

Infrared Spectra of Alkanesulfonic Acids, Chlorosulfonated Polyethylene, and Their Derivatives

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Synopsis

The infrared spectra of methane, *n*-butane-, and *n*-dodecane-sulfonic acids, their esters, alkali metal, silver and amine salts, amides, and chlorides are compared with analogous structures derived from chlorinated and chlorosulfonated polyethylenes. The Bellamy and Williams's linear relationship between ν_{SO_2} (asym.) and ν_{SO_2} (sym.) is valid for both the simple alkane sulfonic acid derivatives and those of chlorinated and chlorosulfonated polyethylenes.

DISCUSSION

The infrared characterization of derivatives prepared from chlorinated and chlorosulfonated polyethylenes (commercially available as Hypalon -20, -30, and -40, from E. I. du Pont de Nemours and Company, Inc.) by comparison with the spectra of simple alkanesulfonic acids and their derivatives has not always been possible, since only sparse and incomplete data concerning the latter are available.¹⁻⁴ The spectra of only a few polymeric sulfonic acid derivatives have been reported,^{5,6} and the data are insufficiently definitive to permit positive identification. This is particularly true in those cases where the groups in question ($-\text{SO}_2\text{Cl}$, $-\text{SO}_2\text{R}$, $-\text{SO}_2\text{NR}'\text{R}''$) fall within a narrow spectral range. Of particular help in assigning symmetric and asymmetric S—O stretching frequencies of compounds containing the $-\text{SO}_2-$ group is the correlation reported by Bellamy and Williams.⁷ They have found that any change in ν_{SO_2} (asym.) is accompanied by a proportional change in ν_{SO_2} (sym.) such that a plot of ν_{SO_2} (asym.) versus ν_{SO_2} (sym.) gave a straight line. Since the S—O stretching frequencies are essentially unaffected by mass and coupling effects, they pointed out that the positions of ν_{SO_2} (asym.) and ν_{SO_2} (sym.) depend on the electronegativity of the substituents attached to the $-\text{SO}_2-$ group. As the electronegativity of these groups is increased, the stronger are the S=O bonds, resulting in a shift to higher vibrational frequencies.

Some 97 compounds containing the $-\text{SO}_2-$ group have been examined by Robinson⁸ and found to fit the linear relationship of Bellamy and Williams.⁷ As the carbon atom of the grouping RSO_2-C was replaced by progressively more electronegative groups (N, O, Cl, F), Robinson observed a propor-

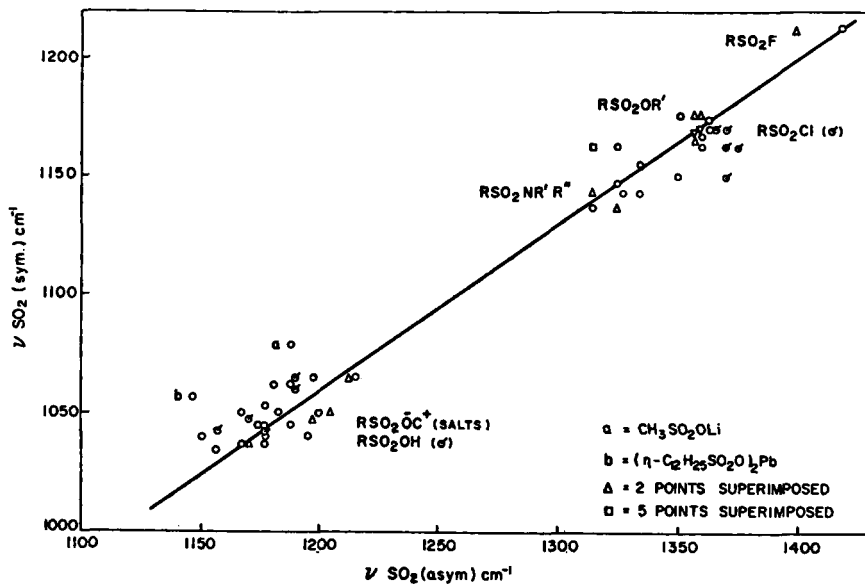


Fig. 1. Correlation of asymmetric and symmetric S—O stretching frequencies of alkanesulfonic acids, chlorosulfonated polyethylenes, and their derivatives.

tionate shift of ν_{SO_2} (asym.) and ν_{SO_2} (sym.) to higher frequencies. His finding that replacement of one or both alkyl groups of RSO_2R by aryl group(s) was sufficient to shift the ν_{SO_2} (asym.) and ν_{SO_2} (sym.) vibrations to higher frequencies, pointed out emphatically the inadvisability of comparing the spectra of chlorinated and chlorosulfonated polyethylene derivatives with the literature spectra of $-\text{SO}_2-$ compounds bounded by alkyl-aryl or aryl-aryl groups. For this reason a number of alkanesulfonic acid derivatives were prepared as model compounds whose infrared spectra could be compared directly with those derived from chlorinated and chlorosulfonated polyethylenes hereafter referred to as chlorosulfonated polyethylene.

The S—O asymmetric and symmetric stretching frequencies of the 39 alkanesulfonic acid derivatives and some 30 chlorosulfonated polyethylene derivatives and analogous polymeric structures reported here were found to fit the linear plot of Bellamy⁷ as shown in Figure 1. Moreover, the ν_{SO_2} (asym.) and ν_{SO_2} (sym.) vibrations are shifted in the direction of higher frequencies when the electronegativities of the $-\text{SO}_2-$ substituents are increased as mentioned above. That this relationship holds for the polymeric derivatives attests to the freedom of the $-\text{SO}_2-$ stretching frequencies from mass and coupling effects.

