactions were always conducted in rather dilute solution, in an only slightly polar, non-solvating, non-dissociating medium (1,2-dichloroethane). These conditions allow to use literature data pertaining to the gaseous state. The values of the bond energies and cyclic strain energies necessary to the calculation of the reaction

TABLE IV

Laidler-type contributing bond energies (CBE) in organo-sulfur and related compounds

Index	Bond	Origin	CBE (kcal · mol^{-1})	Ref.
a	C_{sp_3}—C_{sp_3}	alkanes	85.5	18
b	C═C[a]	alkenes	133.0	18, 19
c	C_{sp_2}—C_{sp_3}	alkenes	90.1	18
d	$(C_{sp_3}—H)''$	alkanes (CH_2 groups)	97.3	18
e	$(C_{sp_3}—H)'_O$	butanols (CH groups)	95.2	18
f	$(C_{sp_3}—H)''_{SO_2}$	sulfones (CH_2 groups)	97.9	18
g	$(C_{sp_2}—H)''$	alkenes (CH_2 groups)	101.2	18
h	$(C_{sp_2}—H)'$	alkenes (CH groups)	100.5	18
i	$(C_{sp_3}—O)$	ethers	91.0	18
j	$(C_{sp_3}—S)$[b]	sulfones ($CH_2—SO_2$ groups)	60.6	20
k	S—O(C)	sulfate esters	69.1	20
l	S—O(H)	sulfuric acid	70.0	20, 21
m	S═O	sulfur trioxide	110.0	22
n	S═O	sulfuric acid, sulfones	109.5	18, 21
p	O—H	sulfuric acid	111.6	21

[a] Atomization enthalpy differences between (E) and (Z)-isomers $(\Delta H_a)_E - (\Delta H_a)_Z = 1.0$ kcal · mol.

[b] Sulfur is always here hexavalent sulfur.

TABLE V

Conventional ring strain energies (CRSE) in cycloalkanes and saturated heterocycles[a]

Index	Cyclic type	Origin (resp. target compounds)	CRSE (kcal · mol^{-1})
	Four membered rings		
	Homocycle	Cyclobutane	26.5
	Heterocycle with O	Oxetane	25.4
	Heterocycle with S	Thietane	19.7
	Heterocycle with SO_2	(Thietane-1,1 dioxide)	19.0 estd[b]
4	Heterocycle with SO_2-O	(β-sultones)	23.0 estd (this work)
	Five membered rings		
	Homocycle	Cyclopentane	6.2
	Heterocycle with O	Oxolane	5.6
	Heterocycle with S	Thiolane	2.0
5	Heterocycle with SO_2-O	(γ-Sultones)	4.0 estd (this work)
	Six membered rings		
	Homocycle	Cyclohexane	0.0
	Heterocycle with O	Oxane	1.1
	Heterocycle with S	Thiane	−0.2
6	Heterocycle with SO_2-O	(δ-sultones)	0.5 estd (this work)

[a] Data from ref. 18 unless otherwise mentioned. Values taken from other works may differ from these ones by ± 0.2 kcal · mol^{-1}.

[b] Ref. 23.

enthalpies ΔH_1 to ΔH_4 are summarized in Tables IV and V. Among several systematic schemes the Laidler type contributing bond energies (CBE) and the conventional ring strain energies (CRSE) of Cox and Pilcher[18] were chosen.

The enthalpies of the SO_3-sulfonation of 1-alkenes giving respectively only one kind of sultone or only 2-alkenesulfonic acids may be calculated as follows* (the

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*SO_3 is assumed to be monomeric in 1,2-dichloroethane solution.

