tween 12 and 14 during a reduction process. In the present reduction potential data, a value between pH 10 and pH 11 is estimated, inasmuch as the reduction potentials measured in the 0.1*M* sodium hydroxide are 140 mv. more negative than those measured in the unstirred potassium chloride.

Effect of Dissolved Oxygen and Current Density. The oxide-film value was measured in deaerated and air-saturated solutions, as a function of current density (0.019, 0.039, 0.078, 0.116, 0.155, 0.233, 0.310, and 0.388 ma. per square cm.) and on various tin-plate specimens with different quantities of surface oxides. In deaerated solutions, the plot of oxide-film value *vs.* current density approached a straight line parallel to the abscissa. Slight deviations caused by a trace of oxygen remaining in the solution were observed. The error in the oxide-film value due to the presence of oxygen in the electrolyte in the air-saturated solutions increased with decreasing current density for a particular oxide level. Similarly, the error increased with increasing oxide-film value when the current density was held constant. This is consistent with the assumption that oxygen was reduced concurrently with the oxide. For long electrolysis times—i.e., for low current densities or high oxide-film values—the quantity of oxygen reduced was greater than that reduced during short times of electrolysis, hence, the greater error. This indicated that the reduction of the oxygen could be a diffusion-controlled process (at least for the times of electrolysis measured in these experiments). Assuming linear diffusion, the current, i, at any time, t, is given by (*4*)

$$i_t = nF\pi^{-1/2}AD^{1/2}Ct^{-1/2} \qquad (1)$$

where A is the electrode area, D is the diffusion coefficient of the oxygen, C is the bulk concentration of the oxygen, and the other terms have their usual significance. To determine the quantity of electricity that flows over a period of time, Equation 1 must be integrated over the time interval. Thus

$$Q = 2nF\pi^{-1/2}AD^{1/2}Ct^{1/2} \qquad (2)$$

where Q is the quantity of electricity, which is a measure of the quantity of oxygen reduced. For a diffusion-controlled process, a plot of the error due to the presence of dissolved oxygen in the electrolyte *vs.* the square root of the time of electrolysis should give a straight line. A plot of the data gives a straight line, in agreement with the theory. Stirring the electrolyte also increased the error; this is consistent with a diffusion-controlled process. At sufficiently high current densities, the oxygen error became almost negligible, especially for tin plate that only had a very thin oxide film.

SUMMARY

The quantitative coulometric determination of tin oxides is affected by the pH and the buffering capacity of the electrolyte. Results in unbuffered electrolytes of pH 5 or greater and in all electrolytes of pH 8 or greater are low because of the dissolution of some of the oxides, the dissolution being caused by the high alkalinity at the electrode surface. The pH at the electrode surface, under these conditions, is estimated to be between 10 and 11. Oxygen dissolved in the electrolyte causes an error proportional to the square root of the time of electrolysis. The evidence indicates that the rate of reduction of the oxygen is diffusion controlled.

LITERATURE CITED

(1) Britton, S. C., Bright, K., *Metallurgia* **56**, 163 (1957).

(2) Campbell, W. E., Thomas, U. B., *Trans. Electrochem. Soc.* **76**, 303 (1939).

(3) Constable, F. H., *Proc. Roy. Soc.* (*London*) **A117**, 376, 386 (1928).

(4) Delahay, P., "New Instrumental Methods in Electrochemistry," p. 51, Interscience, New York, 1954.

(5) Evans, U. R., Stockdale, J., *J. Chem. Soc.* **1929**, 2651.

(6) Katz, W., *Stahl u. Eisen* **76**, 1672 (1956).

(7) Miley, H. A., *Iron Steel Inst. Carnegie Schol. Mem.* **25**, 197 (1936).

(8) Salt, F. W., Thomas, J. G. N., *Nature* **178**, 434 (1956).

(9) Stern, M., *J. Electrochem. Soc.* **102**, 609 (1955).