The infrared spectra of chlorosulfonated polyethylene and its fluoro analog have been published in full⁸ and will be mentioned briefly. All of its other derivatives and those of the model compounds will be treated in greater detail. They are discussed below in the order of decreasing elec-

tronegativity of the substituent X in the grouping RSO_2X , where X is F, Cl, OR', NR'R'', O-C⁺ (salt), and OH.

Halides

Fluorosulfonated polyethylene, prepared from chlorosulfonated polyethylene by 90% conversion of the $-\text{SO}_2\text{Cl}$ groups with NaF, shows ν_{SO_2} (asym.) and ν_{SO_2} (sym.) at 1400 and 1212 cm^{-1} , respectively,⁵ which correspond closely to those reported for poly(vinylsulfonyl fluoride) at 1419 cm^{-1} and 1213 cm^{-1} .⁶ These assignments are in good agreement with those reported for $\text{CH}_3\text{SO}_2\text{F}$ at 1400 cm^{-1} and 1212 cm^{-1} .^{3,4,8}

The ν_{SO_2} (asym.) and ν_{SO_2} (sym.) bands of chlorosulfonated polyethylene appear at 1370 and 1163 cm^{-1} , respectively,⁵ and closely parallel those of poly(vinylsulfonyl chloride) at 1370 and 1150 cm^{-1} .⁶ These bands are in excellent agreement with those of $\text{CH}_3\text{SO}_2\text{Cl}$ (1365 and 1170 cm^{-1}),^{3,4,8} *n*- $\text{C}_4\text{H}_9\text{SO}_2\text{Cl}$ (1375 and 1163 cm^{-1}), and $\text{CH}_3\text{CHClCH}_2\text{SO}_2\text{Cl}$ (1370 and 1170 cm^{-1}).

Esters

The data listed in Table I for both the model compound esters and the methyl sulfonatochloropolyethylenes show strong bands in the region of 1361 and 1177 cm^{-1} characteristic of the asymmetric and symmetric S—O stretching frequencies.^{3,4} Absorption bands, appearing in the 1283 and 1112 cm^{-1} regions of the model compounds correspond with the 1316 and 1102 cm^{-1} bands reported for methyl-*p*-toluenesulfonate.⁹

A previously unreported band appears at 1419 cm^{-1} with remarkable consistency for all the model ester compounds studied. It also appears with dependability in the spectrum of the simple alkanesulfonic acid salts, sulfonamides, sulfonyl chlorides, and the acids themselves. It may be concluded that this absorption is due to some vibrational mode of the $-\text{SO}_2-$ group which is common to all of these derivatives. This band could possibly be assigned to the asymmetrical CH deformation of the C— CH_3 group ($1450 \pm 20 \text{ cm}^{-1}$) shifted by the electronegative $-\text{SO}_2-$ group.¹⁰ However, its appearance in model compounds in which the methyl group is far removed from the inductive effect of $-\text{SO}_2-$, as for example in the C_4H_9- and $\text{C}_{12}\text{H}_{25}-$ sulfonic acid derivatives, makes such an assignment unlikely.

All the model compound methyl esters and the methyl esters of chlorosulfonated polyethylene show an absorption band in the region of 1000 cm^{-1} which seems to be characteristic of this group. However, since it also appears in the butyl esters of the simple alkanesulfonic acids, a definite assignment is difficult.

All the esters of $\text{C}_4\text{H}_9\text{SO}_3\text{H}$ show bands at 1286 and 1083 cm^{-1} which do not appear with regularity for the other esters. Unassigned bands also appear in the regions of 1053, 972, and 944 cm^{-1} .

TABLE I
Principal Frequencies of Alkanesulfonic Acid Esters*

RSO ₃ R'		Frequency, cm. ⁻¹											
R	R'	^ν SO ₂ (asym.)					^ν SO ₂ (sym.)						
Me	Me	1420 M ^{vs}	—	1360 VSbr	—	1176 VSbr	1110 W ^{sh}	—	1059 S ^{sh}	1000 VS	971 S	—	—
Me	Et	1420 M ^{vs}	1395 M ^s	1351 VSbr	—	1176 VSbr	1104 M	—	—	—	976 S	—	922 Sbr
Me	n-Pr	1420 M ^{vs}	1394 S ^{sh}	1358 VSbr	1285 M	1176 VSbr	1100 M ^s	—	1050 S ^s	—	981 S ^{sh}	943 VSbr	913 S
Me	n-Bu	1420 M ^{vs}	1390 S ^{sh}	1360 VSbr	—	1176 VSbr	1124 M	—	1057 S ^s	996 VS ^{sh}	976 VSbr	939 VSbr	—
n-Bu	Me	1420 M ^{vs}	—	1358 VSbr	1285 M ^r	1166 VSbr	1107 M ^s	1085 M	1057 S ^{sh}	—	—	—	922 S ^s
n-Bu	Et	1420 M ^{vs}	1395 S ^{sh}	1358 VSbr	1290 M	1167 VSbr	1107 M ^s	1085 M	—	—	—	—	922 Sbr
n-Bu	n-Pr	1420 M ^{vs}	1395 S ^{sh}	1358 VSbr	1285 M	1168 VSbr	1107 M ^s	1085 M	1053 S ^s	—	976 VS ^{sh}	943 VSbr	920 Sbr
n-Bu	n-Bu	1420 M ^{vs}	1390 M ^{sh}	1358 VSbr	1285 M ^{sh}	1167 VSbr	1124 M	1085 M	1059 S ^s	995 VS	954 S ^{sh}	941 VSbr	926 S ^{sh}
n-C ₁₂ H ₂₅	Me	1420 M ^{vs}	—	1360 VSbr	—	1167 VSbr	1129 W ^{sh}	—	—	995 VSbr	—	—	—
n-C ₁₅ H ₃₁	Et	1420 M ^{vs}	1395 M ^{sh}	1360 VSbr	—	1170 VSbr	1105 M ^{sh}	—	—	—	—	—	922 Sbr
n-C ₁₇ H ₃₅	n-Pr	1420 M ^{vs}	1395 M ^{sh}	1363 VSbr	1290 M ^{sh}	1170 VSbr	1105 W ^{br}	—	1053 S ^s	—	978 S ^{sh}	948 VSbr	914 Sbr
n-C ₁₉ H ₃₉	n-Bu	1420 M ^{vs}	—	1363 VSbr	—	1174 VSbr	1128 M	—	1060 S ^s	998 VS	966 S ^{sh}	946 VSbr	912 W
Hypalon-20	Me	—	—	1360 VSbr	—	1163 VSbr	—	—	—	992 VS	—	—	917 W ^{br}
Hypalon-30	Me	—	—	1360 VSbr	—	1170 VSbr	1112 W	—	1064 S ^s	996 VS	—	—	917 M ^{br}