ΔH_i's ($i = 1$ to 4) indicate the enthalpy changes accompanying the above reactions):

$$\begin{aligned}\Delta H_1 &= (\mathrm{CBE})_b + (\mathrm{CBE})_c + 2(\mathrm{CBE})_g + (\mathrm{CBE})_h + 3(\mathrm{CBE})_m - 2(\mathrm{CBE})_a \\ &\quad - (\mathrm{CBE})_e - 2(\mathrm{CBE})_f - (\mathrm{CBE})_i - (\mathrm{CBE})_j - (\mathrm{CBE})_k - 2(\mathrm{CBE})_n + (\mathrm{CRSE})_4 \\ &= -22.7\ \mathrm{kcal \cdot mol^{-1}}\end{aligned}$$

$$\Delta H_2 = \Delta H_1 - (\mathrm{CRSE})_4 + (\mathrm{CRSE})_5 = -41.7\ \mathrm{kcal \cdot mol^{-1}}$$

$$\Delta H_3 = \Delta H_1 - (\mathrm{CRSE})_4 + (\mathrm{CRSE})_6 = -46.2\ \mathrm{kcal \cdot mol^{-1}}$$

$$\begin{aligned}(\Delta H_4)_E &= (\mathrm{CBE})_a + 2(\mathrm{CBE})_d + 2(\mathrm{CBE})_g + 3(\mathrm{CBE})_m - (\mathrm{CBE})_c \\ &\quad - 2(\mathrm{CBE})_f - (\mathrm{CBE})_h - (\mathrm{CBE})_j - (\mathrm{CBE})_l - 2(\mathrm{CBE})_n - (\mathrm{CBE})_p \\ &= -35.1\ \mathrm{kcal \cdot mol^{-1}}\end{aligned}$$

$$(\Delta H_4)_Z = (\Delta H_4)_E + (\Delta H_a)_E - (\Delta H_a)_Z = -34.1\ \mathrm{kcal \cdot mol^{-1}}$$

These results mean that the order of increasing enthalpic stability of the sulfonated compounds (as a number of isolated molecules) is: β-sultone < 2-alkenesulfonic acids ((E)-isomer slightly more stable than (Z)-isomer) < γ-sultone < δ-sultone. The calculation may also be done for a final state consisting of 1-alkenesulfonic acid (E or Z) if one assumes the CBEs of C_{sp_3}–S and C_{sp_2}–S are equal: this assumption is consistent with the published heat of combustion of divinylsulfone.[18] Combined with other CBEs taken from Table IV, this value leads to a reaction enthalpy with a slightly lower absolute value than $\Delta H_4((\Delta H_4')_E = -29.3\ \mathrm{kcal \cdot mol^{-1}})$, but whose exact figure may not be really significant.

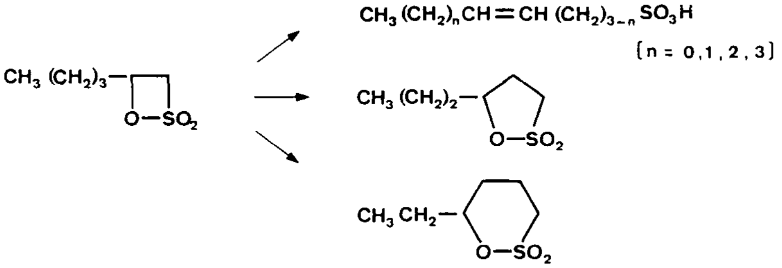
However, in addition to average bond energies only taken into account thus far, one should consider another enthalpic term arising from internal or intermolecular hydrogen bonding of sulfonic acids (solute–solute interaction) in a non-hydroxylic solvent. This term, which may amount to 6–7 kcal · mol^{-1} increases the stability of sulfonic acids relative to sultones but does not change the order found above.

