mate and barium 2-furylcarbamate have been prepared; and certain reactions of the first four have been studied.

Isolation of 2-furyl isocyanate in syntheses in which it is an intermediate compound has been shown to be advantageous in some instances.

The usefulness of the Curtius reaction for the introduction of nitrogen into the alpha position in the furan series has been demonstrated further, and some of the favoring conditions have been determined.

BATON ROUGE, LA. RECEIVED OCTOBER 18, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Raman Spectra of Sodium Alkyl Sulfonates and Sulfinates

BY HAROLD G. HOULTON[1] AND H. V. TARTAR

Introduction

The constitution of the sulfinic acids has long been an open question. In addition, further confirmatory evidence concerning the structure of the sulfonates also should be of considerable interest. The purpose of this investigation was to establish, if possible, their type of valence bonds. The Raman effect has always been characterized by the attribution of certain wave number shifts to certain bonds in the molecule. It is possible by this means to establish the bonds existing in the sulfonic and sulfinic acid groups. In order to have the most rigorous solution to the problem, the simplest molecules containing these groups were taken for investigation, *i. e.*, the lower members of the saturated alkyl series.

Little work has been done in recent years on the lower members of the alkyl sulfonates and sulfinates. One of the first investigations on the structure of sulfinic acid was that of P. Claesson[2] in 1877, on sodium ethyl sulfinate. From that time until 1931 practically no work was done on this series of compounds. Von Braun and Weissbach[3] in 1931 prepared butyl sulfinic acid but did nothing to establish its constitution. In no case have definite directions been given for the preparation of this series of sulfinates and it is deemed advisable to include the details herein.

Some of the earliest work on alkyl sulfonic salts was carried out by Hemilian[4] who reported yields of 90%. Wagner and Reid[5] using the same method obtained only 50–60%. In this investigation we substituted sodium sulfite for the ammonium sulfite used by these workers and the yields ranged 85–90%. Consequently, the details of preparation are also included.

Experimental

Preparation of Sulfonates.—The bromides used were either supplied by the Eastman Kodak Company or were prepared by the method outlined in Gilman.[6] One mole of the bromide, 1.15 moles of sodium sulfite and 750 cc. of water were refluxed for approximately twelve hours, *i. e.*, until the bromide disappeared.

The resulting solution was evaporated to dryness on a steam-bath, dried at 110°, pulverized, and finally extracted twice with petrol ether. The excess of this solvent was removed by heating on a steam-bath. The solid thus obtained was placed in a five-liter, round-bottomed flask, two liters of alcohol (denatured, formula No. 30) added, heated to boiling, and filtered with suction to remove the excess sodium sulfite. The alcoholic solution was then cooled overnight in a refrigerator and again filtered with suction. By this procedure the yield was 75%. The remaining 25% was obtained by distilling the excess alcohol and cooling. The salt was then dried at 110° and recrystallized using one liter of alcohol per mole, 85% yields being obtained. The excess sodium sulfite sometimes approached the colloidal state and consequently all filters, with the exception of suction, clogged badly. If the salt is dried thoroughly after the addition of the petroleum ether the colloidal properties are greatly reduced. By this method, ethyl, propyl, butyl, and amyl sodium sulfonates were prepared.

Preparation of Sulfinates.—To a three-necked, three-liter flask were connected a separatory funnel, a mercury-sealed mechanical stirrer, and a reflux condenser. Three moles of magnesium turnings, previously washed with anhydrous ether, 500 cc. of anhydrous ether, 5 cc. of the bromide concerned (previously distilled from phosphorus pentoxide) and a crystal of iodine were added in the order given. The remainder of the three moles of the bromide dissolved in 500 cc. of anhydrous ether was added from the separatory funnel to the top of which was connected a calcium chloride drying tube. A similar tube was also placed in the top of the reflux condenser. The ether solution of the bromide may be added as fast as the refluxing will permit, and the addition may therefore be decidedly

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[2] Claesson, *J. prakt. Chem.*, **15**, 222 (1877).

[3] Von Braun and Weissbach, *Ber.*, **63**, 2836 (1930).

[4] Hemilian, *Ann.*, **168**, 146 (1873).