(10) Tammann, G., Bochow, K., *Z. anorg. Chem.* **169**, 42 (1928).

(11) Vernon, W. H. J., *Trans. Faraday Soc.* **31**, 1668 (1935).

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Infrared Identification of Some Sulfur Derivatives of Long-Chain Fatty Acids

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► Infrared absorption spectra of some long-chain fatty acid derivatives containing sulfide, sulfoxide, and sulfone groups were studied. The spectra were investigated to determine the effects of such substitutions on the characteristic bands of fatty acids and to establish means for detection and determination of these compounds in the presence of each other. Interruption of the carbon chain by —S—, —SO—, or —SO_2— makes the band progression region less useful for chain-length determination, but introduces spectral detail that can be used to identify individual compounds. Very closely related sulfur derivatives of fatty acids can be distinguished by studying the 1350- to 1180-cm.$^{-1}$ region of solid-state spectra obtained from potassium bromide pellets. For differentiating between the main classes, it is best to utilize the extremely regular dilute solution spectra of the corresponding methyl esters.

THE ANALYTICAL USEFULNESS of the infrared absorption spectra of long-chain fatty acids has been discussed and evaluated by a number of workers, most recently by Jones, McKay, and Sinclair (*4, 12*) and by Meiklejohn, Meyer, Aronovic, Schuette, and Meloche (*7*). The spectra show bands that are characteristic for the carboxyl and methylene groups and for the methyl end groups. In the crystalline state the "band progression," a regular series of evenly spaced absorption maxima, is observed in the 1350- to 1180-cm.$^{-1}$ region. This band progression frequently provides the only practical means of spectrally differentiating various saturated fatty acids because their spectra are otherwise similar.

The present study describes the spectral effects produced by introducing a sulfide, sulfoxide, or sulfone group into the fatty acid chain. Some of the characteristic frequencies of these groups have been established (*1, 9, 10*). It can hardly be expected, however, that introduction of bulky or highly polar groups into fatty acid molecules will leave the characteristic fatty acid features unchanged, especially the band progression which probably depends on crystal structure. It was therefore considered of interest to study the effect of the sulfur-containing groups on fatty acid spectra and to establish spectroscopic means of distinguishing the various sulfur derivatives of fatty acids, particularly with the chemistry of organosulfur compounds continuously growing in interest and usefulness.

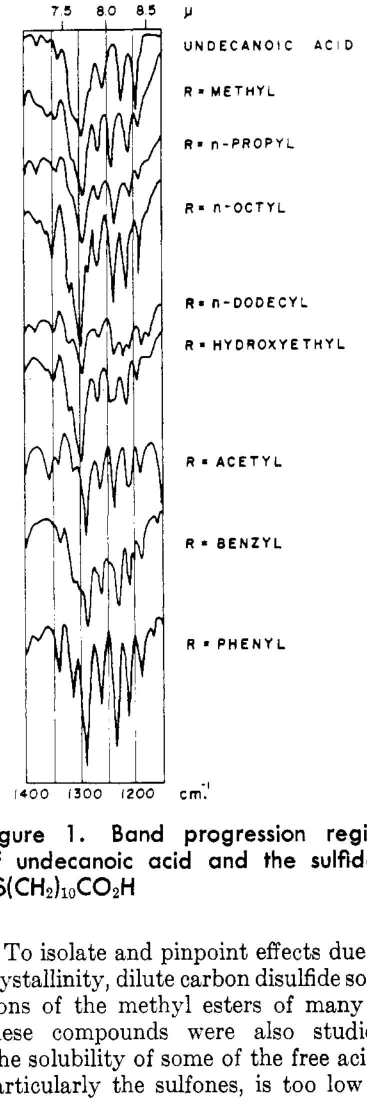

Figure 1. Band progression region of undecanoic acid and the sulfides, $RS(CH_2)_{10}CO_2H$

To isolate and pinpoint effects due to crystallinity, dilute carbon disulfide solutions of the methyl esters of many of these compounds were also studied. The solubility of some of the free acids, particularly the sulfones, is too low to permit such investigations.