Furthermore the determination of the relative stabilities of the various sulfonated species should include entropic considerations. Firstly, the reactions 1–4 are accompanied by a decrease in entropy because only one molecule of products forms from two molecules of reactants. Secondly, the cycloaddition of reactants into sultones surely results in a further marked decrease in entropy. In fact for instance the entropies of cyclization of n-alkanes into cycloalkanes $(CH_2)_n$ are respectively in cal · mol^{-1} · K^{-1}: -10.7 for $n = 4$; -13.4 for $n = 5$ and -21.5 for $n = 6$.[24] Hydrogen bonding in alkenesulfonic acids and entropic destabilization of γ- and δ-sultones reduce the free energy gap between the two types of compounds. However these factors don't reverse the order found on the enthalpy scale, since δ-sultones can be obtained simply by heating sulfonation mixtures rich in alkenesulfonic acids.[25]

Thermodynamically speaking, alkenesulfonic acids and medium-sized ring sultones, even more stable, are then favored products of the sulfonation of linear 1-alkenes with respect to β-sultones. Therefore the higher ratio of β-sultone found in the primary mixtures of our experiments may be explained by kinetic criteria, β-sultone forming more rapidly than alkenesulfonic acids. But in order to determine if alkenesulfonic acids are present since the beginning of the reaction the following kinetic results will usefully complement this study.

(b) *Kinetics*

The isomerization of the β-sultone formed during the early stage of the sulfonation of 1-hexene was followed by GLC. Owing to the increasing amounts of both alkenesulfonic acids and larger ring sultones, the reaction can be written:



The first of these reactions undergoes acid catalysis, observable in free SO_3-sulfonation: in this case it exhibits complex kinetics.[9] For the sake of greater simplicity, the isomerization of β-sultone was studied after SO_3–dioxane sulfonations,* i.e. in media where the concentration of hydrogen ion is quite small. Then plots of Log[β-sultone] versus time gave straight lines indicating first order kinetics with respect to reactant. Up to a 60% conversion the following rate constants and Arrhenius activation energy were obtained from the analysis of the β-sultone (Table VI). So these alkenesulfonic acids (as well as γ- and δ-sultones formed in smaller amounts) do proceed, wholly or only in part, from the primary β-sultone. Now the kinetic experiments only began 30 to 45 min after the addition of SO_3 and there were already some "primary" alkenesulfonic acids at this time, resulting either from the early transformation of the β-sultone or more directly from the SO_3-alkene reaction via another intermediate. Even with so few kinetic data in hand we can now discern if part of the alkenesulfonic acids forms primarily. In fact it is then sufficient to compare at a given temperature the calculated molar ratio of β-sultone to alkenesulfonic acids ($R_{cal} = [\beta\text{-sultone}]_t/[\text{sulfonic acids}]_t$) with the experimental one (R_{exp}). This latter ratio was obtained by chemical quenching of a sulfonation mixture (thermostated at $-1.5°$ C) 35 min after addition of SO_3-dioxane and subsequent GLC analysis. The corresponding value ($R_{exp} = 5.9$) is very close to that reported in Table I after correction for the relative molar responses of the TC detector with respect to the components of the mixture ($R_{exp} = 6.2$). On the other hand, assuming the worst hypothesis, that is β-sultone converted only into alkenesulfonic acids, the expression of R_{cal} is, since a first order rate law holds:

$$R_{cal} = \frac{e^{-kt}}{1 - e^{-kt}}$$

The value of E_a (Table VI) affords the rate constant at $-1.5°$ C ($k = 6.9 \cdot 10^{-7}$ s^{-1}) leading to the calculated ratio ($R_{cal} = 690$). It may therefore be claimed that alkenesulfonic acids are found at the very beginning of the sulfonation and do not entirely originate from β-sultone.

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*Dioxane and SO_3 were mixed in stoichiometric amounts.

