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The Catalysis of Imide Esters in the Presence of Acids.

A Dissertation.

Submitted to the Faculty of the Graduate Schools of Arts Literature and Science in Candidacy for the Degree of Doctor of Philosophy.

Department of Chemistry.

By William Weldon Nickman.

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THE CATALYSIS OF IMIDO ESTERS IN THE PRESENCE OF ACIDS.

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The permanent value of any theory can be ascertained only by putting the conclusions proceeding logically from its applications in different directions to the test of rigorous quantitative experimentation. In the following pages some of the consequences concerning the behavior of imido esters in acid solution--the quantitative study of which has formed the basis of Stieglitz's theory of catalysis of ordinary esters, cane sugar and similar bodies--- have been examined from this point of view. (1)

It may be said that in the order of time in which the three problems treated in this paper were taken up, that discussed first was investigated last. It is placed first because it leads to the most interesting results.

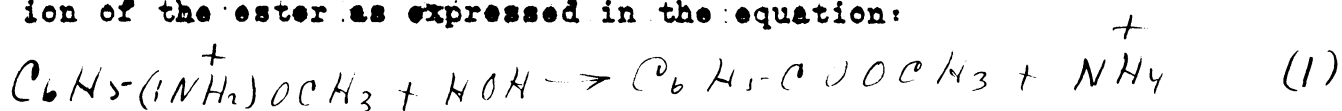
Footnote)

(1) Investigations with other classes of compounds than imido esters are being prosecuted in this laboratory. J. Stieglitz.

I.

The Velocity of Decomposition of Imido Esters as Bromides, Nitrates and Sulphates.

Considerable work has been done in this laboratory (1) on the velocity of the decomposition of the hydrochlorides of imido esters by water and on the effect produced on the velocity by the addition of the alkali hydrochlorides. The conclusions reached may be summarized in the statement that the decomposition seems to be the result of the action of water on the positive ion of the ester as expressed in the equation:



the action proceeding according to the following isothermal equation:

$$\frac{dx}{dt} = K_{v(ion)} \times C_{Pos. Est. Ion.} \times [C_H \times C_{OH}] \quad (2)$$

The addition of alkali salts accelerates this action, as referred to the positive ion as the reacting component, the value of the velocity constant, $K_{v(ion)}$ increasing with the concentration of the added electrolyte; (2) this acceleration is ascribed to a probable increased ionization of water, (3) the third factor in equation (2), under the influence of electrolytes, comparable with the increased ionization of acids, such as acetic, oxalic, formic acid etc. under the influence of neutral salts. (4) In confirmation of

Footnotes)

(1) Stieglitz; Derby; McCracken; Schlesinger. Am. Chem. J. 39, 29, 166, 402, 437, 566, 719.

(2) Barnard.

(3) Arrhenius, Z. Phys. Chem. 1, 126. Euler, Ibid. 32, 348. Stieglitz, Am. Chem. J. 39, 29, 166.

The question whether the so called salt effect may be interpreted as the result of hydrate formation in the solutions will be discussed at length in another place. It does not seem possible.

(4) Arrhenius, Zeit. Phys. Ch. 1, 126, (1887)

such a view Miss Barnard found that the acceleration is the same for the various imido esters investigated, irrespective of the question whether ^{it} is decomposed rapidly or slowly. (1) That is, as demanded by equation (2) $K_{v(\text{ion})}$ under the influence of equivalent quantities of ionized potassium chloride showed the same proportional increase for the various esters, namely about 185% per gram molecule fully ionized salt. Sodium and lithium chlorides, although producing different positive ions, produce the same acceleration, namely 185% per gram molecule fully ionized salt, as does potassium chloride. This conclusion may be formulated mathematically as follows:-

The velocity of decomposition of the imido ester hydrochlorides appears to be dependent on two factors (2)--namely the velocity of decomposition of the positive ester ion by water irrespective of any salt effect, and an increase of this velocity due to the salt effect, which most likely is due, as stated to an increase in the ionization of water, the third factor in the fundamental equation (2). The combined actions may be expressed in the equation:-

$$\underline{K_{v(\text{ion}) \text{ observed}}} = \underline{K_{v(\text{ion})_0}} (1 + A \times m \times \alpha) \quad (3)$$

Footnotes)

(1) Vide also part III. below.