EXPERIMENTAL

Spectra in the 650- to 4000-cm.$^{-1}$ region were obtained with a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Solid samples were examined as potassium bromide pellets (*5*). These were prepared by grinding about 1 mg. of the solid sample with 0.4 gram of potassium bromide in a mechanical vibrator (*5*) and pressing the resulting mixture in a Perkin-Elmer die with a force of 20,000 pounds. The solution spectra were obtained on 1% carbon disulfide solutions in 0.5-mm. sealed rock salt cells. The instrument was calibrated with polystyrene and atmospheric water vapor. Instrumental settings corresponded to "resolution schedule 4," as specified by the manufacturer.

Solid-state spectra of the following 11-substituted undecanoic acids were obtained: sulfides, $RS(CH_2)_{10}CO_2H$, R = methyl, *n*-propyl, *n*-octyl, *n*-dodecyl, 2-hydroxyethyl, acetyl, benzyl, or phenyl; sulfoxides, $RSO(CH_2)_{10}CO_2H$, R = methyl, *n*-octyl, benzyl, or phenyl; and sulfones, $RSO_2(CH_2)_{10}CO_2H$, R = *n*-propyl, *n*-octyl, benzyl, or phenyl. Methyl esters of the sulfoxides, $RSO(CH_2)_{10}CO_2CH_3$, and of the sulfones, $RSO_2(CH_2)_{10}CO_2CH_3$, R = *n*-octyl, benzyl, or phenyl, were studied in dilute carbon disulfide solution.

All of the acids were recrystallized solids of high purity. The preparation of most of the acids has been reported (*6*). Similar procedures were used to prepare three previously unreported acids: 11-(methylsulfinyl)-undecanoic acid, melting point 87° C.; 11-(benzylsulfinyl)-undecanoic acid, melting point 83° C.; 11-(*n*-propylsulfonyl)-undecanoic acid, melting point 101° C. The following esters, all new compounds, were made by refluxing the corresponding acid with a large excess of methanol containing catalytic amounts of naphthalene-2-sulfonic acid: methyl 11-(*n*-octylsulfinyl)-undecanoate, melting point 74° C.; methyl 11-(*n*-octylsulfonyl)-undecanoate, melting point 77° C.; methyl 11-(phenylsulfinyl)-undecanoate, melting point 36 to 38° C.; methyl 11-(phenylsulfonyl)-undecanoate, melting point 64° C.; methyl 11-(benzylsulfinyl)-undecanoate, melting point 69° C.; methyl 11-(benzylsulfonyl)-undecanoate, melting point 80° C.

RESULTS AND DISCUSSION

Sulfides, $RS(CH_2)_{10}CO_2H$. Substituting a sulfur atom in the 11-position causes only minor changes in the fatty acid spectra. The only new bond introduced, the C—S linkage, probably absorbs below the region observable with a rock salt prism. Although a weak band occurs in all of the sulfides between 675 and 700 cm.$^{-1}$, this seems to be too high for the C—S stretching mode (*10*).

Table I. Number of Bands in the 1180- to 1350-Cm.$^{-1}$ Region of Sulfides, $RS(CH_2)_{10}CO_2H$

(Excluding carboxyl band at about 1300 cm.$^{-1}$)

R	No. of —CH_2— Units	No. of Bands
Methyl	10	6
Acetyl	10	6
Phenyl	10	6
Benzyl	10 + 1	6
n-Propyl	10 + 2	6
2-Hydroxyethyl	10 + 2	6
n-Octyl	10 + 7	7
n-Dodecyl	10 + 11	7

The band progression region (1180 to 1350 cm.$^{-1}$), however, warrants some discussion. Meiklejohn and associates (*7*) have recently found that in the case of normal long-chain fatty acids the number of bands in the progression series is approximately equal to half the number of carbons in the chain. Figure 1 shows the results obtained in the present study for the sulfides. Undecanoic acid (melting point 28° C., run as a solid film) is included for comparison. Table I lists the number of bands observed for the various sulfides.