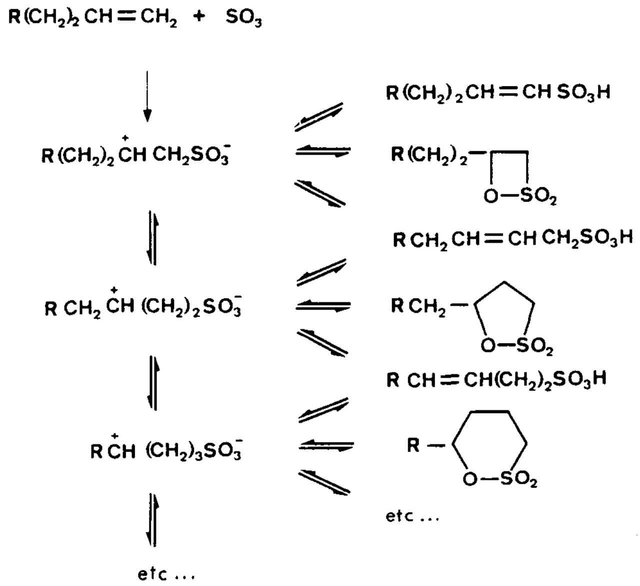
TABLE VI

Isomerization of a β-sultone (2-*n*-butylethanesultone). Kinetic parameters of β-sultone conversion in the presence of dioxane

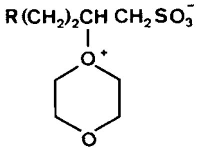
t (°C)	2	20	31	E_{app} (kcal · mol^{-1})
10^6 k (s^{-1}) solvent CH_2Cl_2	1.4	15		
solvent $(CH_2Cl)_2$	1.1	14	53	23

(c) *Reaction Mechanism and Energy Profile*

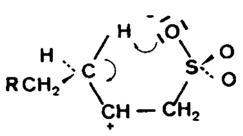
As it has already been postulated,[3] the most probable reaction pathway in the electrophilic addition of SO_3 to 1-alkenes involves a zwitterionic intermediate. During the second step of the mechanism the zwitterion can directly yield either a β-sultone by cyclization or a 1- or 2-alkenesulfonic acid by loss of a methylene proton. But it can otherwise undergo a rearrangement to equally or more stable carbenium ion species, then affording other isomeric alkenesulfonic acids as well as γ- and δ-sultones. In the case of linear substrates for instance the set of reactions may be written as follows:



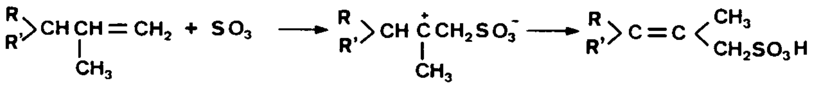
Of course the actual structure of the zwitterion formed during SO_3–dioxane sulfonation rather consists of an oxonium type ion:



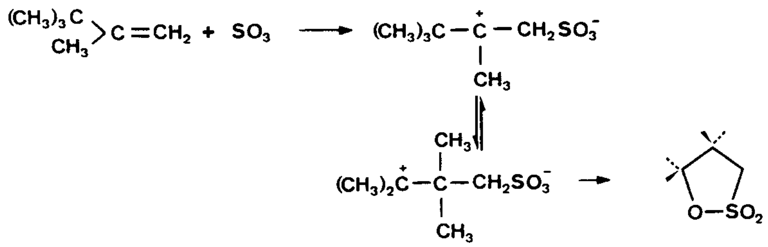
Besides the thermochemical argument with respect to the formation of 1-alkenesulfonic acid, the higher ratio of the Δ^2 isomer may be explained by a greater ability of the sulfonate group to remove a methylene proton through a pseudo-cyclic conformation:



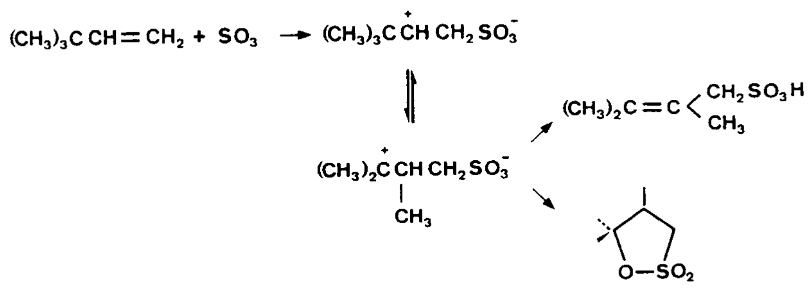
This simplified picture takes into account our observations, but it should be remembered that the presence of other products, especially disultones and "carbyl sulfates" was evidenced by some authors.[6,7]* With respect to branched 1-alkenes most of (but not all) our results were consistent with literature data.[13-15] 2-Methyl 1-pentene and 2,3-dimethyl 1-butene react essentially as follows:



while the zwitterion formed from 2,3,3-trimethyl 1-butene undergoes a rearrangement:



