NOTES.

209. *The Ionization of Saturated* n-*Aliphatic Dicarboxylic Acids in Sulphuric Acid.*

By L. A. WILES.

THE measurement of the basicity of a series of saturated aromatic diketones in sulphuric acid has been described by Wiles and Baughan (*J.*, 1953, 933). As indicated by van't Hoff's i factor, the early members of this series are monoacid bases ($i = 2$), whereas later members, in which the carbonyl groups are separated by three or more methylene groups, are completely ionized as diacid bases ($i = 3$).

A survey of the literature suggested that the ionization of saturated n-aliphatic dicarboxylic acids in sulphuric acid might show the same effect, but the data available are for work done before cryoscopy in sulphuric acid as solvent was firmly established. As shown in the following table, the observations of different workers are not concordant and for this reason the ionizations of the dicarboxylic acids were re-investigated with the results shown in the Table. The present results vindicate Oddo and Casalino's observations (*loc. cit.*).

Acid ($R = CO_2H$)	Values of i		Acid dissn. constants (e)	
	This work	Previous data	$K_1 \times 10^5$	$K_2 \times 10^6$
$R \cdot R$	1·3 *	1·2—1·3 (a)	5800	64
		1·1 (b)		
$R \cdot CH_2 \cdot R$	2·0	1·8—1·9 (a)	149	2·0
		1·4—1·7 (c)		
$R \cdot [CH_2]_2 \cdot R$	2·5	2·2—2·3 (a)	6·4	3·3
		2·2—2·4 (c)		
		3 (d)		
$R \cdot [CH_2]_3 \cdot R$	2·6	2·5—2·6 (a)	4·5	3·8
$R \cdot [CH_2]_6 \cdot R$	2·6	2·5—2·7 (a)	3·0	4·0
$R \cdot [CH_2]_8 \cdot R$	2·6	2·6—2·7 (a)	2·8	†

* Increases with time.   † Data unreliable.

(a) Oddo and Casalino, *Gazzetta*, 1917, **47**, 200. (b) Hantzsch, *Z. physikal. Chem.*, 1908, **65**, 41. (c) *Idem, ibid.*, 1907, **61**, 257. (d) Hammett, "Physical Organic Chemistry," New York, 1940, p. 47. (e) From Dyson, "A Manual of Organic Chemistry," Vol. 1, p. 533, Longmans, 1950.

Oxalic acid is largely un-ionised in sulphuric acid (precise measurement of i is not possible since oxalic acid is decomposed by sulphuric acid; the remaining acids of the series are

completely stable). This lack of ionization is not unexpected since oxalic acid is a relatively strong acid, particularly at the first dissociation stage. Moreover, the addition of a single proton would not form a stable hydrogen-bonded ring as it would only contain five members. Malonic acid, a much weaker acid than oxalic acid, adds a single proton, and there is the possibility of forming a six-membered ring. Succinic acid, and higher acids of the series, are only partly ionized as diacid bases ($i = ca.$ 2·6). These acids are all of the same order of strength, and they are all sufficiently strong to prevent the complete addition of two protons per molecule. The value of $i = 3$, mentioned by Hammett (*op. cit.*) for succinic acid, differs from the results of the present research and of Oddo and Casalino (*loc. cit.*).

In general, the data given here are supported by the work of Kendall and Carpenter (*J. Amer. Chem. Soc.*, 1914, **36**, 2498), who found that weak organic acids (*e.g.*, succinic and glutaric acids) formed addition compounds with sulphuric acid, but that an increase in the acidic strength of the organic acid was accompanied by the loss of this property. The relative i values for the higher members of the series of dicarboxylic acids ($i = 2\cdot6$) and of diketones ($i = 3$) indicate that the acids are weaker bases than the ketones. Further evidence for this is data given by Hammett (*op cit.*, p. 271) which show, from ultra-violet absorption measurements of the degree of ionization in mixtures of sulphuric acid and water, that aromatic monocarboxylic acids are weaker bases than monoketones. Craig, Garrett, and Newman (*ibid.*, 1950, **72**, 163) also found that in methanesulphonic acid, the acidity of which corresponds to sulphuric acid diluted with 25% of water, the i values of organic acids are smaller than those for ketones.

Experimental.—The carboxylic acids were of " analytical reagent " quality and were used, after being dried, without further purification. The apparatus and procedure have been described by Wiles and Baughan (*loc. cit.*). The acids were not recovered from the solvent but, except in the case of oxalic acid, the freezing points showed no diminution even after a day or longer, and the complete stability of the acids in sulphuric acid is therefore inferred.

The assistance of discussions with Dr. B. W. V. Hawes is acknowledged.

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210. *The Infra-red Spectra of Quaternary Methiodides of NN-Disubstituted Thioamides.*

By J. D. S. GOULDEN.

DURING the examination of the infra-red absorption spectra of the Chabrier–Renard compounds reported by Peak and Stansfield (*J.*, 1952, 4067) unusually low values were found for the C=N$^+$ vibration frequency. Examination of the spectra of other compounds in this series now suggests that these low values were due to resonance contributions from the sulphonium forms (I) to the predominating ammonium forms (II).