It is evident that the simple correlation described by the above authors is no longer valid when the carbon chain is interrupted. Further, the individual bands are not easily counted. The band intensities become irregular and splittings occur that are not easily systematized. It appears that the number of bands is determined essentially by the longer uninterrupted hydrocarbon chain. The other (shorter) chain probably gives rise to its own bands, which overlap and partially distort the pattern produced by the longer chain. Various end groups (phenyl, hydroxyl, or acetyl) also cause distortions, but do not change the basic pattern.

These observations tend to substantiate earlier assumptions (*3*, *4*, *8*) about the origin of the band progression—namely, that it arises from coupled motions of methylene groups in a particular spatial arrangement. If the hydrocarbon chain is interrupted by a sulfur atom, the coupling of methylene groups is also interrupted and the hydrocarbon chains on each side of the sulfur atom behave somewhat independently. Likewise, if the structure of the solid aggregate is altered by introducing new groups, the pattern is again modified and distorted. Thus, the effects of substituent groups on the band progression offer a potential means of distinguishing various derivatives of fatty acids. Moreover, as the number of regular bands in the progression region is probably related to the length of the chain segments, study of this region may be of value in locating the position of atoms, groups, or multiple bonds in other long-chain compounds.

Sulfoxides, $RSO(CH_2)_{10}CO_2H$, $RSO(CH_2)_{10}CO_2CH_3$. Introduction of the sulfoxide group gives rise to a strong band between 1000 and 1060 cm.$^{-1}$, associated with the S—O stretching motion. In the solid state the band is split into two to four submaxima, all within the above region. The band progression region is altered to a point where even an estimation of chain length becomes impractical. Figure 2*A* gives the spectra from 900 to 1400 cm.$^{-1}$ of the acids, $RSO(CH_2)_{10}CO_2H$, where R is methyl, octyl, phenyl, or benzyl.

The decreased regularity of the band

progression in the sulfoxides, compared to the sulfides, probably has its origin in the larger size and greater polarity of the —SO— group. Whereas the effect of the sulfur atom is essentially to interrupt the hydrocarbon chain, the —SO— group changes the configuration of the solid aggregate, and thereby further distorts the band progression. On the other hand, these greater variations permit more extended use of the spectra for analytical purposes.

In contrast to the complexity of the solid-state spectra of the acids, the corresponding esters in dilute carbon disulfide solution show extremely regular features, as shown in Figure 3*A*. All major bands can be explained by well-known correlation rules (*2*)—for example, the triplet absorption at about 1170, 1195, and 1250 cm.$^{-1}$ is typical for long-chain methyl esters (*11*). For the determination of sulfoxide derivatives of fatty acids in the presence of unsubstituted acids, the dilute solution spectra of the esters are preferred to the acid spectra because of this regularity. On the other hand, seemingly irregular features of the acid spectra measured in the solid state can be utilized for analytical work on closely related substituted acids.

Sulfones, $RSO_2(CH_2)_{10}CO_2H$, $RSO_2(CH_2)_{10}CO_2CH_3$. Figure 2*B* shows the 900- to 1400-cm.$^{-1}$ region of the sulfones, $RSO_2(CH_2)_{10}CO_2H$, where R is propyl, octyl, phenyl, or benzyl. There is little band progression left. In addition to the effects produced by distorting the crystals through introduction of the highly polar and relatively large —SO$_2$— groups, complications arise from the —SO$_2$— stretching band in the 1325-cm.$^{-1}$ region. In fact, the 1180- to 1350-cm.$^{-1}$ region becomes so complicated that recognition or assignment of individual bands is extremely difficult.

A detailed discussion of these spectra is beyond the scope of this presentation.

The higher —SO$_2$— stretching vibration is difficult to pinpoint because carboxyl and methylene bands occur in the same region.

