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# Studies on Sulfinic Acids

## VI.* The IR-Spectra of Aromatic Sodium Sulfinates and Sulfonates

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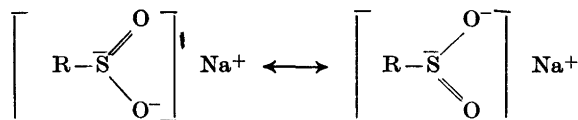*Research Division, Pharmacia AB, Uppsala, Sweden*

The IR-spectra of the sodium salts of a series of substituted aromatic sulfinic acids have been studied in aqueous solution in the region of the SO-stretching vibrations. The wave numbers of both the symmetric and asymmetric vibrations agree with the Hammett equation. The results are compared with the SO-stretching vibrations of related compounds, and for comparison the IR-spectra of a series of substituted aromatic sodium sulfonates have also been recorded in aqueous solution. The bearing of the results on the character of the SO-bonds is discussed.

The IR-spectra of aromatic sulfinic acids have previously been studied in the solid state or in organic solvents. Guryanova and Syrkin [1] reported the IR-spectra of some aromatic sulfinic acids in a study concerned with the structure of sulfinic acids. Detoni and Hadži [2] extended these studies to methyl benzenesulfinate, benzenesulfinyl chloride, and potassium benzenesulfinate, and concluded that of the two possible structures for sulfinic acids (I, II), structure I is favoured. They assigned a band near 1090 cm⁻¹ to the S=O-stretching vibration and a band near 860 to the S—O(H)-stretching vibration.
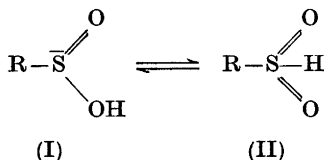


In the salts these bands were shifted to lower and higher frequencies, respectively. The sulfinic acids in this respect resemble the carboxylic acids and these shifts were taken as an evidence for a resonant structure of the sulfinate group in the alkali salts of sulfinic acids.[3]

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$$\left[ R-\overset{O}{\underset{O^-}{\overset{\nearrow}{S}}} \right] Na^+ \longleftrightarrow \left[ R-\overset{O^-}{\underset{O}{\overset{\nearrow}{S}}} \right] Na^+$$

In connection with a study on the structure of iron sulfinates Liepins studied the IR-spectra of some substituted aromatic sulfinic acids and their iron salts in the solid state.[4] Some of these compounds were also studied in dimethyl sulfoxide. She also studied some sodium sulfinates in the solid state and by comparison with the spectra of the iron salts it was concluded that the sulfinate group was non-resonant. A band of moderate intensity near 1045 $cm^{-1}$ was assigned to the S=O-stretching vibration and a strong band near 970 $cm^{-1}$ to the S—O(Na)-stretching vibration. Assuming that the force constants of the sulfur-oxygen bonds decrease by approximately 40 % relative to the corresponding carbon-oxygen bonds, Liepins expected a resonant sulfinate group to give two strong bands near 960 $cm^{-1}$ and 870 $cm^{-1}$ by analogy with the carboxylate group, and thus concluded that the alkali sulfinates were non-resonant:

$$R-\overset{O}{\underset{ONa}{\overset{\nearrow}{S}}}$$
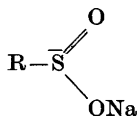
This conclusion is open to doubt and the assignments made are somewhat uncertain because of the complex character of the solid state spectra in these regions. In most of the sulfinic acids three principal bands were observed near 1082 $cm^{-1}$, 1058 $cm^{-1}$ and 1020 $cm^{-1}$. The band at 1082 $cm^{-1}$ became sharper in the sodium and iron salts but its intensity diminished, and it was considered to be associated with the substitution. The two remaining bands were thus assigned to the SO-vibrations. These were considered to be too low to be consistent with a resonant structure of the sulfinate group in the sodium salts. In the iron salts, the corresponding bands were shifted so as to give one single broad band. Since the spectra of carboxylic and sulfinic acids are influenced by hydrogen bonding,[5] the shifts in going from the acids to the salts may not be strictly comparable, and it seems reasonable that the "40 % rule" is only strictly applicable when comparing bonds of equal bond orders.

In the present investigation some of these difficulties have been eliminated by studying the IR-spectra of an extensive series of substituted aromatic sodium sulfinates, with which the previous papers of this series have been concerned, in aqueous solution. The region where the SO-stretching vibrations occur could be investigated satisfactorily in this medium, and the spectra were much simpler than those in the solid state. The bands associated with the SO-vibrations appeared as two very intense single peaks, which were easily distinguished from the vibrations associated with substitution by their broadness. The latter were very sharp and considerably weaker than the former. Since the sodium salts must be regarded as fully ionized in aqueous medium, these spectra must be associated with a resonant sulfinate structure,

and the two intense peaks were assigned to the symmetric and asymmetric SO-stretching vibrations, respectively. These peaks appeared near 965 cm$^{-1}$ and 1015 cm$^{-1}$. If the frequencies of the bands in the solid alkali metal sulfinates assigned to the SO-vibrations by previous authors are compared with those in aqueous solution, it is evident that the former agree best with a resonant structure.

The previous investigations of the IR-spectra of sulfinic acids have been mainly concerned with the hydrogen bonding. Since the character of sulfur-oxygen bonds is still an unresolved question [6] and there are indications that the correlation of IR-shifts with substituent constants can reveal interesting aspects on the character of these bonds,[7] it was deemed of interest to examine the SO-vibrations of the spectroscopically simpler salts more closely, and hence to correlate them with substituent constants and to compare them with the SO-vibrations in related compounds. Both the symmetric and asymmetric SO-stretching vibrations were found to be sensitive to the substituents and the wave numbers could be fairly well correlated with the Hammett equation.[7] The asymmetric vibration was the more sensitive.

For comparison, the IR-spectra of a series of substituted aromatic sodium sulfonates in aqueous solution were also recorded. The first comprehensive presentation of IR-spectra of aromatic sulfonic acids and of their esters and salts was given by Detoni and Hadži.[8] For the acids they assigned two strong bands near 1350 cm$^{-1}$ and 1160 cm$^{-1}$ to the degenerate asymmetric and symmetric SO-vibrations, respectively, and a band near 900 cm$^{-1}$ to the stretching vibration of the S—O(H)-bond. The spectra of metal sulfonates showed characteristic bands near 1200 cm$^{-1}$ and 1140 cm$^{-1}$. La Lau and Dahmen studied some aliphatic cyclohexylammonium sulfonates in carbon disulfide.[9] They found bands near 1180 cm$^{-1}$ and 1050 cm$^{-1}$ and observed broadening or splitting of the band near 1180 cm$^{-1}$. In the present investigation very simple

*Table 1.* SO-stretching vibrations in substituted sulfinic and sulfonic acids and their salts.