* Legend: S = strong, M = medium, W = weak, V = very; superscript letters: s = sharp, sh = shoulder, br = broad, v = very.

Sulfonamides

N-Monosubstituted sulfonamides have been reported to show ν_{SO_2} (asym.) and ν_{SO_2} (sym.) at 1316–1378 and 1145–1165 cm^{-1} , respectively; these frequencies appear at 1335–1350 and 1155–1172 cm^{-1} for the *N,N*-disubstituted analogs.² Both the model compounds and the amides of chlorosulfonated polyethylene show these vibrations occurring at 1315–1350 and 1337–1163 cm^{-1} (Table II). The N–H stretching frequency of the mono-*N*-alkyl sulfonamides appears at 3280 cm^{-1} for the model compounds but were observed for only some of the polymeric analogs. Similarly, although the S–N stretching frequency appears in the region of 1065–1088 cm^{-1} for all the model compounds examined, it was found in only a few of the polymeric derivatives.

Salts

The infrared spectra of the few alkali and heavy metal salts of the alkanesulfonic acids that have been reported^{3,4,8} show ν_{SO_2} (asym.) and ν_{SO_2} (sym.) appearing mainly in the region of 1163–1192 and 1021–1053 cm^{-1} , respectively. Similar observations were made for some 14 model compounds (Table III) containing amino or metallic cations (C^+). These frequencies are also clearly discernible in the chlorosulfonated polyethylene salt derivatives. However, all the model compounds showed strong absorptions in the 1190–1200 cm^{-1} region which could be mistaken for ν_{SO_2} (asym.) appearing close by at 1150–1200 cm^{-1} . Only in a few cases was the former band of equal intensity to the latter and in most cases it was weaker. Because of this, but more particularly since the latter vibration when plotted against ν_{SO_2} (sym.) fitted the straight line of Figure 1 more closely, it was preferentially assigned as ν_{SO_2} (sym.). That the plot of ν_{SO_2} (asym.) versus ν_{SO_2} (sym.) for $\text{CH}_3\text{SO}_2\text{OLi}$ and $(n\text{-C}_{12}\text{H}_{25}\text{SO}_2\text{O})_2\text{Pb}$ fall outside this straight line (points *a* and *b* respectively of Figure 1) may be attributed to the partial covalent nature of the oxygen–metal bonds.

The C–H stretching frequency of the —CHCl— group in chlorosulfonated polyethylene appears at 1258 cm^{-1} and is of weaker intensity than the —CH₂— deformation frequency at 1470 cm^{-1} . In the salt derivatives, however, it appears in combination with some vibrational mode of RSO_3^- and is now of greater intensity than the 1470 cm^{-1} band.

The salts of chlorosulfonated polyethylene were prepared from appropriate alkali metal hydroxides or amines in the presence of methanol which was found to facilitate these preparations. The course of the reaction can be followed spectrophotometrically by observing the disappearance of the methyl ester at 995 cm^{-1} which is noticeable at the beginning of the reaction. When this band is absent and the sodium sulfonate band at 1058 cm^{-1} has reached its maximum, the reaction was considered as being complete.

