

Citation:

J. Böeseken & P.E. Verkade, The mechanism of the acid formation of aliphatic acid anhydrides in an excess of water, in:

KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 718-726

The progressive change of the solubility is also characterised by the fact that after about 25 minutes, when the solubility of phthalic acid (35.2 millimol. per litre) has not yet been attained, the condition is already such that the solution contains a preponderance of acid. The idea that phthalic anhydride should be readily soluble is, therefore, without any foundation; the anhydride concentration can, moreover, not be calculated by simply deducting the solubility of the acid in water from the total solubility.

This last experimental series therefore also confirms our contention: the anhydride passes into solution as such and then becomes hydrated and this so rapidly in comparison with its solubility velocity that the non-variant (p,t) equilibrium is not attained, or at least not permanently so. The anhydride, if we will not credit it with an *abnormally* small solubility velocity (for which there exists no reason, just the contrary), has a much smaller solubility than the acid.

No measurements have as yet been carried out with succinic anhydride, but looking at the parallel behaviour of the two acid anhydrides similar relations may be expected there also.

Owing to the peculiar relations between the homogeneous and the heterogeneous reaction velocities in this kind of systems, we are here at the limitation where we may still speak of actual pseudo ternary systems. In connection therewith and other correlated questions the investigation of different systems is being continued.

Utrecht, Dec. 1913.

VAN 'T HOFF-Laboratory.

Chemistry. — “*The mechanism of the acid formation of aliphatic acid anhydrides in an excess of water*”. By Prof. J. BÖESEKEN and P. E. VERKADE. (Communicated by Prof. HOLLEMAN).

(Communicated in the meeting of December 27, 1913).

The communication of WILSDON and SIDGWICK¹⁾ on the hydration of some acid anhydrides induces us to give a short résumé of the results obtained by us when investigating the hydration of the aliphatic acid anhydrides.

This investigation²⁾ has already been announced by one of us some time ago. He had found that the hydration constant of the cyclic acid anhydrides was connected with the dissociation constant of the acids formed thereof. As it was his intention to get to know

¹⁾ Soc. 103, 1959 (1913).

²⁾ Recueil 31, 90 (1912).

something about the ring tension eventually occurring in those acid anhydrides, it had to be decided whether the dissociation constant of the acids was the only or principal factor which, besides that ring tension, could exert an influence on the hydration velocity. The hydration of the anhydrides of the fatty acids seemed to him the most appropriate one, because in this the factor of the ring tension is excluded, whilst that of the dissociation constant can be readily applied. Moreover, the values of the dissociation constants of the fatty acids do not diverge much, so that other factors can exert their influence distinctly. While the detailed account of this investigation will be published in another form ¹⁾, we give here a short summary of the results obtained.

The hydration velocity of the acid anhydrides was determined in the manner indicated by VOERMAN ²⁾, namely by measuring the conductivity of the aqueous solutions in which it is assumed that only the acid determines the conductivity and that this is not modified by the anhydride still present.

The conductivity of the acids and the dissociation constant to be deduced therefrom had to be accurately known, because from the conductivity found in the hydration the concentration of the acid formed (and consequently that of the anhydride consumed) had to be calculated. As the values given in the literature for the diss. const. often differ considerably, we judged it necessary to make new determinations thereof.

They were carried out in the usual manner already frequently described by us.

A correction for the conductivity of the water itself ($1-1.5 \times 10^{-6}$) was not applied, because this conductivity is caused in the carefully

Dissociation-constants of the fatty acids.

	μ^0_∞	μ^{25}_∞	$K^0 \times 10^5$	$K^{25} \times 10^5$
acetic acid	—	387	—	1.82
propionic „	241	384	1.37	1.31
n. butyric „	239	381	1.55	1.47
isobutyric „	239	381	1.53	1.44
isopropylacetic acid	—	378	—	1.68

¹⁾ Dissertation of P. E. VERKADE to appear shortly.

²⁾ Recueil **23**, 265 (1902). Dissertation Groningen 1903.

cleaned Jena vessels by carbon dioxide and the dissociation thereof is practically repelled by the fatty acids.

The constant given above for *isopropylacetic acid* ($= 1.68$) has been found equal for both the commercial and synthetic product. As the former is contaminated with methylethylacetic acid and as the constant thereof does not differ much from that of the pure *isovalerianic acid*¹⁾, this was to be expected.