| Compound | Number of substituents | State | $\nu_{SO}$ asym. | $\nu_{SO}$ sym. | $\nu_{S=O}$ | $\nu_{S-O(H)}$ | Ref. |
|---|---|---|---|---|---|---|---|
| ArSO$_2$H | 3 | solid | | | 990—1090 | 810—870 | 2 |
| | | CHCl$_3$ | | | 1020 | 860 | 2 |
| ArSO$_2$Na | 1 | solid | 1020 | 970 | | | 2 |
| | 6 | solid | 1040 | 970 | | | 4 |
| | 19 | H$_2$O | 1015 | 965 | | | |
| ArSO$_2$OH | 3 | solid | 1350 | 1160 | | 900 | 8 |
| ArSO$_2$ONa | 3 | solid | 1200 | | | | 8 |
| | aliphatic | CS$_2$ | 1180 | 1050 | | | 9 |
| | 15 | H$_2$O | 1200 | 1035 | | | |
| | | | $\nu_{CO}$ asym. | $\nu_{CO}$ sym. | $\nu_{C=O}$ | $\nu_{C-O(H)}$ | |
| ArCOOH | | | | | 1680—1720 | 1075—1190 1280—1380 | 10 |
| ArCOONa | | H$_2$O | 1550 | 1385 | | | |

*Table 2 a.* IR-spectra of sodium benzenesulfinates, solid KBr.

| Substi-tuent | Observed bands in the region 900—1150 cm⁻¹ | | | | | |
|---|---|---|---|---|---|---|
| H | 973 (7) 980 (8) | 996 (8) 1004 (8) | 1025 (8) | 1048 (10) | 1070 (7) | 1086 (6) 1132 (2) |
| o-CH₃O | 959 (3) | 983 (8) | 1039 (9) | | 1062 (5) | 1138 (3) |
| o-CH₃ | 969 (10) | 1009 (10) | | | 1060 (5) | 1138 (4) |
| o-Cl | 955 (6) | 982 (9) | 1034 (9) | 1047 (10) | 1094 (8) | 1128 (4) |
| o-NO₂ | 998 (8) | 1030 (8) | | 1057 (6) | 1100 (3) | 1148 (1) |
| m-CH₃O | 968 (6) | 978 (7) | 995 (6) 1010 (8) | 1045 (5) | 1070 (2) | 1093 (2) |
| m-CH₃ | 976 (6) | 983 (6) | 996 (6) 1005 (7) | 1049 (9) | 1085 (4) | 1094 (3) |
| m-Cl | 979 (7) | 984 (6) | 995 (6) 1007 (7) | 1049 (9) | 1072 (5) | 1115 (4) |
| m-COONa | 950 (8) | 980 (sh) | 1003 (7) 1018 (7) | 1039 (7) | 1080 (5) | 1148 (4) |
| m-NO₂ | 998 (7) | 1009 (6) | 1036 (8) | 1049 (7) | 1069 (6) | 1084 (4) 1124 (2) |
| p-CH₃O | | 979 (6) | 1000 (7) 1010 (5) | 1031 (6) | 1051 (9) | 1089 (6) 1109 (2) |
| p-CH₃ | 952 (5) | 980 (7) | 1000 (8) 1021 (sh) | 1028 (6) | 1053 (9) | 1085 (6) |
| p-Cl | | 980 (9) | 1004 (9) 1015 (sh) | | 1050 (9) | 1080 (6) 1098 (4) |
| p-COONa | | 998 (8) | 1008 (7) | 1039 (9) | | 1082 (4) |
| p-COOH | 937 (4) | | 1011 (7) | 1027 (8) | 1080 (sh) | 1088 (8) 1129 (3) |
| p-CH₃CONH | 930 (8) | 969 (8) | 1010 (9) | 1030 (sh) | | 1087 (7) |
| p-CN | | 991 (9) | 1010 (9) | | 1055 (9) | 1089 (7) |
| p-NO₂ | 978 (7) | 992 (7) | 1015 (6) | 1022 (7) | 1060 (8) | 1076 (6) 1110 (4) |
| p-NH₃⁺ | 929 (10) | | 1013 (10) | 1028 (9) | | 1080 (6) |

spectra were obtained with the sodium sulfonates in aqueous solution. Two strong bands near 1200 cm⁻¹ and 1035 cm⁻¹ were observed, and the band near 1200 cm⁻¹ was considerably broader than that near 1035 cm⁻¹. These were assigned to the degenerate asymmetric and symmetric internal SO-stretching vibrations, respectively, and could because of their sensitivity to the substituent effects be distinguished from bands due to the aromatic substitution in the same region. The latter were very sharp compared with the asymmetric SO-stretching vibration. The SO-vibrations could, similarly to those of the sulfinate ion, be correlated with the Hammett equation, and the asymmetric stretching vibration was the more sensitive to substituent effects.[7]

In order to investigate the solvent effect, the tributylammonium salts of the sulfinic acids were also studied in carbon tetrachloride solution, but in this medium more complex spectra were obtained.

*Table 2 b.* IR-spectra of sodium benzenesulfinates, 15 % aqueous solution.

| Substituent | $\nu_{SO}$ sym. Broad s | $\nu_{SO}$ asym. Broad s | Arom. subst. | $C_{arom}-S$ | Arom. subst. | Misc. |
|---|---|---|---|---|---|---|
| H | 963.2 | 1011.9 | | 1090 w | | |
| | | | $A_1\beta CH$ | | $B_1\beta CH$ | 1176 w |
| o-CH₃O | 961.6 | 1010 | | 1064 w | 1136 vw | 1185 w |
| o-CH₃ | 962.6 | 1009 | | 1063 w | 1138 vw | 1198 vw |
| o-Cl | 966.5 | 1020.0 | 1035 sh | 1100 w | 1132 vw | |
| o-NO₂ | 970.9 | 1028.1 | | 1055 m | 1114 w | |
| m-CH₃O | 965.0 | 1017.0 | 1073 sh | 1098 w | | 1190 w |
| m-CH₃ | 963.7 | 1010.7 | 1096 w | 1082 w | 1178 vw | 1218 vw |
| m-Cl | 967.2 | 1018.8 | | 1077 w | | 1115 m |
| m-COONa | 964.0 | 1016.6 | 1080 sh | 1087 w | 1170 vw | 1142 w |
| m-NO₂ | 969.9 | 1028.0 | 1067 w | 1082 sh | — | — |
| | | | $B_2u\beta CH$ | | $B_3u\beta CH$ | $Ag\beta CH$ |
| p-NH₂ | 960.0 | 1002.5 | | 1089 m | | 1180 w |
| p-CH₃O | 961.5 | 1010.1 | ~1020 sh | 1089 s | 1112 vw / 1128 vw | 1182 m |
| p-CH₃ | 962.1 | 1008.8 | | | — | — |
| p-Cl | 965.0 | 1018.1 | | 1081 m / 1095 w | — | — |
| p-COONa | 963.5 | 1015.0 | | 1085 w | — | — |
| p-CH₃CONH | 961.6 | 1013.5 | | 1087 m | | 1180 w |
| p-CN | 969.5 | 1027.0 | | 1079 w | | |
| p-NO₂ | 970.0 | 1027.1 | | 1081 w | 1111 vw | |