[5] Wagner and Reid, THIS JOURNAL, **53**, 3407 (1931).

[6] Gilman, "Collected Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1934.

facilitated by cooling the upper part of the flask with ice. It was necessary to have a 3.8-cm. seal on the mechanical stirrer and the cylinder holding the mercury seal should be 10 to 12.5 cm. in length. This was required because negative pressures of approximately 2.5 cm. of mercury were sometimes developed and this length prevents any mercury from getting into the reaction flask. A brass stirrer was used; one made of glass broke due to the solid formed after the addition of sulfur dioxide. After the Grignard was complete a liter of anhydrous ether was added, the separatory funnel removed and replaced by a glass tube (1 cm. diameter) through which previously dried sulfur dioxide or nitrogen might be introduced and the condenser replaced by a two-holed stopper, one hole of which contained a toluene thermometer, the other hole an outlet tube with a mercury trap to develop a half centimeter head. The flask was surrounded by an alcohol-bath to which solid carbon dioxide was added until the temperature within the flask had reached −50°. During this cooling sulfuric acid-dried nitrogen was introduced; without this precaution a 5% lower yield was obtained. It is necessary to carry out the reaction at this low temperature because (a) the reaction is highly exothermic, (b) the solid salt formed, magnesium alkyl sulfinate, coats the inside of the flask causing low heat transfer, and (c) many side reactions take place at the higher temperatures due to the strong reducing properties of the Grignard. The sulfur dioxide was then passed through a set of driers, into the reaction flask at an absorbing rate that kept the temperature below −15°. A too rapid rise in temperature was prevented by shutting off the sulfur dioxide and running in the nitrogen. The completion of the reaction was indicated by a continuous drop in temperature. For a three mole run 15 pounds (7 kg.) of solid carbon dioxide sufficed.

After the reaction was complete, the flask was allowed to come to room temperature and the salt hydrolyzed directly in the reaction flask with 12 N sulfuric acid; the sulfinic acid so produced immediately dissolved in the ether present. Because of the solubility of ether in concentrated sulfuric acid, a concentration greater than 12 N was avoided. The ether layer was decanted into a two-liter separatory funnel and the remaining sulfuric acid layer extracted several times with fresh 100-cc. portions of ether. Owing to the large amounts of magnesium bromide formed, some of the magnesium alkyl sulfinate was not hydrolyzed; this was overcome by grinding the sulfuric–magnesium bromide layer before further washing with the 100-cc. portions of ether. The ether extract was next shaken with 50-cc. portions of a saturated sodium carbonate solution until evolution of carbon dioxide ceased. The ether extract was yellow, due to the presence of the sulfinic acid, and the reduction products were very irritating to the eyes and skin. The sodium carbonate–sulfinate layer was separated and the excess ether distilled off in the presence of excess of sodium carbonate solution. The residue was then added to the previous batch and the whole was evaporated to dryness. The salt thus formed was recrystallized twice from absolute alcohol. Absolute alcohol was necessary because the salts are very hygroscopic and with water form a sirup from which they do not crystallize.

Apparatus.—The arc used was of hot cathode, mercury–neon type, operating at 2500 volts. It has the advantage over the cold cathode type in that much higher currents can be obtained with corresponding increase in light intensity. This type of arc competes with the capillary mercury-arcs for brilliancy while it excels in that its average life is very much longer, about twenty-five hundred hours.

The Pyrex tubing required to carry 300 m. a. is 10 mm. diameter; by water cooling, however, 900 m. a. can be used. The cooling bath was of such size that a temperature of 60° was maintained at all times. No attempt was made to obtain maximum current through the arc by cooling continuously. This would have necessitated a specially built transformer. The arc, therefore, has possibilities not yet investigated. We have no reason to doubt that even better light intensity might be obtained by increasing the current to 3 or even 5 amperes. Three magnetically-shunted transformers were connected in parallel to deliver the 900 m. a. current.