The measurements of the hydration velocity were executed in the same manner as those described previously.²⁾ The anhydride

Propionicanhydride 0°.				Aceticanhydride 25°0.			
<i>t</i>	<i>v</i>	<i>c</i>	0.4343 <i>k</i> ⁰	<i>t</i>	<i>v</i>	<i>c</i>	0.4343 <i>k</i> ²⁵
0	0.0 ₄ 598	0.00481	—	0	0 0 ₃ 132	0.00674	—
3	664	594	0.00689	1	1555	937	0.0721
4	685	631	691	1 1/2	164	0.01048	700
5	705	668	695	2	172	1151	713
6	725	701	686	2 1/2	1795	1250	718
7	745	740	700	3	186	1341	718
8	764	767	679	3 1/2	192	1425	713
9	780	809	699	4	1965	1486	703
11	815	879	706	4 1/2	2015	1560	706
13	844	940	699	5	206	1628	704
15	874	0.01002	698	5 1/2	2095	1680	703
17	902	1070	708	6 1/2	213	1734	705
20	938	1150	698	∞	2505	2380	—
23	973	1238	704	mean: 0.4343 <i>k</i> ²⁵ = 0.0709.			
26	0.0 ₃ 1008	1325	712				
29	1037	1401	712				
32	1064	1473	711				
36	1098	1563	710				
∞	1497	2913	—				

mean: 0.4343 *k*⁰ = **0.00700.**

¹⁾ BILLITZER, Sitz. Ber. Ak. Wien 1899, p. 416.

²⁾ Rec. **31**, 80 (1912).

was shaken with previously warmed (cooled) conductivity water and then filtered rapidly into the resistance vessel.

As 0-point was taken the moment that the irregular initial reaction was over and the bridge readings could take place accurately.

Subjoined are found some of these measurements. (See p. 720).

In this manner the following constants were obtained for different acid anhydrides.

Hydratation-constants of the fatty anhydrides.			
	0.4343 k_0	0.4343 k^{25}	Values found by RIVETT, WILSDON and SIDGWICK.
acetic anhydride	—	0.0713	0.0701
propionic „	0.00700	0.0372	0.0372
n. butyric „	0.00471	0.0243	0.0204
isobutyric „	0.00454	0.0227	
aceticpropionicanhydride	—	0.0522	

This table contains a résumé of the constants obtained at an anhydride concentration of 0.01—0.02 normal. We chose this small concentration, because it had been noticed by SIDGWICK and his coadjutors¹⁾ that the constant decreases when a much greater concentration is taken and also because the higher fatty acids were soluble to the extent of about 0.03 normal only.

Only under these conditions could the constants obtained be compared mutually.

a. From these data it follows in the first place that the influence of the temperature is about the same for the fatty acids mutually:

$$\frac{k^{25}}{k_0} \text{ for acetic acid} = 5.0^2)$$

$$\text{propionic „} = 5.3$$

$$\text{n. butyric „} = 5.2$$

$$\text{isobutyric „} = 5.0,$$

and differs considerably from that found previously for the cyclic anhydrides.³⁾

¹⁾ Soc 97, 732 (1910), 101, 1708 (1912) and 103, 1959 (1913).

²⁾ This has been deduced from the above measurements in connexion with those of RIVETT and SIDGWICK (l.c.) and ORTON and JONES. Soc. 101, 1708 (1912).

³⁾ Recueil 31, 80 (1912).

b. For *iso* and *n* butyric acid the proportion of the hydration constants = 1 : 1,04, and 1 : 1,07 respectively; that of the dissociation constants 1 : 1,01, and 1 : 1,02 respectively. The branching of a saturated group, appears therefore to exert but little influence on the velocity of hydration. This is in accordance with the fact that the hydration constants of the two isomeric *s* dimethylsuccinic anhydrides are proportional to the dissociation constants of the correlated acids.¹⁾

c. If now we assume provisionally that, other influences being equal, the hydration constant is proportional to the dissociation constant, the specific influence of the saturated group may then be expressed in figures.

Therefore we have only got to divide the hydration constants by the dissociation constants; we then obtain, for the influence of this group, for instance at 25°:

		Proportion
For acetic acid	3.92×10^{-3}	
		1.36
For propionic „	2.89×10^{-3}	
		1.75
„ <i>n</i> butyric „	1.65×10^{-3}	
„ isobutyric „	1.58×10^{-3}	

From the corresponding values for butyric acid and isobutyric anhydride follows that the influence of the configuration of the group in regard to other influences must be trifling (see *b*).