(2) Exactly the same is true in considering the velocity of decomposition of any ester or of cane sugar under the influence of acids, Arrhenius having shown that besides the catalyzing effect of the hydrogen ion, there is also always an additional salt effect produced by the catalyzing acid itself.

in which $K_{\text{velim}}^{\text{observed}}$ is the observed velocity constant referred to the concentration of the positive ester ion(1) $K_{\text{velim}}^{\text{e}}$ is the velocity constant for the decomposition of the positive ester ion in the absence of all electrolytes(2), A is the acceleration produced by the salt effect by one gram molecule of fully ionized salt present, m is the concentration of the electrolyte present and α is its degree of ionization. For instance, in the case of the hydrochloride of ethyl imido benzoate, $K_{\text{velim}}^{\text{e}}$ the velocity of decomposition of the positive ion at 25° in the absence of any electrolyte is $\frac{164}{43430}$ and for potassium, sodium and lithium chloride A is 185% as determined by Miss Barnard.

In considering the velocity of decomposition of any imido ester salt, it is therefore necessary to determine two constants(3) viz. $K_{\text{velim}}^{\text{e}}$ the velocity constant irrespective of any salt effect and A the constant of the accelerating salt effect. $K_{\text{velim}}^{\text{e}}$ should be the same for the decomposition of all the salts of a given imido ester, and A should be the same for the effect of any given salt (e.g. potassium chloride) irrespective of the imido ester on which its effect is produced, i.e. irrespective of the value of $K_{\text{velim}}^{\text{e}}$. The results of Miss Barnard's investigations may be briefly summarized in the statement that she

Footnotes)

(1) $K_{\text{velim}}^{\text{observed}}$ = K_v/α , in which K_v is the velocity of decomposition referred to the total imido ester salt and α is the degree of ionization of the imido ester salt.

(2) The value is obtained by extrapolation from the curve, the concentration of the ionized salt and the values of K_v/α for the various concentrations being used on the coordinates.

(3) See footnote (3), p.2.

found the correctness of the second part of this postulate, viz. that A is the same (e.g. 185% for KCl) for the effect of a given salt on all the imido esters studied. In addition to that Miss Barnard found that A is the same for the ~~the~~ similar salts, potassium, sodium and lithium chloride.

In measuring the velocities in more concentrated imido ester hydrochlorides, a similar salt effect is evident, the observed velocity decreasing owing to the decreased ionization of the salts, but the velocity referred to the positive ion, Kellum increasing as a result ~~of~~ of the auto catalytic salt effect of the imido ester salts themselves, (1) exactly as in the presence of foreign salts. The accelerating effect of the imido ester salt ions is smaller than that of the potassium, sodium and lithium chlorides, being 110 % for the hydrochlorides of ethyl and methyl imido benzoate and about 75% for the hydrochloride of methyl imido para toluylate.

In all these investigations the hydrochlorides exclusively have been used. At the suggestion and under the direction of Prof. Stieglitz I undertook the measurement of the decomposition of the hydrobromides and nitrates and finally also of the sulphates of the imido esters with the object of testing the first postulate discussed above, viz. whether the velocity of decomposition of the positive ester ion, Kellum, - in the calculation of which the salt effects have been eliminated - is the same for a given imido ester, irrespective of the acid with which it is combined.

Footnote)

(1) Schlessinger, Am. Chem. J. 39, 719.

