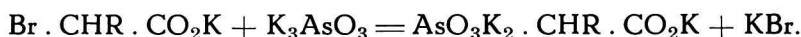


**Chemistry.**— *Optically active  $\alpha$ -arsoncarboxylic acids.* By H. J. BACKER and C. H. K. MULDER. (Communicated by Prof. F. M. JAEGER.)

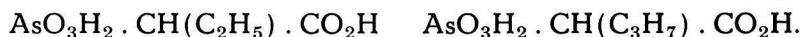
(Communicated at the meeting of March 31, 1928).

The optically active sulfocarboxylic acids show remarkable changes in rotatory power on neutralisation.

For the purpose of comparison we have now prepared some corresponding  $\alpha$ -arsoncarboxylic acids. These acids are obtained in excellent yield by the reaction of the potassium salts of  $\alpha$ -bromocarboxylic acids with potassium arsenite :



Only the first two terms of the series, arsonacetic acid <sup>1)</sup> and  $\alpha$ -arsonpropionic acid <sup>2)</sup>, are known. We have prepared  $\alpha$ -arsonbutyric and  $\alpha$ -arsonvaleric acids :



$\alpha$ -Arsonbutyric acid crystallises from water in anhydrous prisms and sometimes in plates melting at 127°.  $\alpha$ -Arsonvaleric acid, recrystallised from the same solvent, separates in prisms or plates of melting point 114°. These acids may be titrated as dibasic acids, when using phenolphthalein as indicator.

The  $\alpha$ -arsonic acids, derived from propionic, butyric and valeric acids, have an asymmetric carbon atom and should thus be resolvable into optically active enantiomorphs.

In fact the resolution has been successful by means of the secondary quinine salts.

$\alpha$ -Arsonpropionic acid gives a diquinine salt with 6 molecules of water ; the corresponding salt of  $\alpha$ -arsonbutyric acid crystallises with 5 molecules, that of  $\alpha$ -arsonvaleric acid with 4 molecules of water. The solubility of these diquinine salts in water is slight, namely about 0.8, 0.7 and 0.6 % respectively at room temperature.

The quinine salts may be recrystallised from dilute alcohol. They separate in concentric conglomerates of long needles.

Careful decomposition by baryta gave the barium salts, from which hydrochloric acid liberated the active acids.

About six recrystallisations were necessary to obtain the quinine salts in the pure active form.

The rotation of the acids and their salts was measured for different

<sup>1)</sup> PALMER, J. Amer. Chem. Soc. **45**, 3023 (1923). RAMBERG, Svensk Kem. Tidskr. **36**, 119 (1924).

<sup>2)</sup> WIGREN, Svensk Kem. Tidskr. **36**, 127 (1924).

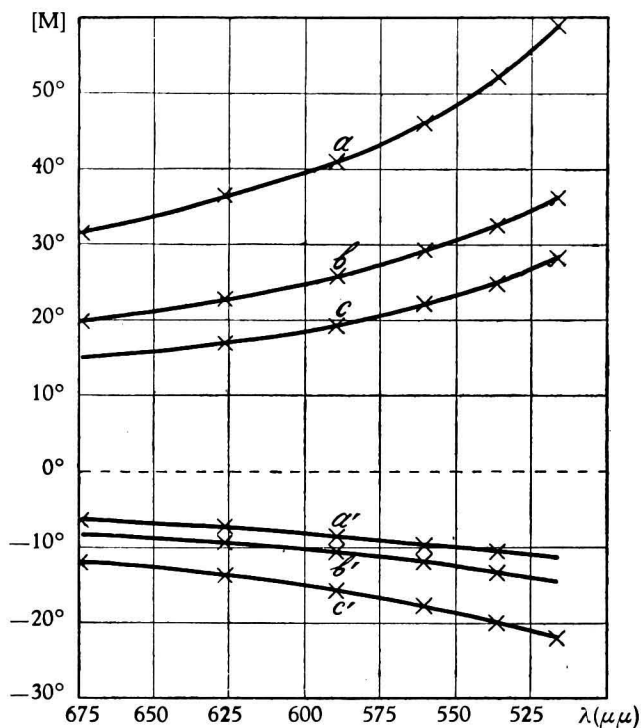
wave-lengths. The curves of rotatory dispersion have been plotted by means of the values, which are given in the following tables.

free acids	$\lambda(\mu\mu)$	674.0	626.5	589.3	560.5	536.5	516.0
d- $\alpha$ -arsonpropionic	[M]	+31.5	+36.1	+41.0	+46.0	+52.2	+58.9
d- $\alpha$ -arsonbutyric	..	+19.7	+22.7	+25.7	+29.1	+32.5	+36.3
d- $\alpha$ -arsonvaleric	..	—	+16.7	+19.3	+22.1	+24.8	+28.3

secondary barium salts	$\lambda(\mu\mu)$	674.0	626.5	589.3	560.5	536.5	516.0
d- $\alpha$ -arsonpropionic	[M]	-6.5	-7.3	-8.5	-9.7	-10.5	—
d- $\alpha$ -arsonbutyric	..	—	-9.4	-10.5	-11.9	-13.4	—
d- $\alpha$ -arsonvaleric	..	-10.2	-13.7	-15.6	-17.7	-20.0	-22.0

The tables and the figure show that neutralisation of two acid functions changes the sign of rotation.



Rotatory dispersion of  $\alpha$ -arsoncarboxylic acids and their secondary barium salts.

- a.  $\alpha$ -Arsonpropionic acid    a'. Salt.  
 b.  $\alpha$ -Arsonbutyric acid.    b'. Salt.  
 c.  $\alpha$ -Arsonvaleric acid.    c'. Salt.

The relation between the molecular rotation of the acid and the salt is  $-4.8$  for  $\alpha$ -arsonpropionic acid,  $-2.4$  for  $\alpha$ -arsonbutyric acid and  $-1.2$  for  $\alpha$ -arsonvaleric acid. Thus this relation changes gradually.

The study of the permanence of rotatory power has given remarkable results.

Whilst optically active sulfocarboxylic acids are less stable in alkaline than in acid solution, the arsoncarboxylic acids show just the opposite behaviour.

The barium salts of the active arsoncarboxylic acids are perfectly stable in aqueous solution, even at  $100^\circ$ .

The activity of the free acids, however, is labile, especially in the presence of strong inorganic acids.

The racemisation was examined kinetically; it proved to be a monomolecular reaction.

The constant increases almost proportionally to the quantity of hydrochloric acid added. The racemisation constant of the pure acids increases with their molecular weight.

A detailed account of the  $\alpha$ -arsoncarboxylic acids and their derivatives will be published elsewhere.

*Organic Chemical Laboratory of the  
State University.*

*Groningen.*