TABLE II*
Principal Frequencies of Alkanesulfonic Acid Amides

RSO ₂ NR'R''		Frequency, cm. ⁻¹												
R	R'	R''	N—H stretching		ν _{SO₂} (asym.)		ν _{SO₂} (sym.)		S—N stretching					
Me	H	Et	3280 VS ^b	1446 S ^b	1420 S ^b	1390 S ^b	1325 VS ^b	—	1163 VS ^b	1105 S ^{sh}	1065 S ^b	—	981 VS ^b	940 M ^b
Me	Et	Et	—	—	1425 S ^b	1395 VS ^b	1325 VS ^b	1213 VS ^b	1147 VS ^b	1110 VS ^b	1080 VS	—	974 VS ^b	938 VS
n-Bu	H	Et	3280 VS ^b	1440 S	1423 S	1395 S ^b	1334 VS ^b	1198 S ^b	1155 VS	1105 S ^b	1076 VS	—	947 VS ^b	926 M ^{sh}
n-Bu	Et	Et	—	—	1425 S ^b	1400 VS ^b	1334 VS ^b	1213 VS ^b	1143 VS ^b	1105 S ^b	1088 S ^{br}	—	981 VS ^b	944 VS ^b
CH ₂ =CH— ^b	H	H	—	—	—	1350	—	—	1150 S ^b	—	—	—	—	—
(—CH ₂ —CH—) ^c	Et	Et	—	—	—	—	1327	1213	1143	—	—	—	—	—
Hypalon-20	H	Me	3390 S	1440 S ^{sh}	—	—	1325 VS ^b	—	1137 VS ^b	—	—	—	1025 S ^{br}	—
Hypalon-20	Me	Me	—	—	—	—	1315 S ^{sh}	—	1137 VS ^b	—	—	—	—	—
Hypalon-20	H	Et	—	—	—	—	1315 S	—	1163 S	—	—	—	1025 VS ^{br}	—
Hypalon-20	Et	Et	—	—	—	—	1315 S ^{br}	—	1163 S	—	—	—	—	—
Hypalon-20	H	n-Pr	—	—	—	—	1315 S	—	1163 S	—	—	—	1025 VS	—
Hypalon-20	n-Pr	n-Pr	—	—	—	—	1315 S	—	1163 S	—	—	—	1082 M	1025 VS
Hypalon-20	H	n-Bu	3390 S	1440 S ^{br}	—	—	1315 S	—	1143 S	—	—	—	1082 M	1032 S ^{br}
Hypalon-20	n-Bu	n-Bu	—	—	—	—	1315 S	—	1163 S	—	—	—	—	—
Hypalon-20	n-Bu	n-Bu	—	—	—	—	1315 VS	—	1143 S	—	—	—	1070 S	1008 S
Hypalon-20	—(CH ₂) _n —	—	—	—	—	—	1325 VS	—	1137 S	—	—	—	—	—
Hypalon-20	—(CH ₂) _n —	—	—	—	—	—	—	—	—	—	—	—	—	—

* See Table I for explanation of symbols.

^b Data of Wiley and Gensheimer, ¹¹ CHCl₃ solution of CH₂=CHSO₂N(Et)₂.

^c Data of Kern et al.⁷

The reaction mechanism, therefore, may be explained by the sequence shown in eqs. (1-5).



Consistent with the above is the known rapid rate of esterification of sulfonyl chlorides by alcohols [eq. (1)] under Schotten-Bauman conditions.^{12,13} Moreover, the methyl sulfonates are recognized as efficient alkylating agents [eq. (3)] which undergo rapid and facile hydrolysis necessitating their preparation under strictly anhydrous conditions.⁹ Direct salt formation, via eq. (5), although not considered to proceed to any great extent, can not be ruled out altogether.

Acids

The ν_{SO_2} (asym.) and ν_{SO_2} (sym.) stretching frequencies of alkanesulfonic acids have been reported in the regions of 1190 and 1065 cm^{-1} , respectively.^{2,3,8} Similar observations have been made for $\text{CH}_3\text{SO}_3\text{H}$ (1190 and 1060 cm^{-1}), $n\text{-C}_4\text{H}_9\text{SO}_3\text{H}$ (1170 and 1047 cm^{-1}), and for $n\text{-C}_{12}\text{H}_{25}\text{SO}_3\text{H}$ (1177 and 1042 cm^{-1}). In chloropolyethylenesulfonic acid these bands appear at 1156 and 1042 cm^{-1} . A characteristic feature of the model compound sulfonic acids is the bonded —OH frequencies at 3030 and 2393 cm^{-1} which serve to distinguish them from the salts whose ν_{SO_2} (sym.) and ν_{SO_2} (asym.) frequencies fall in the same regions as the acids. Only the 3030 cm^{-1} band is observed in the polymeric sulfonic acid but common to both the simple and polymeric sulfonic acids is the extensive broadening of the base line of the C—H stretching frequency in the 2860 cm^{-1} region due to the bonded —OH absorptions.

Summary

The asymmetric and symmetric S—O stretching vibrations of the alkanesulfonic acids and their derivatives, described in the preceding sections, are summarized in Table IV. Since many of the derivatives absorb in the same wavelength region, it is not obvious from this table alone that infrared analysis would be useful in distinguishing between various sulfonic acid derivatives. However, when considered jointly with the nature of the chemical reaction used in the modification of the — SO_2H or — SO_2Cl groups, and with auxiliary absorption bands (such as the bonded OH of the — SO_2H groups and the characteristic 1000 cm^{-1} band of — SO_2CH_3), the data in Table IV should prove useful in structural identification.

