LIX.—*The Relation Between the Absorption Spectra of Acids and their Salts. Part I. Sodium Salts.*

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IT is a matter of common knowledge that many acids show a marked colour change when their acidic hydrogen is replaced by a metal, such as sodium, which in itself is colourless. The various indicators used in acidimetry, for example, litmus or methyl-orange, furnish well-known examples of such phenomena. By the application of photography the investigations have been extended to the invisible regions of the spectrum, with the result that numerous substances (such as the phenols) are now known which show a marked change in their absorption spectra on the addition of sodium hydroxide. This change is most frequently ascribed to a variation in molecular structure taking place on salt-formation; the present investigations, however, seem to indicate that change in absorptive power can occur where such variation is hardly possible.

For the most part the examination has been confined to acids of a simple structure, where there is little possibility of atomic rearrangement taking place on neutralisation. Further, aqueous solutions were used throughout, so that any change in absorptive power which might be produced by alteration of the degree of ionisation would have its full effect. As many of the substances photographed have been previously investigated, the full absorption

curves have not been drawn, but the results are expressed by means of tables.

The Fatty Acids.—As will be seen from the table, these acids all show a decrease in absorptive power on salt-formation. This decrease is most marked in the case of formic acid, and grows less as we ascend the series. In the case of the substituted acetic acids, the spectra of salt and acid were practically identical. In this table, as in all others, the ionisation constant k of each acid is given; these constants were obtained from Kohlrausch's "Leitvermögen der Elektrolyte." The limits of absorption for 10 cm. and 1 cm. are given in wave-lengths.

TABLE I.

	10 cm. Spectrum transmitted to λ .	1 cm. Spectrum transmitted to λ .	κ .
Formic acid, N	2520	2430	0.0214
Sodium formate, N	2430	2330	—
Acetic acid, N	2460	2355	0.0018
Sodium acetate, N	2410	2320	—
Propionic acid, N	2480	2360	0.0013
Sodium propionate, N	2460	2335	—
n -Butyric acid, N	2500	2380	0.0015
Sodium n -butyrate, N	2480	2340	—
<i>iso</i> -Valeric acid, $N/10$	2560	2390	0.0017
Sodium <i>iso</i> valerate, $N/10$	2520	2330	—
Chloroacetic acid, N	2620	2500	0.155
Sodium chloroacetate, N	2610	2490	—
Trichloroacetic acid, N	2730	2590	121 (?)
Sodium trichloroacetate, N	2730	2590	—
Phenylacetic acid, $N/100$	2695	2330	0.0056
Sodium phenylacetate, $N/100$	2700	2330	—

Trichloroacetic acid and its salt were also photographed in more dilute solutions, and their spectra remained identical down to 1 cm. of $N/100$ -solution.

The Dibasic Acids.—In this series, as in the fatty, the change is most marked in the lower members, having almost disappeared in the case of succinic acid. In the neutralisation of N -oxalic acid, potassium was used instead of sodium, as the oxalate of the latter is not sufficiently soluble; both metals were examined in $N/10$ -solution, the two spectra being almost identical. Fumaric acid was examined in order to see if the property of simple unsaturation produced any effect; it will be noted that both acid and salt have the same absorptive power. Calcium malonate and calcium succinate were also photographed, the former in $N/100$ - and the latter in $N/10$ -solution; it being thought that in these cases the

presence of a bivalent metal might give rise to a cyclic compound. Unfortunately at the dilutions used both salts are practically diactinic, so that, even if a ring is formed, it produces no increase in absorptive power, at any rate in aqueous solutions.

It is interesting to note that whilst conjugation of unsaturated centres does not of necessity induce change in absorptive power on salt-formation, still the view put forward in two former papers (Crymble, Stewart, Wright, Rea, and Glendinning, T., 1911, **99**, 541, 1262)—that greater general absorption is shown by compounds possessing such conjugation than by those in which it is absent—finds strong confirmation in the results obtained for this series. Of the first three members oxalic acid shows the greatest absorption, and succinic the least, proving that the effect of conjugation can outweigh that of increasing molecular weight.

TABLE II.

	10 cm. Spectrum transmitted to λ .	1 cm. Spectrum transmitted to λ .	κ .
Oxalic acid, <i>N</i>	3000	2800	10.0 (?)
Potassium oxalate, <i>N</i>	2860	2680	—
Malonic acid, <i>N</i>	2520	2440	0.163
Sodium malenate, <i>N</i>	2485	2385	—
Succinic acid, <i>N</i>	2460	2350	0.0066
Sodium succinate, <i>N</i>	2460	2340	—
Fumaric acid, <i>N</i> /100.....	3005	2720	0.09
Sodium fumarate, <i>N</i> 100	3000	2720	—

More dilute solutions were examined in the cases of oxalic and fumaric acids, the results being in harmony with those obtained for the higher concentrations.