The influence of the mass must be, however, very great as the retardation that occurs by the introduction of two methyl groups in the acetic anhydride (= 1.36) is less than that observed by introducing those same groups into the propionic anhydride (= 1.75).

This stronger retarding influence of the ethyl than that of the methyl group also appears from what has been found in the case of the mixed acetic propionic anhydride. The constant thereof lies between the two constants of the acetic and propionic anhydride, but slightly more towards the constant of propionic anhydride.

In the case of the isovaleric anhydride we have met with very great difficulties; the solubility of this substance in water is exceedingly small so that we could not get solutions containing more than 0,005 mol. %.

Owing, however, to the very small velocity with which the hydration took place and the fairly great conductivity of the isovaleric acid the process could be traced very accurately.

¹⁾ Rec. 31, 80 (1912).

Here it appeared that there was no question of a constant; the calculated constant decreased, but so regularly and (after elimination of all possible disturbing influences) so very concordantly, that we were able to conclude that this decrease might be traced to a very definite cause.

The subjoined table shows one of the many measurements.

Isovaleric anhydride at 25°0.			
t	r	c	$0.4343 k^{25}$
0	0.04670	0.00210	—
1	694	224	0.0247
3	727	244	209
5	757	264	209
7	782	280	201
9	804	294	195
11	822	306	188
14	843	321	179
17	863	335	174
20	879	345	166
25	899	360	156
30	914	371	146
37	929	384	139
45	940	392	123
55	953	401	111
∞	0.031027	463	—

When the constants obtained in the different measurements were plotted against the time, we could draw through the points thus obtained smooth curves which either coincided or ran completely parallel¹⁾, a sign that not only were we not dealing with experimental errors, but that the fall must be attributed to a disturbing reaction and; looking at the regularity, to a follow-reaction.

¹⁾ The latter, because the readings did not always commence exactly at the same moment after the anhydride had been dissolved, as the filtration sometimes took a little longer and because the temperature equilibrium in the resistance vessel was not always attained in the same time.

In consequence of VOERMAN's observations (l. c.) we first believed that the anhydride might be polymerised and that a succession of depolymerisation and hydration was measured. As, however, the anhydride did not give the least indications of polymerisation even in strongly associating liquids, C_6H_6 and $C_6H_5NO_2$, we gave up this idea in favour of the following assumption.

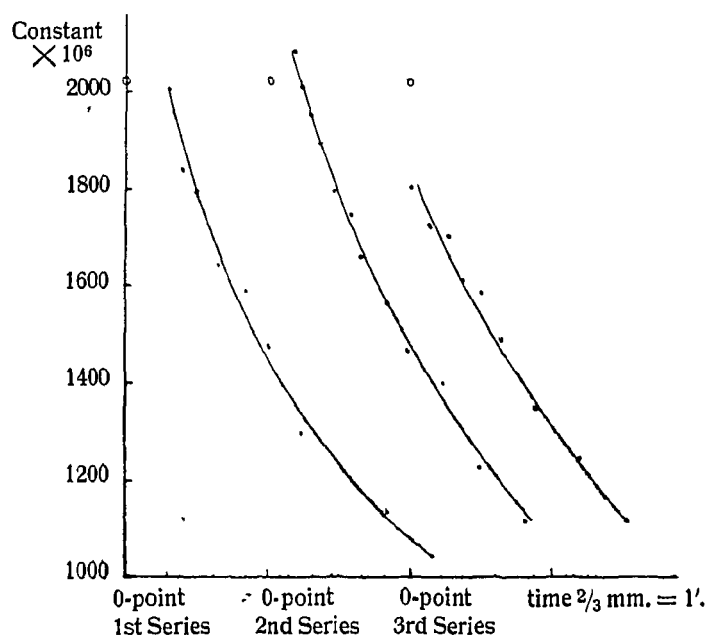
We can imagine the process to be divided into two phases: the first is the union with water or the hydration proper; the second is the splitting of the hydrate into two molecules of acid.

Now in the case of the lower acid anhydrides the first process will take place very rapidly causing the second one to be measured only; hence, the reaction exhibits the form of the simple unimolecular change.