TABLE III^a
Principal Frequencies of Alkanesulfonic Acid Salts

R	RSO ₃ ⁻ C ⁺	NH ₃ ⁺ deformation	Frequency, cm. ⁻¹									
			C ⁺		S		SO ₂ (asym.)		SO ₃ (asym.)		SO ₃ (sym.)	
Me	Li ⁺	—	1440 M ^a	1385 M	1343 M	1245 S	—	1188 VS ^{br}	—	1079 VS	976 M ^a	
		—	1420 M ^a	—	—	—	—	—	—	—	—	
Me	Na ⁺	—	1417 M ^a	1358 M ^{sh}	1285 M	1250 VS ^a	1217 VS ^{sh}	1198 VS ^{sh}	—	1065 VS ^{sh}	992 W	
		—	—	1340 S	—	—	—	—	—	—	—	
Me	K ⁺	—	1430 M ^a	1385 M	1334 M	1245 S	1229 S	1188 VS ^{br}	—	1062 VS ^a	1056 VS ^a	
Me	Cs ⁺	—	1440 M ^a	1385 M	1348 S	—	—	1188 VS ^a	—	1045 VS ^a	992 M ^a	
		—	—	—	1328 S	—	—	—	—	—	982 M ^a	
CH ₂ CH(OH)CH ₃	Na ⁺	—	1420 M ^a	1380 M	1315 M	1240 VS ^a	1205 VS	1177 VS	—	1053 VS ^a	—	
n-Bu	Na ⁺	—	1417 M ^a	—	—	1238 VS ^{sh}	1218 VS ^a	1181 VS	—	1062 VS ^{sh}	997 W	
n-C ₁₁ H ₂₃	Na ⁺	—	1420 M ^a	1362 M ^{sh}	1300 M	1242 VS ^{sh}	1205 VS	1174 VS	—	1045 S	—	
		—	—	—	1285 M	—	—	—	—	—	—	
Me	Ag ⁺	—	1423 M ^a	1350 S	—	1254 VS ^{sh}	1213 VS	1195 VS	1070 M ^{br}	1040 S	—	
		—	—	1326 S	—	—	—	—	—	—	—	
n-Bu	Ag ⁺	—	1423 M ^a	—	1308 S	1254 S ^{sh}	1205 S	1177 VS	1070 M ^{sh}	1040 S	—	
		—	—	—	1294 S ^a	—	—	—	—	—	—	
n-C ₁₁ H ₂₃	Ag ⁺	—	1417 M ^a	—	1308 M ^{sh}	1263 S	1198 S	1167 VS	1083 S	1050 S	—	
		—	—	—	1300 M	—	—	—	—	—	—	
n-C ₁₁ H ₂₃	1/2Pb ⁺⁺	—	1423 M ^{sh}	—	1308 M	1244 S	1156 VS ^{sh}	1146 VS	1083 S	1057 S	1002 S	
		—	1415 M ^a	—	1295 M	—	—	—	—	—	—	
		—	—	—	1280 M	—	—	—	—	—	—	

Me	EtNH ₃ ⁺	1622 VS	1535 S	1430 M ^a	1340 S	—	1250 S	1208 VS ^{br}	1150 VS ^{br}	1083 S	1040 VS	—
n-Bu	EtNH ₃ ⁺	1640 M ^{br}	1525 M ^{br}	1423 M ^a	1344	1315 M	1242 S ^{sh}	1213 VS ^{br}	1177 VS	1070 S	1037 VS	—
n-C ₁₅ H ₃₃	EtNH ₃ ⁺	1625 S ^{br}	1515 M ^{br}	1420 M ^{br}	1334 M ^{sh}	1285 M	—	1180 S	1156 VS	1175 S	1034 VS	1002 M
Hypalon-20	Li ⁺	—	—	—	1360 M	1295 M	1248 S	—	1213 VS	—	1065 VS	1021 M
Hypalon-20	Na ⁺	—	—	—	—	1308 M	1250 S ^{sh}	1210 VS ^{br}	1183 VS ^{sh}	—	1050 VS ^a	1018 M ^a
Hypalon-20	K ⁺	—	—	—	1352 M ^{sh}	1300 S ^{sh}	1250 S	—	1200 VS	—	1050 VS ^a	1021 M ^{sh}
Hypalon-30	Li ⁺	—	—	—	1380 M	1310 S	1250 S ^{sh}	—	1215 VS ^{br}	—	1065 VS	1021 M
Hypalon-30	Na ⁺	—	—	—	—	1308 M ^{sh}	1255 VS ^{sh}	1235 VS ^{sh}	1205 VS ^{br}	—	1050 VS ^a	1018 M ^a
Hypalon-30	K ⁺	—	—	—	—	1315 M ^{sh}	1258 VS ^{sh}	1235 VS ^{sh}	1198 VS ^{br}	—	1047 VS ^a	—
Hypalon-40	Li ⁺	—	—	—	1360 M	1290 S ^{sh}	1250 S ^{sh}	1235 VS ^{sh}	1205 VS ^{br}	—	1050 VS ^a	1018 M ^a
Hypalon-40	Na ⁺	—	—	—	—	1312 S ^{sh}	1253 S ^{sh}	—	1198 VS ^{br}	—	1047 VS ^a	1021 M
Hypalon-40	K ⁺	1628 M	1523 M	—	1375 M	—	1250 S	1198 VS	1177 VS	1070 S ^{sh}	1045 VS ^a	—
Hypalon-20	EtNH ₃ ⁺	1620 M ^{br}	1515 M ^{br}	—	—	1308 S ^{br}	1255 VS ^{sh}	1190 VS	1167 VS ^{sh}	1064 S	1037 VS ^a	—
Hypalon-30	HOCH ₂ CH ₂ NH ₃ ⁺	1614 M ^{br}	1510 M	—	—	1308 S ^{sh}	1258 VS ^{sh}	1188 VS ^{br}	1170 VS ^{sh}	1067 S	1037 VS ^a	1015 S ^{sh}
Hypalon-40	HOCH ₂ CH ₂ NH ₃ ⁺	1625 W ^{br}	1515 W	—	—	1308 S ^{sh}	1251 VS	1195 VS	1170 VS ^{sh}	1064 S	1037 VS ^a	108 VS ^a

^a See Table I for explanation of symbols.