The general features so far mentioned have been summarized in Table 1, where the values represent means. For the discussion of the shifts of the SO-frequencies in the transition from acid to salt, the corresponding shifts in the benzoic acids have also been included in Table 1. The results for the benzoates are taken from an investigation of the asymmetric and symmetric CO-stretching vibrations in a series of substituted sodium benzoates, which will be reported elsewhere.[11]

## RESULTS

*Sulfinates.* Typical spectra of some substituted sodium benzenesulfinates in the solid state and in aqueous solution are shown in Fig. 1. In Table 2a the vibrations observed in the SO-stretching region in the solid sulfinates are shown together with their relative intensities (scale 0—10). Table 2b shows the corresponding vibrations in aqueous solution. In this region there are several sharp bands due to the aromatic substitution. These are generally weak in the aqueous solution, and the assignments have been made using the data of
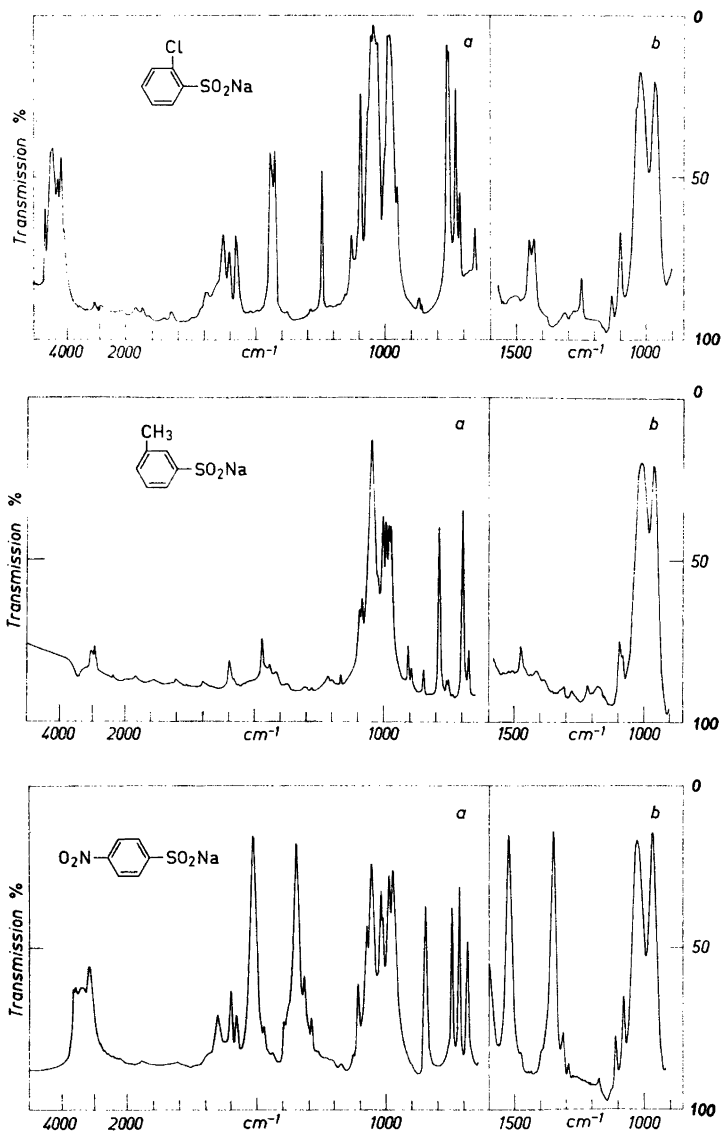
*Fig. 1.* IR-spectra of sodium *o*-Cl, *m*-CH₃, and *p*-NO₂ benzenesulfinate, a) Solid KBr, b) 15 % aqueous solution.

Randle and Whiffen.[12] The SO-stretching vibration bands are strong and broad. The asymmetric band is the broadest and has a half-width about 16 times that of the symmetric vibration. Both are dependent on the nature of the substituents and have, in the previous paper of this series, been plotted

*Table 3.* Statistical data for the correlation of SO-vibrations with substituent constants in aromatic sodium sulfinates.

| Vibration | $\varrho$ | $\nu_0$ cm$^{-1}$ | $s$ | $r$ |
|---|---|---|---|---|
| $\nu_{SO\ asym.}$ | 18.6 | 1013.7 | 1.4 | 0.986 |
| $\nu_{SO\ sym.}$ | 7.9 | 963.7 | 0.9 | 0.963 |

against the Hammett substituent constants for the *meta-* and *para*-substituted members. The statistical data for the Hammett plots are given in Table 3. In Fig. 2 the *ortho*-substituted members have been compared with the Hammett plot using the polar substituent constants given by Taft.[13] The steric effect seems to be small or moderate.

A fairly stable sharp band near 1080 cm$^{-1}$ appears in all sulfinates. This band has been observed in several other aromatic sulfur compounds.[8,14-16] It has been discussed by Kresze *et al.*,[16] who regard it as a characteristic C$_{aromatic}$—S vibration.

*Solvent effect.* The tributylammonium salts of the sulfinic acids were prepared in carbon tetrachloride solution by shaking the sodium salts with a solution containing an equivalent amount of tributylammonium chloride and filtering off the precipitated sodium chloride. The spectra were recorded using an equivalent concentration of tributylammonium chloride in the compensating cell in order to eliminate as far as possible bands from the
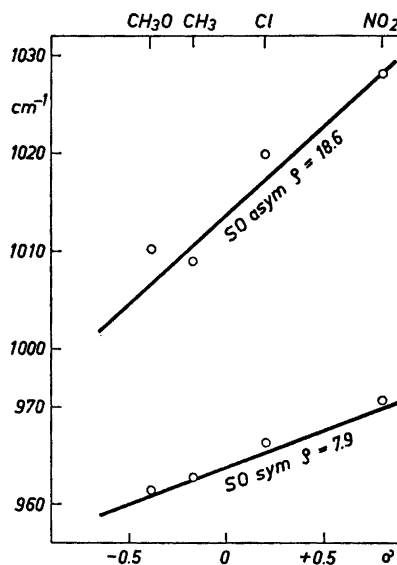


*Fig. 2.* Asymmetric and symmetric SO-stretching vibrations for *ortho*-substituted sodium benzenesulfinates, 15 % aqueous solution. Regression lines from *meta-* and *para*-substituted members, Ref. 7.

*Table 4.* IR-spectra of tributylammonium sulfinates, 0.1 N $CCl_4$ solution, (br = broad).