The water cooled arc was a helix of ten loops through the center of which passed the Raman tube with glass-sealed filtering tubes. On the outside of the arc was a chromium-plated brass cylinder (12.7-cm. diameter) which concentrated to the utmost the high light intensity. The Raman tube passing through the galvanized iron water-bath was made water tight by a pack nut. A draw-band was first tried but proved unsatisfactory. The arc, reflector, and Raman tube with filters were supported by an aluminum frame. The entire set-up could be assembled in less than five minutes and gave the strong Raman lines of carbon tetrachloride in less than a minute.

In order to obtain monochromatic light, liquid filters finally were adopted. Noviol O and Ultra Purple glass[7] from the Corning Glass Company were tried, but were found less satisfactory than the liquid type. The three solutions recommended by Murray and Andrews[8] for the isolation of the 4358 mercury line, were tried but the added inconvenience did not seem to warrant the purity obtained and the final filters decided upon were 11 mm. of a saturated sodium nitrite solution[9] for the isolation of the 4358 line, and 11 mm. of a 15% solution of a saturated solution of iodine in carbon tetrachloride dissolved in carbon tetrachloride, to isolate the 4046 line of mercury.

The liquid to be investigated was placed in a Raman tube developed by Wood,[10] which consisted of a Pyrex glass tube 2.5 cm. in diameter, closed at one end with a plane window (this window was spun directly onto the end of the tube) and terminated at the other with a blackened horn (blackened by friction tape). The edge of the window was painted with black Duco lacquer to prevent the Rayleigh scattering. The outer filter tube was attached with inner seals at each end of the Raman tube.

To remove the fog (halation) resulting from over-exposure of the exciting line, a mechanical filter was employed. This consisted of a brass rod (3.2-mm. diameter) which passed horizontally through the camera box just in front of the plate holder. A lock-nut was attached

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[7] Wood, "Physical Optics," 3rd ed., The Macmillan Co., New York, N. Y., 1934.

[8] Murray and Andrews, *J. Chem. Phys.*, **1**, 406 (1933).

[9] Pfund, *Phys. Rev.*, **42**, 581 (1932).

[10] Wood, *Phil. Mag.*, **7**, 858 (1928).

outside to this rod. Within the camera box there was attached to the rod, by means of a slip-fit and solder, a series of vertical blackened steel wires of approximately the same diameter as the line passing to the plate from the slit of the spectrograph. These steel wires were filed flat on one side, and the flattened surface was at right angles to the oncoming light. The lock-nut thus allowed the wires to be placed in front of the lines during the exposure or tilted horizontal when the mercury arc spectrum or the iron comparison spectrum was wanted.

A Hilger constant deviation spectrograph was used with Eastman 40, Eastman Hypersensitive or Eastman Spectrographic I J plates.

The following precautions were taken in measuring the plate with comparator: (1) the line to be measured was always approached from the same side (avoiding backlash screw); (2) each plate was measured twice in opposite directions, by turning the plate around and advancing the microscope in the same direction as before. Approximately fifteen comparator readings were taken per line and an average calculated three plates of each spectra were taken.

Results

The water used to dissolve the purified salts was distilled from phosphoric acid as recommended by Ellis and Kiehl.[11] With two exceptions, sodium butyl sulfonate and sodium butyl sulfinate, the salts gave excellent spectra. These particular salts gave a continuous background which was not removed even when recrystallized three times from alcohol and twice from water. Finally it was necessary to filter the solution through a collodion Berkefelt filter. Solutions of the sulfonates in all cases contained 100 g. of salt in 150 g. water, a concentration which approaches saturation. Solutions of the sulfinates contained 100 g. of salt in 100 g. water. It was important with these latter salts not to allow their solutions to stand before using, for on long standing the following reaction takes place which produces a cloudy solution

$$2RSO_2Na \longrightarrow RSR + Na_2SO_4 \qquad (1)$$

The wave number differences of the several compounds are given in Table I. Three separate spectra were obtained for each compound and the results given are the mean values. In all cases the lines obtained from the three plates checked within an accuracy of 1 Å. The sulfonate solutions were water white and gave Raman lines with only a one-hour exposure. To establish with certainty that all the Raman lines of the sulfonates were obtained, twenty-four hour exposures were taken. No new lines were obtained even with seventy-four hour exposures. The sulfinates on the other hand gave solutions decidedly yellow in color and, though no cloudiness existed in solution, their exposures necessitated three hours duration to bring out the lines. With these compounds also, twenty-four hour exposures were used; and seventy-four hour exposures brought out no new lines. The bands listed in Table I at 1650 and 3400 are those of water.