Various Aromatic Acids.—Acids which contain an aromatic nucleus often exhibit a greater change in absorptive power on neutralisation than do those of an aliphatic nature. The indicators, and the "pseudo-acids" of Hantzsch, all possess this property in a marked degree; fundamental difference of structure between the acid and its salt being in these cases the generally accepted explanation. Numerous compounds of a phenolic nature, as investigated by Baly and others (T., 1905, **87**, 1345; 1910, **97**, 1494) also show considerable change on the addition of sodium hydroxide, but the cause of the change is not quite so evident. Finally, there are many acids of an aromatic nature the spectra of which are either identical with those of their sodium salts, or else differ from the latter only in a very slight degree. In this last group we may place benzoic acid, and the homologous compounds, phenyl-

acetic and phenylpropionic acid. The following table contains the results for a few of the more simple compounds photographed in aqueous solutions.

TABLE III.

	10 cm. Spectrum transmitted to λ .	1 cm. Spectrum transmitted to λ .	κ .
Benzoic acid, <i>N</i> /100	2935	2875	0.0060
Sodium benzoate, <i>N</i> /100	2865	2790	—
Phenylacetic acid, <i>N</i> /100	2695	2330	0.0056
Sodium phenylacetate, <i>N</i> /100	2700	2330	—
Phenylpropionic, <i>N</i> /100	2710	2310	0.0023
Sodium phenylpropionate, <i>N</i> /100	2710	2300	—
Cinnamic acid, <i>N</i> /1000	3190	3100	0.0035
Sodium cinnamate, <i>N</i> /1000	3090	3005	—
Salicylic acid, <i>N</i> /100	3400	3320	0.102
Sodium salicylate, <i>N</i> /100	3490	3350	—
Phenol, <i>N</i> /10	2920	2875	very small
Sodium phenoxide, <i>N</i> /10	3180	3135	—
Picric acid, <i>N</i> /10,000	4350	2320	very great
Sodium picrate, <i>N</i> /10,000	4350	2320	—
Hippuric acid, <i>N</i> /100	2895	2820	0.0222
Sodium hippurate, <i>N</i> /100	2890	2820	—

The absorption bands which exist in phenol and its derivatives have been left out of account in the above table; also, most of the compounds were examined in more dilute solutions, the results being in agreement with those given.

Inorganic Acids.—For the most part the inorganic acids are unsuitable for this type of investigation, for since the property of homology is absent, it is not possible to draw comparisons between acids of gradually varying structure; moreover, a considerable number of the inorganic acids and salts are too diactinic to admit of investigation. Mention should be made of the work of Hartley, who has shown that nitric acid and its potassium salt give identical spectra (*T.*, 1902, 81, 556), whilst Ostwald has made a large number of experiments with the permanganates and other coloured salts.

Two cases of interest will be mentioned out of the few acids examined. Hydrogen sulphide and arsenious acid both show a large increase in absorption on neutralisation with sodium hydroxide.

TABLE IV.

	Acid.		Salt.	
	10 cm.	1 cm.	10 cm.	1 cm.
Hydrogen sulphide, <i>N</i> /10	2480	2330	2790	2685
Arsenious acid, <i>M</i> /10	2435	2320	2695	2570

EXPERIMENTAL.

The water used in this investigation was distilled from silica, the vapour being passed over red-hot silica wool. A sample of 10 cm. thickness was diactinic to $\lambda = 2260$.

As a rule, the salts were prepared by the addition of excess of sodium hydroxide to the acid. The sodium hydroxide used was prepared from metallic sodium. A 10 cm. length of 2*N*-solution was diactinic to $\lambda = 2330$. The substances used were purified so as to give constant melting or boiling points. The hydrogen sulphide was prepared from iron sulphide, and was purified by passing the dry gas over iodine; it was then well washed before being absorbed. The strength of the solution was estimated by means of iron alum and potassium permanganate.

In every case the acid and its salt were photographed on the same plate, thus avoiding errors due to difference of development; moreover, various other thicknesses were examined besides those tabulated.

Summary.

Although it is hardly possible with the present data to state definitely when an acid will show an absorption spectrum different from that of its sodium salt; still, the following points seem clear.

1. The change in degree of ionisation which takes place on the neutralisation of an acid does not in itself of necessity produce a change in the absorption spectrum.

2. Many acids show spectra differing from those of their sodium salts, even when the structure of the acid is so simple as to scarcely admit of molecular rearrangement.

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