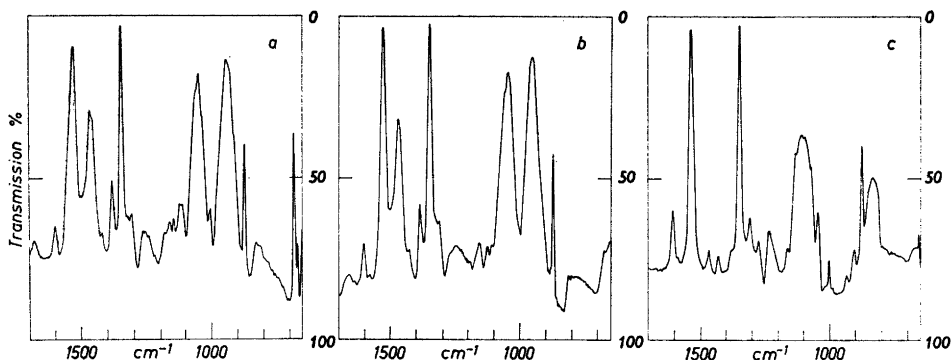| Substituent | range-1150 cm⁻¹ (900) | $\nu_{SO}$ sym. | $A_1$ ring | $A_1\ \beta CH$ | $\nu_{SO}$ asym. | $B_1\ \beta CH$ | $C_{arom}$—S ($\nu_{SO}$ sulfinic acid) | $B_1\ \beta CH$ |
|---|---|---|---|---|---|---|---|---|
| H | 900 | backgr. w ? | 1000 m | 1018 s | 1036 m | 1070 vw | | 1126 s |
| o-CH₃O | 950 | | | 1019 s | 1032 m br | | 1052 m    1092 m | 1141 m |
| o-CH₃ | 950 | | | 1017 s | ~1035 shvw | | 1067 vw    1091 m | — |
| o-Cl | 650 | 927 w ? | | 1016 s | 1033 m br | | 1067 s    1092 w | 1136 m |
| o-NO₂ | 650 | 943 s br | | 1033 sh | 1042 s br | | 1070 s    1108 w | 1123 w |
| | | | | | | | | *Misc.* |
| m-CH₃ | 950 | backgr. w ? | 998 m | | 1033 s | 1082 m | 1090 w | 1112 m |
| m-Cl | 950 | | 1002 m | 1038 sh | 1038 s br | 1074 sh | 1089 m | 1142 m |
| m-NO₂ | 650 | 938 s br | 1004 w | | 1052 s br | | 1067 sh    1109 w | 1148 w |
| | | | | *B₂u βCH* | | | | *B₃u βCH* |
| p-CH₃O | 950 | | | 1008 m | 1029 s br | | 1070 vw    1108 w | 1123 s |
| p-CH₃ | 950 | | | 1013 s | 1035 m | | 1068 w    1110 shvw | 1123 m |
| p-Cl | 900 | 927 vw ? | | 1010 s | 1033 m | | 1078 vw    1089 m | 1124 m |
| p-NO₂ | 650 | 935 s br | | 1015 w | 1051 s br | | 1071 sh m  1109 m | 1122 w |

*Fig. 3.* IR-spectra of *meta*-nitrobenzenesulfinic acid, a) 0.1 N tributylammonium salt in CCl$_4$, b) Do. in CHCl$_3$, c) 0.1 N acid in CHCl$_3$.

ammonium ion. In this medium, only sharp bands were obtained in the asymmetric SO-region. The region where the symmetric SO-vibrations occur was not adequately covered in all cases and the results in this region are somewhat doubtful because of the weakness of observed absorptions. Only in the case of the nitro-substituted salts a strong broad band that could with any degree of certainty be assigned to the symmetric SO-stretching mode was obtained in this region. In this case the band assigned to the asymmetric SO-stretching mode was also significantly broader than the other bands, whereas the corresponding bands in the rest of the salts were less broad. The spectra of the nitrobenzenesulfinic acid salts are shown in Fig. 3a, b.

The results are given in Table 4. The sharp band near 1020 cm$^{-1}$ assigned to a $\beta$CH vibration is ordinarily masked in aqueous solution. Bands in the C$_{aromatic}$—S bond region can also be recognized.

The sulfinic acids are sufficiently strong [17] to exist almost completely as salts in the presence of tributylamine. It is, however, difficult to say exactly what form these salts may have in carbon tetrachloride solution. They could well exist as strongly associated ion pairs. The solvent effect could also possibly influence the acid or basic strengths in such a manner that the salts could be partly protolysed. In this case bands due to the sulfinic acid could also be expected in the region investigated. Such bands would be most favoured by the least electronegative substituents. Some of the bands near 1060 cm$^{-1}$ could perhaps be partly due to sulfinic acid.

*Nitrobenzenesulfinic acids.* In order to investigate this question more closely, the spectra of the nitrobenzenesulfinic acids, which are the strongest in the series under study, were examined. With KBr disc technique and nujol mulls, complex spectra with numerous bands were obtained. The results are given in Table 5. These acids could not be examined in carbon tetrachloride because of poor solubility. They were therefore examined in chloroform in which they were adequately soluble, and for comparison the corresponding tributylammonium salts were also examined in chloroform. The

*Table 5.* IR-spectra of nitro-substituted aromatic sulfinic acids and their tributylammonium salts.

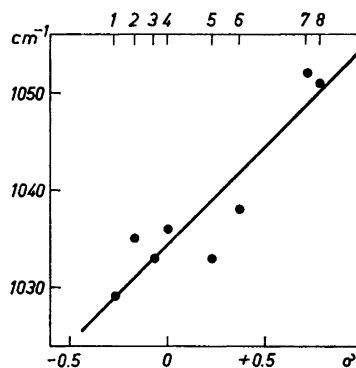| Substituent | State | $\nu_{S-O(H)}$ acid | Arom. subst. | $\nu_{SO}$ sym. salt | Arom. subst. | $\nu_{SO}$ asym. salt | $C_{arom}-S$ | $\nu_{S=O}$ acid | Arom. subst. |
|---|---|---|---|---|---|---|---|---|---|
| **o-NO₂** | | | **B₂,γ CH** | | | | | | **B₁βCH** |
| acid | Solid KBr | *794 s, 841 s* | 857 s | — | 1003 s | — | 1048 m | *1081 s* | 1119 m |
| | CHCl₃ sat. | *810 s* | 896 m | — | | — | | *1100 sh* | 1125 s |
| salt | CCl₄ 0.1 N | — | 859 s | *943* vs br | | *1042* vs br | 1070 s | — | 1108 w ? |
| | CHCl₃ 0.1 N | — | 851 s | *950* vs br | | *1041* vs br | 1063 s | — | 1106 m ? |
| | H₂O 15 % | — | 853 m | *970.9* vs br | | *1028.1* vs br | 1055 m | — | 1114 w |
| **m-NO₂** | | | | | **A₁ ring** | | | | |
| acid | Solid KBr | *817 s, 848 s* | 877 s | — | 998 s | — | 1072 s | *1065 s* | |
| | CHCl₃ sat. | *832 s* | 910 w | — | 1010 s | — | | *1105 svbr* | |
| salt | CCl₄ 0.1 N | — | 875 s | *938* vs br | 1004 w | *1053* vs br | 1072 sh | — | |
| | CHCl₃ 0.1 N | — | 869 s | *953* vs br | 1003 m | *1048* vs br | ∼1070 sh | — | |
| | H₂O 15 % | — | 877 m | *969.9* vs br | | *1028.0* vs br | 1082 sh | — | |
| **p-NO₂** | | | | | **B₂υβCH** | | | | **B₃υβCH** |
| acid | Solid KBr | *832 m* | 878 s | — | 1005 s | — | 1060 s | *1082 s* | 1111 m |
| | CHCl₃ sat. | *∼790 s* | 890 m | — | | — | | *1105 svbr* | 1125 s |
| salt | CCl₄ 0.1 N | — | 858 s | *935* vs br | 1016 m | *1052* vs br | 1072 sh | — | 1107 m ? |
| | CHCl₃ 0.1 N | — | 853 s | *952* vs br | 1016 s | *1048* vs br | 1074 s | — | 1108 m ? |
| | H₂O 15 % | — | 855 s | *970.0* vs br | | *1027.1* vs br | 1081 w | — | 1111 vw |