The lower —SO$_2$— stretch occurs around 1125 cm.$^{-1}$ However, when the —SO$_2$— group is attached directly to a benzene ring, the frequency is increased to about 1150 cm.$^{-1}$ (*1*).

All four sulfones [$RSO_2(CH_2)_{10}CO_2H$] studied show a medium to weak band around 775 cm.$^{-1}$ No explanation is attempted at present.

Figure 3*B* gives the spectra of carbon disulfide solutions of the sulfone methyl esters, $RSO_2(CH_2)_{10}CO_2CH_3$, where R = octyl, phenyl, or benzyl. Again, once the complexities inherent in solid-state

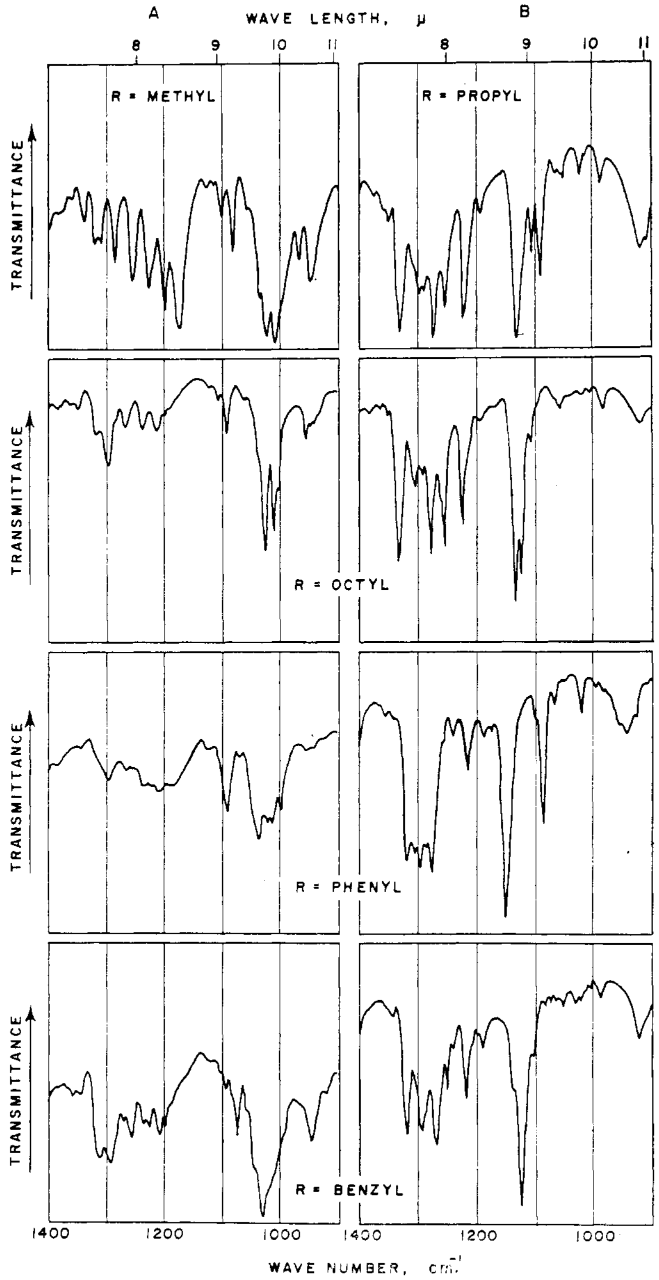

Figure 2. The 900- to 1400-cm.$^{-1}$ region

A. Acid sulfoxides, $RSO(CH_2)_{10}CO_2H$
B. Acid sulfones, $RSO_2(CH_2)_{10}CO_2H$

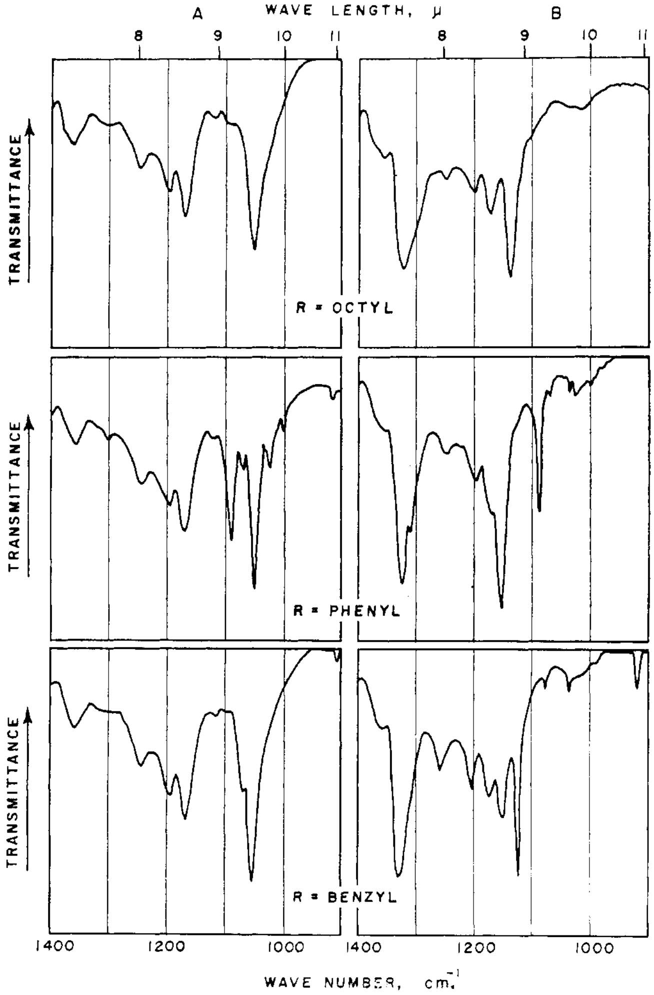

Figure 3. The 900- to 1400-cm.$^{-1}$ region

A. Sulfoxide methyl esters, $RSO(CH_2)_{10}CO_2CH_3$
B. Sulfone methyl esters, $RSO_2(CH_2)_{10}CO_2CH_3$

spectroscopy are removed, the spectra can easily be interpreted by well-known correlation rules. The only irregularity noted is in methyl 11-(benzylsulfonyl)-undecanoate, where two bands occur between 1120 and 1150 cm.