If the reacting component is the positive ester ion- a theory of fundamental importance for the catalytic action of acids(1)- then the velocity of decomposition, k_{ion} , should be the same irrespective of the origin of the ion. If various salts could be used without exhibiting the disturbing influence of an accelerating "salt effect," one could in fact say categorically that all the various salts must show the same velocity constants referred to the concentration of the positive ester ions, if the theory of Stieglitz of the catalysis of esters, imido esters etc. is correct. The fact, however, that there is a secondary accelerating factor, the salt effect, must be taken into consideration. In the simplest case, if the accelerating salt effect caused by the salts of different negative ions, e.g. $\overline{\text{Cl}}$ and $\overline{\text{Br}}$, should prove to be the same, the velocity constant, k_{ion} , obtained for the different salts would still remain the same. The factor A for the effect of the salts of these negative ions can be controlled by studying the imido ester salts not only in aqueous solution but also in the presence of added salts of the acid under investigation, exactly as Miss Barnard did with the hydrochlorides of the imido esters.

The fact that the hydrochlorides of the positive ions, potassium, sodium and lithium, gave the same acceleration (2) led us to hope that such might prove the case, at least, for salts of the univalent negative ions, $\overline{\text{Cl}}$, $\overline{\text{Br}}$, and $\overline{\text{NO}_3}$, -- a result which would simplify the problem.

As a matter of experiment, careful determinations of

Footnotes)

(1) Stieglitz, Am. Chem. J. 39, 29.

(2) Edith E. Barnard.

the degree of ionization by conductivity measurements and velocity determinations made with the hydrobromides in the presence of potassium and sodium bromide showed the potassium and sodium bromide have the same accelerating effect, 185%, as sodium and potassium chloride. This conclusion is borne out by the facts presented, for instance, in the following table, in which the results of the velocity determinations of Miss Barnard's work on the hydrochloride of ethyl imido benzoate in the presence of potassium chloride are compared with the results of my determinations with the hydrobromides of the same salts.

Table I.

K Hal. m	KCl		KBr	
	43430 K_v/α_1		43430 K_v/α_1	
	Found	Calculated.	Found	Calculated.
0	176	176	176	177
0.1	191	190	191	190
0.2	213	214	209	216
0.25	227	228	230	227
0.333	247	246	(238)	247

In the table, column 1 gives the concentration of the potassium salt used, column 2 and 4 contain the values found for the velocity constant referred to the concentration of the positive ester ion in the hydrochloride and hydrobromide respectively.

$K_{ion} = K_v/\alpha_1$ when α_1 is the degree of ionization of the imido ester salt and

$$K_v = \frac{1}{t_2 - t_1} \times \text{Log. nat.} \left(\frac{C - x_1}{C - x_2} \right)$$

represents the concentration of the imido ester salt at any moment. Columns 3 and 5 are calculated on the basis of the fundamental equation, (3) p. 3, 43430 $K_{ion}c$ being taken as 184. The accelerating factor, A , was taken as 185% for both the hydrochloride and the hydrobromide.

It is quite evident from the table that the two salts, potassium chloride and bromide, have exactly the same effect on $k_{\frac{1}{2}}$, ~~the velocity of the action referred to the concentration of the positive ester ion. That being the case, if the reacting component in the decomposition of imido esters by water is the positive ion of the ester, solutions of an imido ester hydrochloride, hydrobromide and nitrate, of the same degree of ionization, should show the same velocity constants, K_v (observed) or $K_{v/\alpha}$, the secondary salt effect being the same for all of them. That such is the case is shown by the following tables.~~

In the first column is found the molecular concentrations of the imido ester salts used; in the columns headed α is given the percent of ionization of each salt for the indicated concentration; in the columns headed K_v are given the constants of decomposition ~~as computed from the equation $K_v = \frac{1}{c_0} \times \log. \text{rat. } \frac{c_0 - x}{x}$~~ as referred to the concentration of the positive ester ion. ~~Common logarithms are used in place of natural logarithms and the constants are multiplied by 10^5 and the values are consequently 43430 too large, but as we wish to see only the comparative values they are left in this shape.~~

in the columns headed $K_{v/\alpha}$ are given the constants of decomposition as referred to the concentration of the positive ion. Common logarithms were used in place of natural logarithms and the constants were multiplied by 10^5 and the values given are consequently 43430 times too large, but as we wish to see only the comparative values they are left in this shape.