TABLE IV
S—O Stretching Frequencies of Model
Compound Sulfonic Acids and Their Derivatives

Group	Frequency, cm. ⁻¹	
	Asymmetric	Symmetric
Halides		
Fluorides	1400	1212
Chlorides	1365-1375	1163-1170
Esters	1351-1363	1166-1176
Sulfonamides		
RSO ₂ NHR'	1316-1378	1145-1165
RSO ₂ NR'R''	1335-1350	1152-1172
Salts		
Li, Na, K, Cs	1174-1198	1045-1079
Ag	1167-1195	1040-1050
Pb	1145	1057
Acids	1177-1190	1042-1060

EXPERIMENTAL

Halides

Chlorosulfonated Polyethylenes. Du Pont's chlorosulfonated polyethylenes,^{14,15} designated Hypalon-20, -30, and -40 were used for the preparation of all polymeric sulfonic acid derivatives reported here.

CH₃SO₂Cl. CH₃SO₂Cl, from Eastman Kodak, was distilled and collected at 65°C./20 mm.¹⁶

***n*-C₄H₉SO₂Cl.** The *n*-C₄H₉SO₂Cl, also from Eastman Kodak, was distilled and collected at 90°C./11 mm.¹⁷

CH₃CH(Cl)CH₂SO₂Cl. This compound was prepared by the chlorine oxidation at 2-5°C. of 2-chloropropyl mercaptan¹⁸ according to the procedure of Stewart and Cordts.¹⁹ There was obtained a 91% yield of colorless product boiling at 52-53°C./0.5 mm.

ANAL. Calcd. for C₃H₆Cl₂O₂S: C, 20.35%; H, 3.42%; Cl, 40.05%; S, 18.10%. Found: C, 20.8%; H, 3.4%; Cl, 39.5%; S, 17.8%.

Esters

The preparation and properties of the model compound esters and those from chlorosulfonated polyethylenes are listed in Table V. The procedure of Emmons and Ferris,²⁰ who prepared esters of CH₃SO₃H by treating its silver salt in room temperature CH₃CN with alkyl halides proved to be satisfactory for the preparation of the methyl, ethyl, propyl, and butyl esters of C₄H₉SO₃H and C₁₂H₂₅SO₃H. Yields of 90% or better were obtained, and the method is applicable to higher molecular weight acids like C₁₂H₂₅SO₃H when hot CH₃CN is employed to insure dissolution of its silver salt. The method of Sekera and Marvel¹³ was used for the preparation of the esters of CH₃SO₃H.

TABLE V
 Preparation of Alkanesulfonic Acid Esters

RSO ₂ R'		R'	Method ^a	Yield, %	B.p., °C./mm.	Calculated			Found		
R	C, %					H, %	S, %	C, %	H, %	S, %	
Me	Me	Me	1	25	100/25	21.82	5.50	29.1	21.9	5.5	29.2
Me	Et	Et	2	57	88.5/11	29.03	6.50	25.8	29.3	6.7	26.5
Me	<i>n</i> -Pr	<i>n</i> -Pr	2	61	94/8.8	34.78	7.30	23.2	35.1	7.5	23.5
Me	<i>n</i> -Bu	<i>n</i> -Bu	2	90	105/8.5	39.45	7.95	21.07	39.4	7.6	20.6
<i>n</i> -Bu	Me	Me	3	100	74/2	39.45	7.95	21.07	39.3	8.0	20.9
<i>n</i> -Bu	Et	Et	3	94	75.5/1.4	43.40	8.49	19.30	43.4	8.3	19.3
<i>n</i> -Bu	<i>n</i> -Pr	<i>n</i> -Pr	3	94	79-80/1	46.68	8.95	17.78	46.7	9.0	17.7
<i>n</i> -Bu	<i>n</i> -Bu	<i>n</i> -Bu	3	91	88-90/1	49.50	9.44	16.50	49.3	9.2	16.4
<i>n</i> -C ₁₂ H ₂₅	Me	Me	3	96	130-133/0.3	59.10	10.67	12.13	59.2	10.8	12.1
<i>n</i> -C ₁₂ H ₂₅	Et	Et	3	90	132-135/0.3	60.40	10.86	11.51	60.4	10.9	11.5
<i>n</i> -C ₁₂ H ₂₅	<i>n</i> -Pr	<i>n</i> -Pr	3	90	142-143/0.3	63.13	8.83	11.23	63.1	8.8	11.2
<i>n</i> -C ₁₂ H ₂₅	<i>n</i> -Bu	<i>n</i> -Bu	3	90	150-152/0.3	62.70	11.17	10.46	62.6	11.1	10.1

$$\text{CH}_3\text{OSOCH}_3 \begin{array}{c} \text{O} \\ || \\ \text{CH}_2\text{CN} \end{array}$$
^a Method 1: rearrangement of CH₃OSOCH₃ with tri-*n*-butylamine;⁹ method 2: RSO₂Cl + R'OH in pyridine;¹² method 3: RSO₂Ag + R'I in CH₃CN.⁸

The preparation of ester derivatives of chlorosulfonated polyethylenes from alcohols and inorganic or organic basis having a dissociation constant K_b of greater than 2×10^{-9} has been described.²¹ The use of triethylamine, reported to be the preferred base, was found to give a mixture of ester and sulfonic acid amino salt. Nearly pure methyl esters were more conveniently prepared using NaOAc as the base.

Since most of the esters given in Table V are believed to be new compounds, the following slightly modified literature methods given below will serve to illustrate the two general procedures used.

