

Citation:

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acid (No. 19) notwithstanding its very low division factor yet promotes the development not so well as, for instance, 3,4 dioxycarboxylic acid. (Notice the amount required for a maximum development, last column Table 5).

Presumably, this is also the reason why *o*-toluic acid with its large division factor acts somewhat less retarding than *p*-toluic acid; we have shown that *o*-toluic acid is oxidised to a substance which is also formed during the assimilation of *o*-phthalic acid; it is, therefore, very probable that *o*-toluic acid is first oxidised to the favourable *o*-phthalic acid.

The research will be continued by us in various directions.

It is our pleasant duty to thank Prof. Dr. BEYERINCK and Mr. JACOBSEN for their kind support in the biological part of the research.

Org. Chem. Lab. Techn.

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University Delft.

Chemistry. — “*On the velocity of hydration of some cyclic acid anhydrides.*” By Prof. J. BÖESEKEN, A. SCHWEIZER and G. F. VAN DER WANT. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of November 25, 1911).

In connection with the research of A. SCHWEIZER and myself, of which a communication is inserted in these Proceedings (November 26, 1910, p. 534), we have measured the velocity of hydration of some saturated cyclic acid anhydrides in order to collect more data as to the value of the figures thus obtained as a measure of the ring tension.

In the said communication we already pointed out that it is not excluded that the velocity of hydration of those anhydrides will be affected by their affinity for water and their ring tension so that in the figure found both these causes will find their expression.

It is, of course, not feasible to ascertain what part is due to the affinity, yet, we may expect that this affinity will be connected with the dissociation constant of the acids obtained from the anhydrides.

The dissociation constant is up to a certain degree a measure for the velocity with which the acid is further divided into its ions; we may expect that the quicker this takes place the more rapidly will the disappeared acid molecules be replenished from the anhydride.

If we compare the figures for the hydration constant, obtained by ourselves and other investigators, with those of the electrolytic dissociation, a parallelism cannot be denied, particularly when we choose analogous substances for comparison.

The number of substances investigated is, as yet, far too small to enable us to draw general conclusions; still in the succinic acid

Hydration constant of some acid anhydrides calculated for a monomolecular reaction with the minute as time unit; and the dissociation constant K .

Group	Anhydride of	$0.4343 \times K_{\text{gas}}$	$0.4343 \times K_0$	Investigators	Dissociation constant K of the acids
I	succinic acid	0.0736	0.0088	Voerman	} 0.00652 (V.)
	»	0.0693		Rivett and Sidgwick	
	»			Böeseken and Schweizer	
	methyl succinic acid	0.0965		Riv. and Sidg.	0.0086 (O.)
	s.dimethyl m.p. = 87°	0.110		} Bö. and V. d. Want	0.0132 (V.d.W.)
	s.dimethyl m.p. = 42°	0.153			0.0194 »
II	maleic acid	0.690	0.125	Riv. and Sidg.	} 1.17 (Schw.)
	»			Bö. and Schw.	
	itaconic acid	0.0776		} Riv. and Sidg.	0.012 (O.)
	citraconic acid	0.459			0.34 »
	o.phthalic acid	0.2766			0.121 »
III	glutaric acid	0.0742	0.0117	Voerman	0.0047 (V.)
	acetyl β oxyglutaric acid	0.096		Bö. and Schw.	0.0157 (Schw.)

group the increase of the velocity of hydration with that of the dissociation constant is so striking that it cannot be quite accidental.

The same is true for the maleic acid group to which even o-phthalic acid is connected.

The slight increase of the velocity of hydration, noticed by VOERMAN, when one passes from succinic anhydride to glutaric anhydride now finds a very simple explanation in the slight dissociation constant of glutaric acid, as compared with that of the succinic acid.

From this point of view the difference in tension between this 6-ring and the 5-ring of succinic anhydride would be considerably

greater than might be surmised from a comparison of VOERMAN'S figures.

In both the symmetric dimethylsuccinic anhydrides ¹⁾, we notice that the two constant-couples are almost proportionate, so that the relation of the dissociation constant with the hydration is particularly striking; the influence of the ring tension (to be expected on account of the difference in configuration) appears to become quite inconspicuous.

In other cases, this affinity is less pronounced, so that we can say, as a rule, that the hydration changes in the same sense as the dissociation constant, but that the changes do not keep equal pace. Whether this bears a relation to the ring tension remains to be seen when a much greater number of experiments have been made.

At present we can, however, state with great probability that in the hydration of acid anhydrides the affinity of water for anhydride plays a very important role.

The description of the experimental part of this research carried out with the assistance of MESSRS. A. SCHWEIZER and G. F. VAN DER WANT will shortly appear in the *Recueil des travaux Chimiques*.

Org. Chem. Lab. Techn. University.

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¹⁾ I call attention to the fact that some confusion exists in the denomination of the two symmetric acids. They are indicated by the names *cis* and *trans*, *fumaroid* and *maleinoid*, *para* and *anti*, *racemic* and *meso (anti)*.

The last is undoubtedly the most rational one, but it cannot be applied, because it is not known, as yet, to which of the stereoisomers the racemic configuration appertains.

One is accustomed to give to the acid with the highest melting point the name of *para*- or *trans*-dimethylsuccinic acid in the idea that this is the racemic acid; but this is only based on some speculative ideas of BISCHOFF (*B* 24 p. 1086) and v. BAEYER (*Ann.* 258 p. 180) as to the privileged position of the groups, which in this case have now little value.

So long as not one of these acids has been resolved into its optical components, there is no certainty; it is even more probable that the acid with the lowest melting point (128°) will prove to be the racemic acid because the anhydride of this acid, which melts at 87°, is stable and because we may expect that the methyl-groups on both sides of the ring will render the same more stable than when they are situated at the same side. The *trans*-anhydride belongs to the racemic acid (Compare also MICHAEL *Journ. f. pr. Ch.* [2] 46 p. 422).

Provisionally, I have indicated the anhydrides with their melting points. (J. B.).