TABLE I

RAMAN SHIFTS FOR THE SODIUM ALKYL SULFINATES AND SULFONATES

Substance	Raman shifts[a]
$C_2H_5SO_3Na$	392m, 543m, 762s, 1053s, 1177m, 1295w, 1439m, 1650mb, 2791m, 2945s, 2996m, 3421s, 3504sb
$C_2H_5SO_2Na$	386s, 508w, 663s, 752w, 952s, 1029m, 1243w, 1425m, 1636wb, 2933s, 3470sb
$C_3H_7SO_3Na$	320m, 376m, 538m, 608w, 742w, 796s, 904w, 1048s, 1182m, 1295w, 1360w, 1458m, 1645wb, 2880w, 2941s, 2984s
$C_3H_7SO_2Na$	310m, 366w, 503w, 633s, 722m, 942s, 1024m, 1186m(?), 1290w, 1416m, 1453m, 2888s
$C_4H_9SO_3Na$	300m, 351m, 427w, 523m, 598w, 786s, 884m, 1044s, 1177m, 1300m, 1439s, 2872s, 2929s
$C_4H_9SO_2Na$	289m, 376m, 538w, 638m, 723m, 955m, 1046m, 1199w, 1313m, 1456w, 2883m, 2939m
$C_5H_{11}SO_3Na$	279m, 366m, 432w, 533m, 613w, 786s, 889m, 1044s, 1172m, 1304m, 1444s, 1650w, 2751w(?), 2868s, 2933s
$C_5H_{11}SO_2Na$	285m, 385m, 624m, 702m, 956m, 1042m, 1218w, 1445w

[a] m = medium, w = weak, s = strong, b = band.

Discussion and Conclusion

The sulfonates and sulfinates caused a marked effect in the appearance of the water band. The sulfonates showed only one water band at 3450 cm.$^{-1}$ which was a band quite sharp in character being only 100 cm.$^{-1}$ in width. The sulfinates on the other hand broaden the water band to 1000 cm.$^{-1}$ with a maximum (estimated with difficulty) at approximately 3500 cm.$^{-1}$.

To afford an adequate basis for the interpretation of our data, the results of other workers on sulfur-containing compounds are included in Table II. In all cases the additional data are taken from Hibben's excellent and extensive summaries.[12] The possible structures for sodium alkyl sulfonate and sodium alkyl sulfinate are as follows

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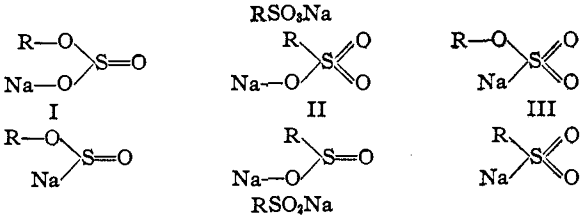
[11] Ellis and Kiehl, THIS JOURNAL, 57, 2145 (1935).

[12] Hibben, *Chem. Rev.*, 13, 345 (1933); 18, 1 (1935).