CH₃SO₂OC₄H₉. To a stirred mixture of *n*-butanol (22.0 g., 0.295 mole) and methanesulfonyl chloride (34.4 g., 0.300 mole) at 0°C. was added dropwise 147 ml. of pyridine over a 2¹/₂-hr. period while maintaining the temperature at 0–5°C. The mixture was stirred for 2 hr. more at 0–5°C. and then overnight at 10–15°C. It was acidified with a cold solution of 270 ml. of concentrated HCl in 900 ml. of water while maintaining the temperature below 20°C. After saturation with NaCl, it was extracted with ether and dried over anhydrous K₂CO₃. After removal of the ether at 150 mm., the residue was distilled at 8.5 mm., yielding 31.5 g. (90% of theory) of colorless product boiling at 105°C. (see Table V for analysis).

C₁₂H₂₅SO₃CH₃. To a stirred solution of C₁₂H₂₅SO₃Ag (17.9 g., 0.05 mole) in 200 ml. of CH₃CN at 80°C., CH₃I (10 g., 0.07 mole) was added dropwise at a rate to maintain a gentle reflux. After 1 hr. at reflux the mixture was cooled to room temperature and filtered through a sintered glass funnel. The solvent was removed from the filtrate under vacuum, and the residue was distilled to give 12.7 g. (96% of theory) of a colorless liquid boiling at 130–133°C. at 0.3 mm. (see Table V for analysis).

Methylsulfonatochloropolyethylene. To a stirred solution of 100 g. of chlorosulfonated polyethylene (Cl, 43%; S, 1.55%) in 1000 ml. of benzene was added 40 g. of NaOAc · 3H₂O dissolved in 118 ml. of methanol and 15 ml. of water. The mixture was then heated for one hour at reflux and coagulated in a Waring Blendor with methanol. After several methanol washes, it was dried at 50°C. and 100 mm. (see Table V for analysis).





Amides

The properties of the model compound amides and those from chlorosulfonated polyethylene are given in Table VI. The following procedures will serve to illustrate their preparations.

C₄H₉SO₂NHC₂H₅. To a stirred solution of 1-butanefulfonyl chloride (31.3 g., 0.2 mole) in 100 ml. of dry benzene at 0°C. was added dropwise a solution of ethylamine (22.5 g., 0.5 mole) in 25 ml. of benzene. The mixture was heated at reflux for 1¹/₂ hr., cooled to room temperature, and filtered to remove C₂H₅NH₂ · HCl. The solvent and excess amine were removed at 200 mm. and the residue fractionated to give 31.3 g. (95% of theory) of colorless liquid boiling at 100–102°C./0.3 mm.

Amides from Chlorosulfonated Polyethylene. To a stirred solution of 200 g. of Hypalon synthetic rubber (containing ~0.08 mole of SO₂Cl) in 1

TABLE VI
 Preparation of Alkanesulfonic Acid Amides

R	RSO ₂ NR'R''		Reaction conditions				Yield, %	Boiling range, °C./mm.	S, %		N, %	
	R'	R''	Solvent	Time, hr.	Temp., °C.	Calcd.			Found	Calcd.	Found	
Me	H	Et	C ₆ H ₆	1 1/2	Reflux	90	105.5-107/0.30	26.03	26.0	—	—	
Me	Et	Et	C ₆ H ₆	1 1/2	Reflux	92	58.5/0.35	21.20	21.1	—	—	
<i>n</i> -Bu	H	Et	C ₆ H ₆	1 1/2	Reflux	95	100-102/0.30	19.41	19.2	—	—	
<i>n</i> -Bu	Et	Et	C ₆ H ₆	1 1/2	Reflux	85	77/0.30	16.58	16.5	—	—	
Hypalon-20	H	Me	CCl ₄	20	25	Quant.	—	1.03	1.00	0.45	0.45	
Hypalon-20	Me	Me	CCl ₄	1	50	Quant.	—	1.03	1.10	0.44	0.50	
Hypalon-20	H	Et	CCl ₄	1	50	Quant.	—	1.03	0.93	0.45	0.46	
Hypalon-20	Et	Et	Dioxane	1	50	Quant.	—	1.03	1.00	0.44	0.37	
Hypalon-20	H	<i>n</i> -Pr	CCl ₄	2	50	Quant.	—	1.02	0.95	0.45	0.42	
Hypalon-20	<i>n</i> -Pr	<i>n</i> -Pr	CH ₃ COC ₂ H ₅	1	50	Quant.	—	1.01	1.00	0.44	0.34	
Hypalon-20	H	<i>n</i> -Bu	CCl ₄	2	50	Quant.	—	1.00	1.00	0.45	0.40	
Hypalon-20	<i>n</i> -Bu	<i>n</i> -Bu	Dioxane	2	65	Quant.	—	1.00	0.84	0.44	0.33	
Hypalon-20			CCl ₄	2	65	Quant.	—	1.02	1.10	0.45	0.50	
Hypalon-20			CCl ₄	1 1/4	50	Quant.	—	1.02	1.01	0.45	0.49	

liter of solvent at room temperature was added dropwise a solution of the amine (0.16 mole) in 50 ml. of solvent. The mixture was stirred at 25°C. and then at an elevated temperature according to the data given in Table VI. The polymer was precipitated with isopropanol and washed with water several times in a Waring Blendor and lastly with isopropanol. It was dried at 50°C. and 100 mm.

Salts

The preparation and properties of the alkanesulfonic acid salts are given in Table VII.

Acids

CH₃SO₃H. CH₃SO₃H was obtained from Eastman Kodak, distilled, and collected at 167°C./10 mm.¹⁷

***n*-C₄H₉SO₃H.** This was prepared by the hydrolysis of C₄H₉SO₂Cl according to the method of Asinger et al.²³ The product, boiling at 126–128°C./0.3 mm., was obtained in 84% yield.