$^{-1}$ instead of the usual single —SO_2— stretching band. Sulfone derivatives of fatty acids in the presence of unsubstituted acids or their sulfide or sulfoxide derivatives are best determined in dilute solution, utilizing the esters; for analytical work on various members of the sulfone series, the solid-state spectra of the acids are preferred.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Barnard, D., Fabian, J. M., Koch, H. P., *J. Chem. Soc.* **1949,** 2442.

(2) Bellamy, L. J., "Infrared Spectra of Complex Molecules," Wiley, New York, 1954.

(3) Ferguson, E. E., *J. Chem. Phys.* **24,** 1115 (1956).

(4) Jones, R. N., McKay, A. F., Sinclair, R. G., *J. Am. Chem. Soc.* **74,** 2575 (1952).

(5) Kirkland, J. J., Anal. Chem. **27,** 1537 (1955).

(6) Koenig, N. H., Swern, D., *J. Am. Chem. Soc.* **79,** 4235 (1957).

(7) Meiklejohn, R. A., Meyer, R. J., Aronovic, S. M., Schuette, H. A., Meloche, V. W., Anal. Chem. **29,** 329 (1957).

(8) Primas, H., Günthard, H. H., *Helv. Chim. Acta* **36,** 1659, 1791 (1953).

(9) Schreiber, K. C., Anal. Chem. **21,** 1168 (1949).

(10) Sheppard, N., *Trans. Faraday Soc.* **46,** 429 (1950).

(11) Shreve, O. D., Heether, M. R., Knight, H. B., Swern, D., Anal. Chem. **22,** 1498 (1950).