3,3-Dimethyl 1-butene behaves intermediately because of the tertiary carbocation bearing an α—CH group, and leads to both γ-sultone (mainly) and 2-alkenesulfonic acid (in smaller amount):



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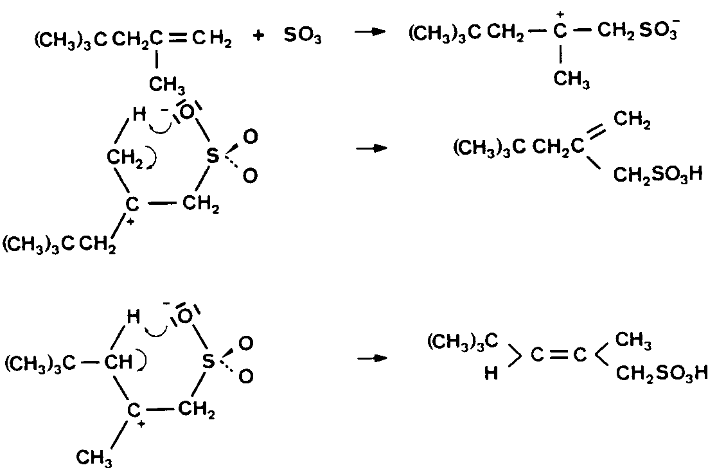
*In fact the GLC analyses carried out in this work were restricted to rather volatile compounds: methyl sulfonates, γ- and δ-sultones.

In our previous report[1] the structural formula of the main sulfonation product given by 2,4,4-trimethyl 1-pentene was erroneously stated as being a 2,4,4-trimethyl 2-pentene sulfonic acid ((Z)-isomer). Further careful examination of ^1H and ^{13}C NMR spectra of the isolated compound led to the more plausible structures and reactions:



2-Methylene 4,4-dimethylpentanesulfonic acid and (E)-2,4,4-trimethyl 2-pentenesulfonic acid are respectively the major and the minor products. An interpretation of the preferred process may lie in the greater availability of the methyl proton with respect to the methylene one α to the bulky *t*-butyl group.

However, on the basis of stereochemical studies Nagayama *et al.*[26] assumed a concerted mechanism (2 + 2 cycloaddition) to explain the occurrence of a β-sultone. Such a mechanism seems rather unlikely owing to the above argument (competitive formation of alkenesulfonic acids and β-sultone) and also for theoretical reasons. In fact the interaction between the LV orbital of SO_3 (π^* type; symmetry a''_2; energy: 0.145 a.u.) and the HO of a 1-alkene (π type; energy: -0.3157 a.u. in propene) constitutes the driving force of the reaction. The highly polar character of the S—O bond in SO_3 (according to MNDO and STO-3G calculations, the sulfur atom bears a positive charge $Q = 1.34 \pm 0.01$[27]) makes him a hard acid and a hard electrophile, while alkenes are soft bases. In short the large energy gap between the two frontier orbitals does not correspond to the conditions allowing orbital control.

Finally we can draw the energy profile of the three principal elementary steps taking place during the SO_3-sulfonation of 1-alkenes. A graph of potential energy F versus reaction coordinate should show (Figure 2):

—the enthalpy changes ΔH_1 and ΔH_4 of the main two-step reactions leading respectively to β-sultone (kinetically controlled path) and (E) 2-alkenesulfonic acid (thermodynamically controlled one),

—the low activation energies of the first common step giving the zwitterion and the second step yielding β-sultone,

—the measured apparent activation energy E_{app} from β-sultone to the transition state reached between the zwitterion Z and alkenesulfonic acid; this value is the algebraic sum of the actual activation energy E_a and the enthalpy change ΔH_5 between the zwitterion and β-sultone (ΔH_5 also contributes to ΔH_1).