ANAL. Calcd. for C₄H₁₀O₃S: C, 34.79%; H, 7.30%; S, 23.20%; Found: C, 34.8%; H, 7.3%; S, 22.9%.

***n*-C₁₂H₂₅SO₃H.** This compound was prepared after the method of Noller and Gordon.²² It was obtained in anhydrous form by drying over P₂O₅ at 80°C. and 1 mm.

ANAL. Calcd. for C₁₂H₂₆O₃S: C, 57.60%; H, 10.46%. Found: C, 57.0%; H, 10.7%.

Chloropolyethylenesulfonic Acid. A solution of 50 g. of chlorinated polyethylene (30.4% Cl) in 500 ml. of CCl₄ was dried by azeotropic distillation. The solution was cooled to 60°C. and agitated while 2.4 g. of chlorosulfonic acid in 25 ml. of dry CCl₄ was added dropwise. The reaction mixture was stirred at 60°C. for 1 hr. and coagulated with isopropanol. After washing in a Waring Blendor four times with methanol, it was dried at 50°C. and 100 mm.

ANAL. Calcd.: S, 1.27%. Found: S, 1.00%.

Infrared Spectra

All spectra (660–5000 cm.⁻¹) were determined on a Perkin-Elmer Model 21 recording spectrophotometer. The liquid model compound alkanesulfonic acids and their derivatives were used undiluted and the solid derivatives were determined as Nujol mulls. Derivatives of the chlorosulfonated polymers were deposited as films on NaCl windows by evaporation *in vacuo* of tetrahydrofuran–methanol solutions of the free sulfonic acid, its salts, and esters, and of CCl₄ solutions of the amides.

References

1. Barnard, D., J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, **1949**, 2442.
2. Baxter, J. N., J. Cymerman-Craig, and J. B. Willis, *J. Chem. Soc.*, **1955**, 669.
3. Haszeldine, R. N., and J. M. Kidd, *J. Chem. Soc.*, **1954**, 4228.
4. Haszeldine, R. N., and J. M. Kidd, *J. Chem. Soc.*, **1955**, 2901.
5. Smook, M. A., F. T. Pieski, and C. F. Hammer, *Ind. Eng. Chem.*, **45**, 2737 (1953).
6. Kern, W., R. C. Shulz, and H. Schlesmann, *Makromol. Chem.*, **39**, 1 (1960).
7. Bellamy, L. J., and R. L. Williams, *J. Chem. Soc.*, **1957**, 863.
8. Robinson, E. A., *Can. J. Chem.*, **39**, 247 (1961).
9. Bissinger, W. E., F. E. Kung, and C. W. Hamilton, *J. Am. Chem. Soc.*, **70**, 3940 (1948).
10. Bellamy, L. J., *The Infra-Red Spectra of Complex Molecules*, Wiley, New York, 1st Ed., 1954, p. 13.
11. Wiley, R. H., and D. E. Gensheimer, *J. Polymer Sci.*, **42**, 121 (1960).
12. Tipson, R. S., *J. Org. Chem.*, **9**, 235 (1944).
13. Sekera, V. C., and C. S. Marvel, *J. Am. Chem. Soc.*, **55**, 346 (1933).
14. McAlevy, A. (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,586,363 (February 19, 1952).
15. Heuse, R. O. (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,982,759 (May 2, 1961).
16. Noller, R. C., and P. J. Hearst, *J. Am. Chem. Soc.*, **70**, 3955 (1948).
17. Vivian, D. L., and E. E. Reid, *J. Am. Chem. Soc.*, **57**, 2559 (1935).
18. Davies, W., and W. E. Savige, *J. Chem. Soc.*, **1950**, 321.
19. Stewart, J. M., and H. P. Cordts, *J. Am. Chem. Soc.*, **74**, 5880 (1952).
20. Emmons, W. D., and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 2257 (1953).
21. Busse, W. F., and Smook, M. A. (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,723,255 (November 8, 1955).
22. Noller, C. R., and J. J. Gordon, *J. Am. Chem. Soc.*, **55**, 1090 (1933).
23. Asinger, F., G. Geiseler, and M. Hoppe, *Chem. Ber.*, **91**, 2137 (1958).
24. Taylor, R. C. (to Atlantic Refining Co.), U. S. Pat. 2,413,199 (December 24, 1946).

Résumé

On a comparé les spectres infra rouges du méthane, *n*-butane, et *n*-dodécane d'acides sulfoniques et de leurs esters, chlorures et amides ainsi que des sels de métal alcalin, d'argent et d'amines qui en dérivent, aux structures analogues dérivées de polyéthylènes chlorés et chlorosulfonés. La relation linéaire de Bellamy et Willim entre ν_{SO_2} (asym) et ν_{SO_2} (sym) est vérifiée à la fois pour les dérivés d'acide alcane-sulfonique et pour ceux de polyéthylène chlorés et chlorosulfonés.

Zusammenfassung

Die Infrarotspektren von Methan-, *n*-Butan- und *n*-Dodekansulfonsäuren, ihren Estern, Alkalimetall-, Silber- und Aminsalzen und Chloriden werden mit denjenigen analoger, von chlorierten und chloresulfonierten Polyäthylenen abgeleiteten Strukturen verglichen. Die lineare Beziehung von Bellamy und Williams zwischen ν_{SO_2} (asym.) und ν_{SO_2} (sym.) gilt sowohl für die einfachen Alkansulfonsäurederivate als auch für diejenigen chlorierter und chloresulfonierter Polyäthylene.

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