Although Randall, Fowler, Fuson, and Dangl (" Infra-red Determination of Organic Structures," Van Nostrand Co. Inc., New York, 1949, p. 5) state that the C=N group in acyclic systems absorbs in the region 1695—1639 cm.$^{-1}$, the highest value found here for this bond in the quaternary methiodides of *NN*-disubstituted thioamides was 1607 cm.$^{-1}$. The presence of a positive charge on the nitrogen atom would be expected to give rise to
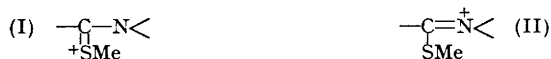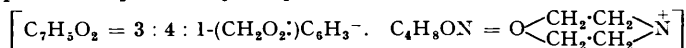

a higher C=N frequency value, since the positive charge would counter the electron-withdrawing effects of groups attached to the carbon and nitrogen atoms and thus prevent a lowering of the C=N frequency value. This effect is demonstrated in the case of 2-phenyl-*N*-piperonylidene-ethylamine (1) and its methiodide (4). When an SMe group is attached to the carbon atom in the C=N group, however, quaternization leads to a fall in the value of the C=N frequency, as can be seen from the Table (Nos. 3 and 8).

These results show that, although substitution changes on the carbon atom of a C=N$^+$

group cause little change in the $C\overline{}N$ frequency, yet those on the nitrogen atom have pronounced effects upon it. Ingold (*J.*, 1933, 1120) has shown that the $-I$ effect of a nitro-

$C\overline{}N$ *Frequencies* (*in* cm.$^{-1}$) *of* $R_1R_2C{:}NR_3$ *and* $R_1R_2C{:}\overset{+}{N}R_3R_4\}I^-$ *compounds in chloroform.*

$R_1R_2C{:}NR_3$ Type

(1) $R_1 = H$, $R_2 = C_7H_5O_2$, $R_3 = CH_2\cdot CH_2Ph$	-1646
(2) $R_1 = MeS$, $R_2 = Ph$, $R_3 = Me$	-1622
(3) $R_1 = MeS$, $R_2 = Ph$, $R_3 = Ph$	-1611

$R_1R_2C{:}\overset{+}{N}R_3R_4\}I^-$ Type

(4) $R_1 = H$, $R_2 = C_7H_5O_2$, $R_3 = CH_2\cdot CH_2Ph$, $R_4 = Me$	-1659
(5) $R_1 = MeS$, $R_2 = Me$, $R_3 = R_4 = Me$	-1607
(6) $R_1 = MeS$, $R_2 = Me$, $NR_3R_4 = C_4H_8ON$	-1581
(7) $R_1 = MeS$, $R_2 = Ph$, $NR_3R_4 = C_4H_8ON$	-1580
(8) $R_1 = MeS$, $R_2 = Ph$, $R_3 = Ph$, $R_4 = Me$	-1562
(9) $R_1 = MeS$, $R_2 = Ph$, $R_3 = R_4 = Ph$	$-$ *ca.* 1510

$$\left[C_7H_5O_2 = 3:4:1\text{-}(CH_2O_2{:})C_6H_3{}^-. \quad C_4H_8ON = O{\Big\langle}{\overset{CH_2\cdot CH_2}{\underset{CH_2\cdot CH_2}{}}}{\Big\rangle}\overset{+}{N}\right]$$

gen atom attached to a phenyl group is normally overpowered by the $+T$ effect of the nitrogen atom. It would seem, however, that the $-I$ effect becomes more powerful when the nitrogen atom carries a positive charge, since the substitution of phenyl groups on the positively charged nitrogen atom results in an increasing amount of the positive charge being transferred to the sulphur atom, as is shown by the lowering of the $C\overline{}N$ frequency. Even in the case of *N*-α-methylthiobenzylidene-*NN*-diphenylammonium iodide (9), the $C\overline{}N$ frequency is nearer to that of the $C\overline{}N$ bond at *ca.* 1650 cm.^{1} than to that of the $C-N$ bond at *ca.* 1300 cm.^{1}, showing that in all the methiodides examined here, the ammonium form (II) makes a larger contribution than the sulphonium form (I) to the molecular structure.

It is noteworthy that conjugation effects leading to a decrease in frequency value generally give rise to an increase in the ε_{molar} value of the absorption band. In the case of the quaternary methiodides of *NN*-disubstituted thioamides, it was observed that the ε_{molar} values decreased slightly as the frequency value decreased, their values being in the region of 200. This high ε_{molar} value enabled the $C\overline{}N$ frequency to be easily distinguished from the weaker benzene-ring absorption bands in the same spectral region.

The difficulty of identifying the weak $C-S$ frequency amongst the strong skeletal vibrations in the 570—710 cm.^{1} region made it impossible to follow the corresponding changes in the $C-S$ frequency.

Experimental.—Spectra were obtained with a Grubb–Parsons S.3 single-beam spectrometer, a rock-salt prism and an a.c. thermocouple detector being used. Solutions containing about 50 mg./ml. were examined in pure chloroform solution in 0·13-mm. and 0·23-mm. cells. Frequency values are considered to be accurate to $\pm$ 2 cm.$^{-1}$ except in the case of *N*-α-methylthiobenzylidene-*NN*-diphenylammonium iodide (9), where the width of the band reduced the accuracy to about $\pm$ 10 cm.$^{-1}$.

N - α - *Methylthiobenzylidene* - NN - *diphenylammonium iodide.* Thiobenzodiphenylamide (Russell, *J.*, 1910, **97**, 956) was refluxed for 1 hr. with excess of methyl iodide to form the *iodide*. After cooling, this was filtered off, dissolved in dry ethanol, and precipitated by slow addition of dry ether. Yellow crystals which turned brown at 115—117° and decomposed at 120—123° were obtained in 95% yield (Found : C, 55·7; H, 4·6. $C_{20}H_{18}NIS$ requires C, 55·7; H, 4·2%).

N-Piperonylidene-2-phenylethylamine and its methiodide were prepared by Hamilton and Robinson's method (*J.*, 1916, **109**, 1033). All the other compounds listed were described by Peak and Stansfield (*loc. cit.*).

The author thanks Dr. F. Stansfield for supplying most of the compounds, and Mr. B. Peutrell for assistance in preparing the others.