*Fig. 4.* Asymmetric SO-stretching vibration for substituted sodium benzenesulfinates, 0.1 N CCl₄ solution. Substituents: 1 $p$-CH$_3$O, 2 $p$-CH$_3$, 3 $m$-CH$_3$, 4 none, 5 $p$-Cl, 6 $m$-Cl, 7 $m$-NO$_2$, 8 $p$-NO$_2$. $\varrho = 20$.

results are given in Table 5, and the spectrum of $m$-nitrobenzenesulfinic acid is given in Fig. 3c.

The results confirm that the tributylammonium nitrobenzenesulfinates exist in the ionic form in carbon tetrachloride, and justify the assignments made for the asymmetric and symmetric SO-stretching vibrations. From Table 5, it can be seen that the solvent effect in going from water to the organic solvents causes an increased separation of the SO-stretching vibrations, but the mean value of the two bands remains almost the same. A Hammett plot for the asymmetric SO-stretching vibrations, although poorer than for the corresponding values in aqueous solution, gives a similar slope as in aqueous solution (Fig. 4). These results support the assignments made for the asymmetric SO-vibration.

*Sulfonates.* Typical spectra of some substituted aromatic sodium sulfonates in the solid state and in aqueous solution are shown in Fig. 5. In Table 6 the vibrations observed in the SO-stretching region in aqueous solution are shown. The band associated with the degenerate asymmetric stretching vibration is easily recognized by its broadness and is situated near 1200 cm$^{-1}$. In the case of the sulfonates, the bands due to the aromatic substitution are strong and sharp and only the asymmetric SO-band is broadened with a half-width of about 6 times that of the symmetric band. The symmetric SO-stretching vibration was recognized by its dependence on the substituent effect. The observed frequencies for benzenesulfonate correlate excellently with the equation derived by Exner for vibrations of the sulfonyl group:[18]

$$\frac{1}{2}\,(\nu_{\mathrm{s}} + \nu_{\mathrm{as}}) = 907 + X_i X_j$$
$$\frac{1}{2}\,(1037 + 1197.5) = 1117 \ (\mathrm{Obs.})$$
$$907 + X_{\mathrm{C_6H_5}} \times X_{\mathrm{O^-}} = 1118 \ (\mathrm{Calc.})$$

The asymmetric and symmetric bands have been plotted against the Hammett substituent constants in the previous paper of this series, and the statistical data for the plots are given in Table 7. The plots are similar to the corresponding plots for the sulfinates. The symmetric band occurs near 1035 cm$^{-1}$ and is accordingly less sensitive to the substituent effects than the asymmetric
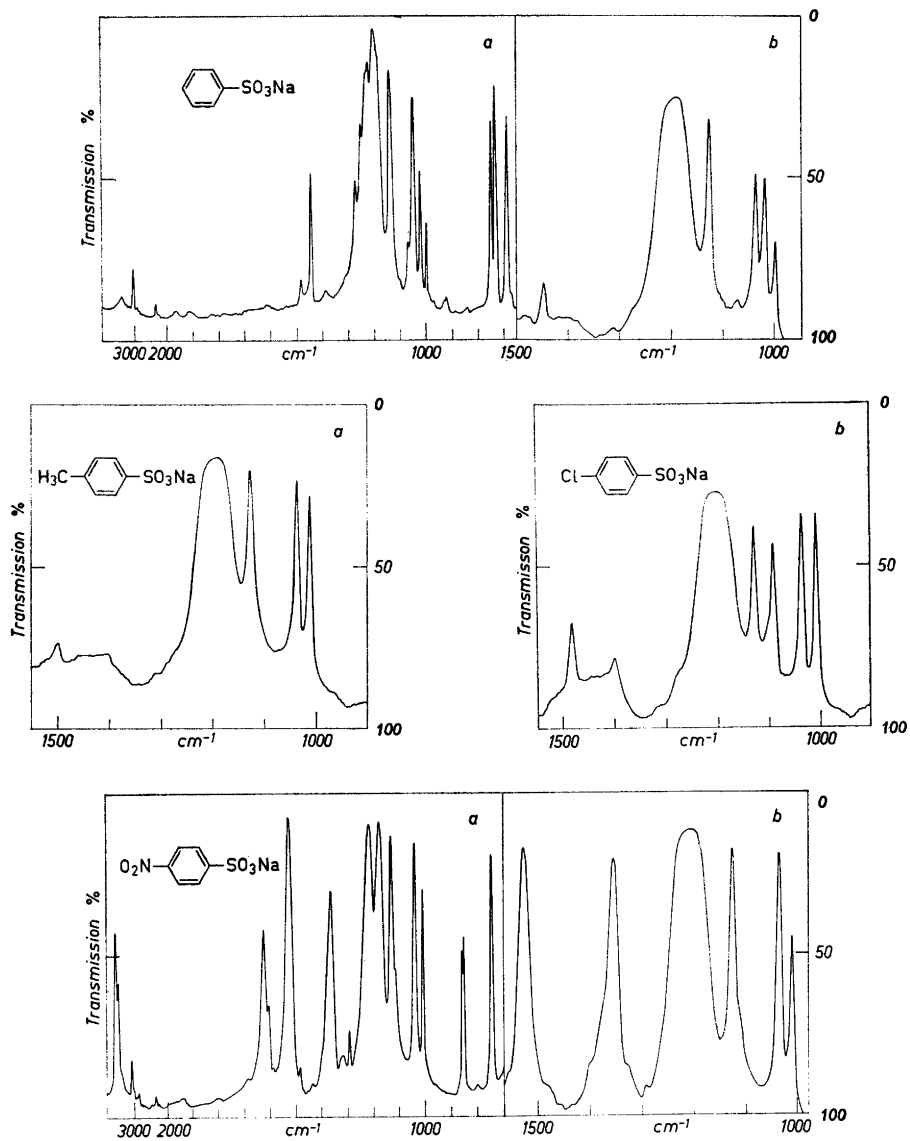
*Fig. 5.* IR-spectra of sodium benzenesulfonate and sodium *p*-CH₃, *p*-Cl, and *p*-NO₂ benzenesulfonate, a) Solid KBr, b) 12 % aqueous solution.

band. These bands have higher wave numbers and are more separated than the sulfinate bands.