RSO₃Na

I II III

RSO₂Na

The following points are to be noted from Table II: below 250 cm.$^{-1}$ in compounds 1, 2, 3 occur frequency shifts not found in the other compounds, and they must therefore be due to the influence of the chlorine therein. From 280–290 cm.$^{-1}$ appear lines common to the compounds 2, 3, and 9, but not in compound 1 and must therefore be excited by an S–O bond, but due to its non-appearance must be inactive in the other "sulfur-oxygen" compounds. From 340–390 cm.$^{-1}$ however, common lines are noticed in compounds 2, 3, 9, 11, and 12, which definitely establishes some type of S–O vibration. Little can be said regarding frequency shifts in the lower 400 cm.$^{-1}$ since evidently they are due to vibrations from the S–Cl bond. In the upper 400 cm.$^{-1}$ compounds 13, 14, and 15 show a likeness. Between 510 and 560 cm.$^{-1}$ appears another very characteristic line which can also be attributed to compounds with S–O bonds. Again compounds 13, 14, and 15 appear unique with a frequency shift at 600 cm.$^{-1}$, and again at 985 cm.$^{-1}$. At approximately 670 cm.$^{-1}$ appears a line which occurs only in compounds containing the C–S bond, not considering the very very weak line found in 9 which is questionable. Also from 750 to 790 cm.$^{-1}$ appear frequency shifts found only in compounds containing the C–S bond. These two groups therefore characterize the C–S binding. The 950 cm.$^{-1}$ shift which occurs in the sulfinic salt but in no other compound needs explanation. The shift from 1030–1050 cm.$^{-1}$ is found in compounds 10, 11, 12, and 15, while the shift 1140 to 1180 is found in compounds 3, 7, 10, 11, and 15. Because of its absence in 2 and 12 it may be attributed to the SO_2 asymmetric vibration. The following conclusions may therefore be drawn

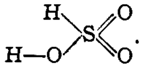
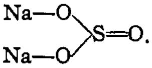
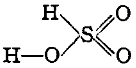
(a) 340 to 390 cm.$^{-1}$ is characteristic of the S–O bond
510 to 560 cm.$^{-1}$ is characteristic of the S–O bond
670 to 700 cm.$^{-1}$ is characteristic of the C=S bond
750 to 790 cm.$^{-1}$ is characteristic of the C=S bond
1030 to 1050 cm.$^{-1}$ is characteristic of the S–O bond
1140 to 1180 cm.$^{-1}$ is characteristic of the S–O bond

(b) Compounds 13, 14, and 15 are unique in that they possess three common shifts 450, 600, and 985 cm.$^{-1}$. (c) No C–O bond occurs in the so-

TABLE II

RAMAN SHIFTS FOR A STUDY OF CERTAIN SULFUR LINKAGES

(1) S_2Cl_2	(2) $SOCl_2$	(3) SO_2Cl_2	(4) SO_2OHCl	(5) COS	(6) CS_2	(7) SO_2	(8) SO_3	(9) S_2O_6	(10) H_2SO_3	(11) RSO_3Na	(12) RSO_2Na	(13) Na_2SO_3	(14) Na_2SO_4	(15) H_2SO_4
190s	..	..	..	..	..	..	...	...	..	..	..	...	..	..
206w	193s	213m	..	..	..	..	...	...	..	..	..	...	..	..
247	..	..	..	..	..	..	...	...	..	..	..	...	..	..
..	282m	278	..	..	..	..	...	290m	..	..	..	...	..	..
..	343s*	(365)*	312	..	..	..	...	...	..	..	..	...	..	..
..	..	387*	..	..	..	..	...	370s*	..	392m*	386s*	...	..	..
..	..	409	419	..	412s	..	...	...	..	..	..	...	..	..
447s	444w	..	..	..	..	..	...	...	..	..	..	...	..	..
..	488	..	..	..	..	..	...	...	..	..	..	471	460	421
(545)	..	559m	513	524	..	576	535	...	569	543m	508	...	..	..
		(576)												
..	..	..	..	..	..	..	...	...	..	..	..	602	617	574
					647			666w						
..	..	..	623	(678)	655s	..	...	697w	..	..	663s	...	..	..
..	..	..	..	..	799w	..	...	...	..	762s	752w	...	..	..
..	..	..	..	859s	(848)	..	...	...	..	..	..	...	..	..
..	..	..	919s	..	..	..	...	...	..	..	952s	...	..	..
..	..	..	..	..	..	..	...	...	..	..	..	984m	984s	985s
..	..	..	..	..	..	..	...	...	1047	1053s	1929m	...	..	1047
..	..	..	..	..	..	..	...	...	..	..	..	...	1109	..
..	..	1187m	1155s	..	..	1145s	...	...	1142	1177m	..	...	..	1170
			1199m						1199					
..	1229	..	..	..	..	..	...	...	..	1295w	1243w	...	..	..
						1334								
..	..	..	..	1383	..	1340	...	...	..	..	..	...	..	1359

dium alkyl sulfonates or sulfinates and therefore structure II is the correct one. (d) Since structure II is correct and compound 10 possesses the 1170 frequency shift characteristic of SO_2 vibration, the structural formula of sulfurous acid must be . (e) The structure of sodium sulfite resembles that of sodium sulfate and sulfuric acid and must therefore be . From this we conclude that sulfurous acid must exist as two tautomers; the form represented by the formula  predominates in solution.