(12) Sinclair, R. G., McKay, A. F., Jones, R. N., *J. Am. Chem. Soc.* **74,** 2570 (1952).

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Determination of Equivalent Weight of Esters and Halides with Cation Exchange Resins

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▶ Salts are formed during the heating of ethanolamine with phosphorus or sulfur esters, and alkyl halides. The solutions are passed through cation exchange resins (in the hydrogen form) where the cation of the salt is exchanged for hydrogen. The free acid in the effluent solution is titrated directly with alkali.

Cation exchange resins are useful for the estimation of the equivalent weight of salts (*6*). The resins retain effective exchange capacity even in nonaqueous media (*2*). Therefore, they can be used to follow the progress of reactions which produce salts. When such a reaction proceeds to completion the equivalent weight of the starting material can be determined—e.g., the saponification of carboxylate esters with alkali leads to the formation of the salt of the carboxylate anion. Wiesenberger (*7*) used this fact to estimate the acetate from the saponification of esters and amides. The usual estimation of the equivalent weight of carboxylate esters requires the titration of the excess alkali. However, the reaction mixture can be passed through a column of a strongly acidic resin in the hydrogen form, liberating the free acid in the column effluent. Thus the acid formed in the reaction can be titrated directly.

In the present investigation, methods were devised for determining equivalent weights of a number of typical phosphorus or sulfur esters and alkyl halides. Salts formed in a preliminary reaction were treated with cation exchangers.

While the saponification of carboxylate ester proceeds satisfactorily with sodium hydroxide or sodium alkoxide, this reaction is much slower with the esters of phosphorus or sulfur. Advantage was taken of the well known alkylation properties of the esters of the inorganic acids (*1, 5*). The heating of phosphate and sulfonate esters with ethanolamine produced salts. The resulting salt solution readily exchanged its cation for hydrogen when passed through a bed of cation exchange resin in the hydrogen form. Under the conditions used, only one alkyl group was removed from the polyesters of phosphorus. The reaction for salt formation may be represented:

$$(RO)_3PO + R'NH_2 \rightarrow (RO)_2P(O)O^- \overset{+}{N}H_2RR'$$

Rauscher (*3, 4*) used ethanolamine for the quantitative identification of carboxylate esters. Carboxylate esters react with amines to form amides which are not affected by the ion exchange resin as it is used here.

Alkyl halides reacted with ethanolamine in an alkylation type of reaction leading to a substituted ammonium salt.

$$RX + R'NH_2 \rightarrow [RR'NH_2{}^+]X^-$$

The halogen acid was liberated quantitatively by the resin. The compound, ethyl chloroacetate, reacted with ethanolamine, and hydrochloric acid was liberated quantitatively by the resin without interference from the carboxylate.

The equivalent weights were calculated using the equation:

$$\text{Equivalent weight} = \frac{\text{weight of sample (mg.)}}{[\text{alkali required in test (ml.)} - \text{alkali in blank (ml.)}] \times \text{normality of alkali}}$$

where the blank was 0.04 ml. of 0.1N sodium hydroxide with ethanolamine; it was often four to five times higher with caustic digestion.

The ion exchange technique was used to follow the rate of dealkylation of esters for the synthesis of acids and for the study of reaction kinetics. The principle of this method can be extended to include any salt solution for which a satisfactory solvent can be found. There is reason to believe, also, that it can be extended to the determination of the equivalent weight of organic compounds, which are converted to the corresponding bases, on passing the compounds through anion exchange resins in the hydroxyl form.

EXPERIMENTAL

Materials. The esters and halides were synthesized by well known procedures or were the best commercial grades which were distilled or crystallized before use. Propanol was refluxed with sodium and distilled; only the middle two thirds was used.

Reaction Mixtures. A. Approximately 30 mg. of sample was weighed into a round-bottomed boiling flask fitted with a ground-glass joint. Five milliliters of sodium propoxide (made daily by dissolving 0.12 gram of freshly