In the cases where nitro-substituents were present the asymmetric and symmetric NO-stretching vibrations were also measured. In Table 8 the results

*Table 6.* IR-spectra of sodium benzenesulfonates, 12 % aqueous solution.

| Substituent | Arom. subst. | $\nu_{SO\ sym.}$ s | $C_{arom} - S$ | Arom. | subst. | $\nu_{SO\ asym.}$ s vbr |
|---|---|---|---|---|---|---|
| | $A_1$ ring | | | | $B_1\ \beta CH$ | |
| H | 999 m 1019 s | 1037 | | | 1128 s | 1197.5 |
| | $A_1\ \beta CH$ | | | | $B_1\ \beta CH$ | |
| $o$-NH$_2$ | 1019.5 s | 1038 m | 1073 m | | 1120 m | 1193 |
| | $A_1$ ring | | | $A_1\beta CH$ | $B_1\ \beta CH$ | |
| $m$-COONa | 999 w | 1037 | 1103 s | 1085 sh | | 1198 |
| $m$-COOH | 999 w | 1038 | 1103 s | 1085 sh w | 1158 sh | 1207 |
| $m$-NO$_2$ | 1000 m | 1040 | 1092 m | 1080 sh | 1151 m | 1211 |
| | $B_2\ u\beta CH$ | | | $B_3\ u\ \beta\ CH$ | | |
| $p$-(CH$_3$)$_2$N | 1011 m | 1032.5 | | 1123 s | | 1191.7 |
| $p$-NH$_2$ | 1007 m | 1031 | | 1125 s | | 1188 |
| $p$-OH | 1009 m | 1032.5 | 1108 sh | 1128 s | | 1195 |
| $p$-CH$_3$ | 1011 s | 1037 | | 1128 s | | 1197 |
| $p$-Cl | 1009 s | 1038 | 1092 s | 1130 s | | 1204 |
| $p$-COONa | 1010 s | 1035 | | 1119 s | 1149 w | 1201 |
| $p$-COOH | 1011 s | 1037 | | 1115 s | 1138 w | 1206 |
| $p$-SO$_3$Na | 1004 s | 1038 | 1110 sh w | 1135 s | | 1205 |
| $p$-NO$_2$ | 1010 s | 1036 | 1110 sh w | 1127 s | | 1210 |
| $p$-(CH$_3$)$_3$N$^+$ | 1010 m | 1042 | | 1114 m | 1142 w | ~1217 |

are shown together with the asymmetric and symmetric vibrations for the other groups discussed. In this table, it can be seen that the constant, $\varrho$, for the asymmetric XO-vibrations decreases with the frequency of the vibration whereas for the symmetric vibrations it increases.

*Accuracy.* The simplification of the spectra by the use of water as solvent which necessitates high concentrations, is obtained at the expense of the broadening of some bands. We have also seen that some bands are masked

*Table 7.* Statistical data for the correlation of SO-vibrations with substituent constants in aromatic sodium sulfonates.

| Vibration | $\varrho$ | $\nu_0$ cm$^{-1}$ | $s$ | $r$ |
|---|---|---|---|---|
| $\nu_{SO\ asym.}$ | 16.4 | 1199.6 | 1.9 | 0.973 |
| $\nu_{SO\ sym.}$ | 5.3 | 1035.6 | 1.6 | 0.795 |

by the broadened bands. It is difficult to estimate how far the assumption that the broader bands, especially the asymmetric, represent only SO-stretching vibrations, renders the results inaccurate. The fairly good fits to the Hammett equation are, however, an indication that these bands are dominated by the SO-stretching vibrations, and as they in most cases are very symmetrical, the evaluation of their wave numbers is comparatively easy. The maximum uncertainty in the evaluation of the wave numbers from the peaks is $\pm 3$ $cm^{-1}$, but in most cases it is less, approaching $\pm 1$ $cm^{-1}$. The accuracy of the measurements is estimated to $\pm 2$ $cm^{-1}$.

For both sulfinates and sulfonates the ordinary $\sigma$ constants give the best correlation with the Hammett equation. The $\sigma^+$ or $\sigma^-$ constants, which in some cases give better correlations with IR-data than the $\sigma$ constants, give poorer fits with the present material. For the plots [7] and calculations the $\sigma$ constants given by Jaffé [37] were used. These gave better fits than more recent $\sigma$ constants given by Ritchie and Sager [38] for the following substituents: $p$-$N(CH_3)_2$, $m$, $p$-$COO^-$, and $p$-$SO_3^-$.
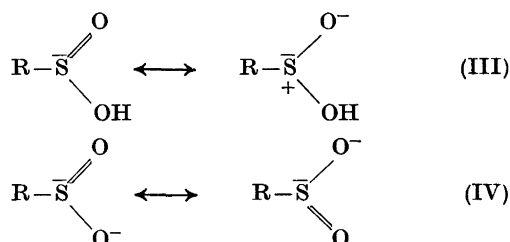
## DISCUSSION

*Shifts from acids to salts.* If the shifts from acids to salts in Table 1 are compared, the most striking fact is the small difference between the S=O-stretching frequency in sulfinic acids and the asymmetric SO-stretching frequency in the salt. Comparing this difference with the corresponding difference in carboxylic acids, Liepins, as already mentioned, concluded that the sulfinic acid salts were non-resonant.[4] It has now been shown that the asymmetric and symmetric SO-stretching frequencies are essentially the same in aqueous solution as in the solid salts (Table 1), and that their dependence on substituent effects is similar to that of the corresponding vibrations in sulfonic and benzoic acids. The sulfinic acid salts are therefore most probably resonant also in the solid state.
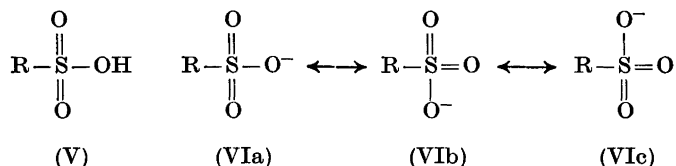
The S=O-stretching vibration of sulfinic acids occurs in the same region as that of sulfoxides. Increasing evidence is accumulating in the literature, that the SO-bond in sulfoxides is best represented as intermediate between a double and a semipolar bond:[6]
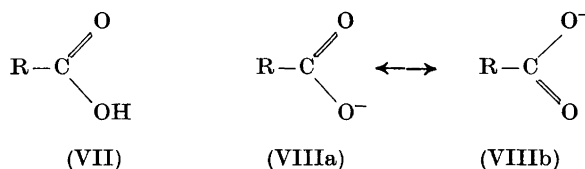
$$\diagdown\!\!{}_{\diagup}\overset{|}{S}{=}O \qquad\qquad \diagdown\!\!{}_{\diagup}\overset{|}{S}{}^{+}{-}O^{-}$$