This structure is in agreement with Nisi[13] and Gerding and Nijveld.[14]

It should be noted that with propyl sulfinates and sulfonates the lower frequencies split into doublets. The 1186 cm.$^{-1}$ line of propyl and butyl sodium sulfinate would contradict the structure II selected. However, its complete absence in ethyl sodium sulfinate, and the ease by which the higher sodium sulfinates are oxidized, appears to be indicative that the structure II is correct.

Reaction (1) progressed too far with butyl and amyl sodium sulfinate, and produced a continuous background of such an intensity that only a few Raman lines were obtained.

The assignment of 1054 cm.$^{-1}$ to S–O vibration is open to question for Woodward[15] has shown that pure sulfuric acid does not possess this vibration but, when slight traces of water are present, 1054 cm.$^{-1}$ does appear and, therefore, he attributed this to the HSO_4^- ion. This frequency must be either incorrectly assigned or some fundamental relation must exist between the series. The data are at present too meager to be conclusive but it should be noticed that it appears to the second harmonic of the fundamental 526.

Perhaps no other substance gives such divergent results as does water; however, this discrepancy is slowly giving way to more accurate assignments, particularly through the work of Bolla,[16] Silveira,[17] Magat,[18] and Hibben.[19] In the past this divergence has been attributed to the broadness of the bands concerned and to the previous history of the water. This latter point is one of very great importance, particularly in obtaining reproducible results. The very precautionary measures of Silveira and Magat to purify water are indeed necessary when the water is distilled from alkaline permanganate. However, these measures may be eliminated by distilling the water from phosphoric acid as recommended by Ellis and Kiehl.[20]

The existence of the 1650 cm.$^{-1}$ band, which appears to have caused much difficulty to previous workers, evidently has not yet been established thoroughly. We were able to obtain this band quite distinctly in a twelve-hour exposure, using either the 4046 or the 4358 mercury line. The band extending from 441–914 cm.$^{-1}$ had a maximum intensity at 743 cm.$^{-1}$. The band extending from 3176–3640 cm.$^{-1}$ had two maxima, one at 3240 cm.$^{-1}$ and the other at 3452 cm.$^{-1}$ which agrees exactly with Magat. We agree with Magat in the non-existence of a maximum at 3600 cm.$^{-1}$, which Bolla evidently found quite easily. The reason for this is not known; this point should be investigated more thoroughly since our data were taken at 60° while those of Magat were found at 12–18°. Then, too, the 3400 cm.$^{-1}$ band of water was obtained with only one-minute exposure so there was no chance of overlooking this band at 3580 (or 3600 cm.$^{-1}$ approximately). Unquestionably the band extends into the region 3600 cm.$^{-1}$ but no maximum is evident.

Summary

1. The technique of Wood for Raman investigation has been modified to give light intensities of great brilliance.
2. Details of the preparation of sodium alkyl sulfonates and sulfinates have been given.
3. Raman spectra of these compounds have been obtained and submitted as evidence concerning their structure.

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[13] Nisi, *Jap. J. Phys.*, **6**, 1 (1930).

[14] Gerding and Nijveld, *Nature*, **137**, 1070 (1936).

[15] Woodward, *Physik. Z.*, **32**, 212, 777 (1931).

[16] Bolla, *Nuovo cimento*, **10**, 101 (1933).

[17] Silveira, *Compt. rend.*, **195**, 652 (1932).

[18] Magat, (a) *ibid.*, **196**, 1981 (1933); (b) *J. Phys. Rad.*, **5**, 347 (1934).

[19] Hibben, *J. Chem. Phys.*, **5**, 166 (1937).

[20] Ellis and Kiehl, THIS JOURNAL, **57**, 2145 (1935).