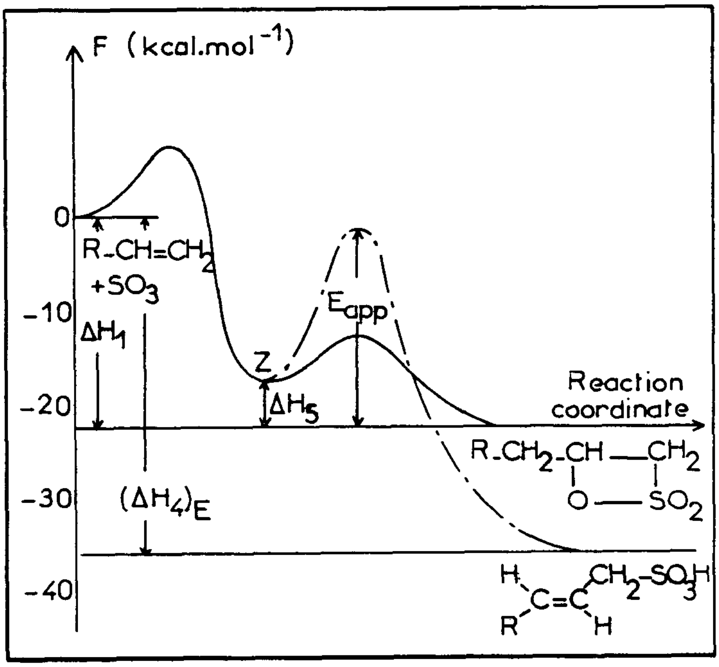
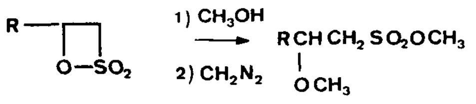


FIGURE 2 SO_3-sulfonation of linear 1-alkenes: energy profile of the main reactions. Z = $R\overset{+}{C}HCH_2—SO_3^-$.

EXPERIMENTAL

Sulfonation reactions. The purification of the reagents and solvents used has already been described. Sulfonations were conducted in 1,2-dichloroethane as previously mentioned.[1]

Kinetic experiments. In order to study the transformation of primary products to secondary ones, the reaction mixture was brought to the desired temperature about 30 min. after the addition of SO_3: 3 ml samples, taken at suitable time intervals, were quenched by methanol. Sulfonic groups were methylated by diazomethane before GLC analysis:



Degradative oxidations. Long chain linear sodium alkenesulfonates were oxidized at the double bond according to Lemieux and Von Rudloff.[28]

GLC analysis. The methyl carboxylates resulting from the above mentioned degradations and subsequent methylations were chromatographed isothermally at 110°C (stationary phase: SE30, 10% on Chromosorb® WNAW; l = 2 m; ϕ = 1/8″), the other conditions being as follows: flowrate of the carrier gas (He): 50 ml. min.$^{-1}$; temperature of the injection port: 250°C; thermal conductivity detector thermostated at 230°C. Standardization according to the internal normalization procedure was performed by using known mixtures of fatty acid methyl esters, but owing to the occurrence of one major component in our experimental mixtures the effect of the different relative molar responses was very small.

After methanolysis of the primary mixtures and, in all cases, methylation sulfonated compounds up to seven carbon atoms in the chain were chromatographed isothermally at 130°C (stationary phase:

DC-QF1; 10% on Chromosorb® WAW; $l = 1.5$ m; $\phi = 1/8''$ or DC-QF1, 5% on Chromosorb® WAW; $l = 2$ m; $\phi = 1/4''$; temperature of the injection port: 235°C; other conditions cited above). Quantitative analysis was allowed by using an internal standard, dimethyl bromoterephtalate, synthesized from *p*-xylene by classical methods and added to the sulfonation medium just after the consumption of SO_3. For kinetic measurements, calibration was done by means of known mixtures of alkenesulfonic acids, methoxyalkanesulfonic acids and internal standard.

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