It therefore seems reasonable to represent the sulfinic acids and their salts by the resonant pairs III and IV, respectively:

$$R-\overline{S}\diagup^{\displaystyle O}_{\diagdown\,OH} \quad\longleftrightarrow\quad R-\overline{S}\diagup^{\displaystyle O^{-}}_{\overset{+}{\diagdown}\,OH} \qquad\qquad \text{(III)}$$

$$R-\overline{S}\diagup^{\displaystyle O}_{\diagdown\,O^{-}} \quad\longleftrightarrow\quad R-\overline{S}\diagup^{\displaystyle O^{-}}_{\diagdown\!\!\diagdown\,O} \qquad\qquad \text{(IV)}$$

These correspond to a SO-bond order of 1.5 in both acids and salts. In the sulfonic acids where the electronegativity on the sulfur is increased by another oxygen ligand and where no electron pair can reduce it, one would expect a higher SO-bond order. It may therefore be reasonable to represent the sulfonic acids and their salts by the structures V and VI:

$$
\underset{(\text{V})}{R-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH}
\qquad
\underset{(\text{VIa})}{R-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-O^-}
\longleftrightarrow
\underset{(\text{VIb})}{R-\overset{\displaystyle O}{\underset{\displaystyle O^-}{\overset{\|}{\underset{|}{S}}}}=O}
\longleftrightarrow
\underset{(\text{VIc})}{R-\overset{\displaystyle O^-}{\underset{\displaystyle O}{\overset{|}{\underset{\|}{S}}}}=O}
$$

With this formulation, the bond orders determining the SO-frequencies decrease from 2 to 1.7 in going from acid to salt, and hence greater shifts could be expected. Similarly, if the carboxylic acids and their salts are represented by the structures VII and VIII, the corresponding bond orders decrease from 2 to 1.5 and hence large shifts could also be expected in this case. The shifts in Table 1 are in qualitative agreement with this.

$$
\underset{(\text{VII})}{R-C\overset{\displaystyle O}{\underset{\displaystyle OH}{}}}
\qquad
\underset{(\text{VIIIa})}{R-C\overset{\displaystyle O}{\underset{\displaystyle O^-}{}}}
\longleftrightarrow
\underset{(\text{VIIIb})}{R-C\overset{\displaystyle O^-}{\underset{\displaystyle O}{}}}
$$

Gillespie and Robinson have proposed a simple treatment for correlating IR-frequencies with bond orders.[19] For an $AB_x$ group with degeneracy $(x - 1)$, the average frequency for the asymmetric stretching is defined by the so-called average rule:

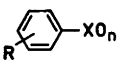$$\nu_{AB} = \frac{1}{x}\left[\nu_{\text{sym}} + (x - 1)\,\nu_{\text{asym}}\right]$$

In the case of SO-bonds this frequency is related to the bond order by the following equations:

$$k_{SO} = 0.63\ \nu_{SO}^2$$
$$n = 1.11 \times 10^{-6}\ k + 0.7$$

Here $k$ and $n$ represent force constants and bond orders, respectively. Bond orders calculated in this way from the data in Table 1 are given in Table 9. In this table the $\nu_{SO}$ shifts from acids to salts are also compared with the shifts in bond orders. The bond order of the SO-bond in sulfinic acids is close to that of dimethyl sulfoxide calculated by Gillespie and Robinson (1.56). The results are in good agreement with the deductions based on the structures proposed above.

*Solvent effect.* The solvent effect on the SO-stretching frequency in various sulfoxides has been studied by Biscarini and Ghersetti.[26] The frequency diminishes with increasing polarity of the solvent, and the solvents studied by these authors affect the SO-vibration according to the following order: $C_6H_6 > CCl_4 > CS_2 > trans\text{-}ClCH_2CH_2Cl > cis\text{-}ClCH_2CH_2Cl > CH_3NO_2 > CHCl_3$. The same order between $CCl_4$ and $CHCl_3$ holds for the asymmetric SO-stretching vibration in the sulfinates (Tables 5 and 8) and including water the follow-

*Table 8.* Solvent effect on NO-stretching vibrations and the dependence of $\varrho$ on vibration frequency in $XO_n$ groups.

| $XO_n$ | R | $\nu_{XOas}$ | $\nu_{XOs}$ | $\nu_{XOas}$ | $\nu_{XOs}$ | $\nu_{XOs}$ | $\nu_{XOas}$ | $\varrho_{as}$ | $\varrho_s$ |
|---|---|---|---|---|---|---|---|---|---|
| | | CCl_4 | | CHCl_3 | | H_2O | | | |
| $CO_2^-$ | Mean[a] | | | | | 1548 | 1390 | 25 | 2 |
| $NO_2$ | $o,m,p$-SO$_2^-$ | *1525* | *1345* | *1530* | *1347* | *1524* | *1357* | | |
| | $o,m,p$-SOOH | | | 1534 | 1350 | | | | |
| | $p$-SO$_3^-$ | | | | | 1534 | 1357 | | |
| | $m,p$-CO$_2^-$ | | | | | 1534 | 1356 | | |
| | Mean | | | $\varrho = 23^{21}$ | | 1530 | 1354 | | |
| $SO_3^-$ | Mean[a] | | | | | 1200 | 1036 | 16.4 | 5.3 |
| $SO_2^-$ | Mean[a] | 1036 | ~930 | 1030 | | 1014 | 964 | 18.6 | 7.9 |
| | $o,m,p$-NO$_2$ | *1049* | *939* | *1046* | *952* | *1028* | *970* | | |

[a] $\nu$ values for $\sigma = 0$ in the Hammett plots are given.

ing order is obtained: $CCl_4 > CHCl_3 > H_2O$. For the symmetric SO-stretching vibration in the nitro-substituted members, the opposite order holds but the total solvent effect on the mean frequency is small. In Table 8, the solvent effect on the NO-vibrations of the nitro group is shown. It is very slight for the asymmetric vibration and follows the same order for the symmetric vibration as the symmetric SO-vibration in the sulfinates. Finally, in Table 10, the dependence of the SO-vibration on the inductive substituent constant $\sigma_I$ for X in compounds of the type RSOX is shown. The general tendency is that the frequency increases with increasing $\sigma_I$. The order of the solvent effect between $CCl_4$ and $CHCl_3$ is $CCl_4 > CHCl_3$ in all cases. The $\varrho$'s increase with increasing polarity of the solvent.
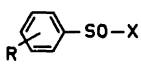
## CONCLUSION

In previous papers of this series it has been shown that the reactivity of the aromatic sulfinate ion can be correlated satisfactorily with the Hammett equation using the ordinary $\sigma$ constants.[28,29] The fact that the asymmetric

*Table 9.* Relationship between SO-stretching frequencies and SO-bond orders, $n$, in aromatic sulfinic and sulfonic acids and their salts.