If the velocity of the first in regard to the second is no longer practically infinite, we are then dealing with the succession of two unimolecular processes occurring in the same direction and the unimolecular-calculated constant will exhibit a regular change¹⁾.

We give here three of these observation series obtained with very carefully purified synthetic *isovaleric* anhydride.

Falling constant of the hydration of the *isovaleric* anhydride.



The further discussion of these observations in connection with the

¹⁾ OSTWALD. Lehrbuch Allg. Ch. II, 2, 285.

relation applying to the unimolecular follow reactions will be given elsewhere; we call, however, already now the attention to the fact that BENRATH¹⁾ has found that in glacial acetic acid the reaction between *equivalent* quantities of water and acetic anhydride proceeds unimolecularly, which can only be explained by assuming that in glacial acetic acid they are dissolved jointly as hydrate (in fact that the hydration proceeds exceedingly rapidly) and that this hydrate splits up into the acid molecules²⁾.

Further, we have also succeeded in demonstrating the formation of other additional compounds with the acid anhydrides of which those with *isovaleric* anhydride exhibit a greater stability than those with the lower acid anhydrides.

Thus we could isolate the additive products of hydroferricyanic acid with *isovaleric* and heptylic anhydride in a crystalline condition and analyse the same whereas these two gave with 70% perchloric acid colorations that pointed to additive action.

With great probability we may conclude already now that the conversion of acid anhydrides into acids proceeds in two phases; presumably there first takes place a linking of the anhydride to the watermolecules which occurs very rapidly with the lower terms; this is then succeeded by the splitting reaction which takes place more slowly.

The analogy existing between the acid anhydrides, the esters, and the ethers and between the acid formation, the saponification and the alcohol formation causes the elucidation of the first reaction to become of a more general significance.

If, on further working out the results obtained, it appears that the process studied by us proves with certainty the linking of water followed by hydrolysis, we may expect this to be also the case with the other processes mentioned.

Like in so many other chemical transformations we again get here the impression that the reaction proper is preceded by a previous stage, namely the mutual influence of the molecules.

This is often shown by the formation of an additive product, but here, as in the case of the catalytic phenomena, the reaction proper will proceed more rapidly when this additive product forms more quickly and possesses less stability.

¹⁾ Z. Ph. Ch. 67. 501 (1909).

²⁾ BENRATH measures the density of a mixture of acetic anhydride, glacial acetic acid and water during the hydration; he finds a change in density of about one unit in the second decimal.

SUMMARY.

1. We determined the progressive change of the acid formation from some aliphatic saturated acid anhydrides in presence of an excess of water at 0° and 25°.
2. In the case of the lower acid anhydrides including the butyric acids this proved to be a unimolecular reaction with a relative small temperature coefficient.
3. As from previous investigations it had appeared that the reaction constant is closely connected with the dissociation constant of the acids forming, it could be deduced, by eliminating this influence, that the hydratation constant decreases as the mass of the saturated group increases, and that the branching of the saturated carbon chain has little influence on this constant.
4. From the fall of the "constant" for the acid formation from *isovaleric* anhydride it was deduced that the formation of acid usually takes place in two phases: *a.* Absorption of water, *b.* splitting of the hydrate; that with the lower acid anhydrides the first reaction occurs very rapidly so that only the last unimolecular reaction gets measured; that in the case of the *isovaleric* anhydride the first reaction no longer takes place infinitely in regard to the second so that we must get the image of a follow-reaction with unequal reaction constants.

Delft, December 1913.

Lab. Org. Chem. Techn. Univ., Delft.

Mathematics. — "*Bilinear congruences and complexes of plane algebraic curves.*" By Prof. JAN DE VRIES.

1. We shall consider a doubly infinite system of plane curves of order n , consequently a congruence $[\gamma^n]$. We suppose that through an arbitrary point only *one* curve passes, and that an arbitrary straight line is cut in n points by only *one* curve. The congruence is in that case of the *first order*, and of the *first class*; we shall call it for the sake of brevity a *bilinear congruence*.

As a γ^n of the congruence is determined by a straight line r of its plane φ , all planes φ must pass through a fixed point F , which we shall call the *pole*.

A ray f passing through F (*polar ray*) bears ∞^1 planes φ ; the curves γ^n lying in it form a surface Σ of order $(n+1)$, for any point of f lies on only one curve γ^n .