| Compound | $\nu_{SO}$ asym. / $\nu_{CO}$ asym. | $\nu_{SO}$ sym. / $\nu_{CO}$ sym. | $\nu_{S=O}$ acid / $\nu_{C=O}$ acid | $\nu_{SO}$ calc. / $\nu_{CO}$ calc. | $n$ | Shifts from acid to salt | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $\Delta n$ | $\Delta$ $\nu_{acid} - \nu_{calc.}$ | $\Delta$ $\nu_{acid} - \nu_{asym.}$ |
| ArSOOH | 1014 | 964 | 1050 | | 1.47 | 0.08 | 61 | 35 |
| ArSO$_2$Na | 1350 | 1160 | | 989 | 1.39 | 0.23 | 137 | 150 |
| ArSO$_2$OH | 1200 | 1036 | | 1255 | 1.80 | | | |
| ArSO$_3$Na | | | | 1118 | 1.57 | | | |
| ArCOOH | 1548 | 1390 | 1700 | | ~2.0 | ~0.5 | 232 | 152 |
| ArCO$_2$Na | | | | 1468 | ~1.5 | | | |

*Table 10.* Solvent effect and inductive effect of X on SO-stretching vibrations in -SOX groups.

| R-⬡-SO-X | | $CCl_4$ | | $CHCl_3$ | | $H_2O$ | | Ref. |
|---|---|---|---|---|---|---|---|---|
| X | $\sigma_I$ | $\nu_{SO}$ | $\varrho$ | $\nu_{SO}$ | $\varrho$ | $\nu_{SO}$ | $\varrho$ | |
| $O^-$ | $-0.12^a$ | 1036 as | 20 | 1030 as | | 1014 as | 18.6 | |
| $NH_2$ | 0.11 | 1048 | solid$^c$ | | | | | 15 |
| ⬡ | 0.08 | 1052 | 4.3 | 1041 | 9.3 | | | 22 |
| $CH_3$ | $-0.03$ | 1057 | ~5 | 1045 | 11.5 | | | 22 |
| OH | 0.31 | ~1090 | | | | | | 2 |
| S-⬡ | ~0.3$^b$ | 1108 | 11.3 | 1091 | | | | 23, 24 |
| $OCH_3$ | 0.33 | 1138 | 6.5 | 1128 | 10.6 | | | 25 |
| Cl | 0.51 | 1160 | 9.5 | 1150 | 11.6 | | | 25 |

$^a$ From Taft *et al.*[26] For the other substituents the corrected $\sigma_I$ constants of Exner have been used.[27]

$^b$ From Exner.[18]

$^c$ *p*-CH$_3$.

and symmetric SO-stretching vibrations of the aromatic sulfinate ion is best correlated with the ordinary $\sigma$ constants indicates that the substituent effects on these vibrations and the reactivity mainly depend on the same factors.

The general vibrational behaviour of the SO-bonds in the aromatic sulfinate ion is best explained by a resonant structure with an SO-bond order of about 1.5.

## EXPERIMENTAL

*Preparation of sulfinates.* The preparation of most of the sodium sulfinates has been described in earlier papers.[29,30]

p-*Carboxybenzenesulfinic acid* was prepared by reduction of *p*-carboxybenzenesulphonyl chloride with sodium sulfite according to Smiles and Harrison.[31] 18 g of carboxybenzenesulphonyl chloride gave after one recrystallization 13 g of product. (Found: C 45.3; H 3.3; S 17.1. Calc. for $C_7H_6SO_4$: C 45.1; H 3.2; S 17.2. $E_{NaOH}$ 185.8; $E_{calc.}$ 186.2). The disodium salt was prepared by neutralization with aqueous sodium hydroxide and precipitation with ethanol (Found: C 37.0; H 2.0; S 13.7. Calc. for $C_7H_4SO_4Na_2$: C 36.5; H 1.7; S 13.9).

p-*Carboxybenzenesulfonyl chloride* was prepared by treating sodium *p*-carboxybenzenesulfonate with chlorosulfonic acid according to Smiles and Harrison.[31]

*Monosodium* p-*carboxybenzenesulfonate* was prepared by oxidation of sodium *p*-toluenesulfonate with potassium permanganate in neutral solution according to Smiles and Harrison.[31]

m-*Carboxybenzenesulfinic acid* was prepared by reduction of *m*-carboxybenzenesulfonyl chloride with sodium sulfite according to Davis and Smiles[32] with the modification that the monochloride was used instead of the dichloride. The acid was extracted with ether from the reaction mixture, the ether was allowed to evaporate and the residue

was dissolved in water and reextracted with ether. By neutralization of the ether extract with sodium ethoxide, the disodium salt was obtained as a precipitate. 15 g of m-carboxy-benzenesulfonyl chloride gave 5.8 g of disodium salt. (Found: S 14.3. Calc. for $C_7H_4SO_4Na_2$: S 13.9. $E_{KMnO_4}$ 115.8; $E_{calc.}$ 115.4).

m-*Carboxybenzenesulfonyl chloride* was prepared by chlorosulfonation of benzoyl chloride with chlorosulfonic acid.[33]

*Preparation of sulfonates.* Sodium salts of p-OH, p-Cl, m-COOH, m- and p-NO$_2$ benzene-sulfonic acids were available as analytical reagents. Sodium salts of p-NH$_2$, o-NH$_2$, p-CH$_3$, and unsubstituted benzenesulfonic acid were prepared by neutralization of the commercial analytical reagent grade acids. Disodium salts of m- and p-carboxybenzene-sulfonic acids were prepared by neutralization of the corresponding monosodium salts.

p-*Benzenedisulfonic acid* was prepared by treating diazotized sulfanilic acid in concentrated hydrochloric acid with sulfur dioxide in glacial acetic acid with copper(I) chloride as a catalyst according to Meerwein et al.[34] The disodium salt was isolated by salting out with sodium chloride, and recrystallizing from saturated sodium chloride solution. The isolated salt contained some sodium chloride from the isolation procedure.

*Sodium* p-*dimethylaminobenzenesulfonate* was prepared by treating sulfanilic acid with dimethyl sulfate in strong alkali according to Fierz-David and Blangey.[35] Yield 30 %. (Found: N 6.2; S 14.2. Calc. for $C_8H_{10}NO_3SNa$: N 6.3; S 14.3).

p-*Trimethylammoniumbenzenesulfonate* was prepared by treating sodium p-dimethyl-aminobenzenesulfonate (I) with trimethylsulfoxonium iodide [36] (II) in dimethyl sulfoxide. 3.3 g (0.015 mole) of I was dissolved in 8 ml of DMSO. 3.3 g (0.015 mole) of II was dissolved in 19 ml of DMSO. The solutions were mixed and heated to 120° for 5 min. Upon cooling, 1.5 g of white crystals were obtained. Recrystallization from water-ethanol 1:1 gave 1.2 g of product. Yield 37 %. (Found: C 49.9; H 6.2; N 6.2; S 14.9. Calc. for $C_9H_{13}NO_3S$: C 50.9; H 6.1; N 6.5; S 14.9).

*IR-Spectra.* The IR-spectra were recorded with a Unicam SP 100 spectrophoto-meter. Polystyrene was used for calibration. A liquid cell with Irtran-2 windows was used for the aqueous solutions and a liquid cell with KBr windows for the carbon tetra-chloride and chloroform solutions.

The spectra of the monosodium m- and p-carboxybenzenesulfonates were recorded at pH 2.0, at which the carboxyl group exists mainly in acid form and the sulfonic group exists mainly in ionized form.

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