Table II.

Ethyl Imido Benzoate.

	Hydrochloride			Hydrobromides.			Nitrates.		
	$\alpha^{(1)}$	$K_v^{(2)}$	$K_{1/2}$	α	K_v	$K_{1/2}$	α	K_v	$K_{1/2}$
35	77.8	138	175.0	75.88	133	173	75.11	133	177
1	71.8	132	184.6	69.38	128	184	68.33	127	186
2	64.5	121	188.0	61.71	119	193	60.46	118	195
333	57.7	114	198.0	54.70	108	198	52.88	107	201

Table III.

Methyl Imido Benzoate.

m	Hydrochloride.			Hydrobromide.		
	$\alpha^{(1)}$	$K_v^{(2)}$	$K_{1/2}$	α	K_v	$K_{1/2}$
0.05	77.0	249	323	78.31	252	321
0.1	71.5	244	341	73.11	242	331
0.2	64.8	232	359	66.09	231	350
0.333	58.4	(222) ⁽³⁾	380	59.51	209(?)	351(?)

A comparison of the values under $K_{1/2}$ for equi-molar solutions shows a very close agreement as the theory predicted. The differences are all within the limits of experimental error.

It is evident then that for the hydrochlorides, hydrobromides and nitrates of these imido esters, the value of the constant K_{imido} for the velocity of decomposition of the positive ester ion, shorn of ~~any~~ any salt effect, may be considered the same, - the same constant 134 for the ethyl esters and 295 for the methyl esters respectively having served for the calculations of columns 3 and 5 in table I.

After the investigation of the hydrobromides and nitrates our attention was turned to the sulphate of the ethyl and methyl imido benzoates. The work on these salts was handicapped somewhat (Footnotes)

(1) From Miss Barnard's results.

(2) From Schlesinger's results.

(3) By interpolation

by the fact the solid salts could not be isolated in pure condition. They are so hygroscopic and sensitive to moisture that recourse had to be taken to preparing the salts in aqueous solution for every experiment by mixing equivalent quantities of the free base and of the acid. It is thought, however, from the concordance of the results obtained, that this handicap does not vitiate the ~~results obtained~~ reliability of the determinations, although further experiments will be necessary to confirm the unexpected conclusions to which the experimental results lead.

According to our conductivity measurements, the sulphates of the imido esters like other sulphates ^{are} ~~are~~ less ionized in equivalent solutions than are the salts of monobasic acids. Neglecting for the moment the salt effect, one would anticipate that in reactions in which the positive salt ion is the reacting component, the sulphates would react more slowly than would these other salts. (1) All of our determinations for the action of water on the sulphates of the imido esters show uniformly a greater speed of reaction than for the hydrochlorides, hydrobromides and nitrates in equivalent solutions, and in view of the reduced ionization, the rate of change calculated for the positive ester ion, $K_{1/2}$, proved to be quite a little greater for the sulphates than for the other salts investigated.

Footnote)

(1) For the imido ester salts this conclusion was confirmed by Miss Blunt in the case of the action of ammonia on the imido ester salts. The sulphates react more slowly than the hydrochlorides in proportion to the degrees of ionization,

$\frac{K_r(\text{chloride})}{\alpha_{\text{chloride}}}$ proved equal to $\frac{K_r(\text{sulphate})}{\alpha_{\text{sulphate}}}$.

This rather unexpected result led to the suspicion that the accelerating salt effect, A , of the salts of the sulphate ion (1) might be greater than for the salts of the univalent ions used. If such is the case, the same greater degree of ~~ionization~~ acceleration of the speed of decomposition should result from the addition of the sulphate ion from some other source, for instance from the addition of an alkali sulphate. And furthermore the same proportionate acceleration should be shown for the sulphates of different imido esters. (2) The experimental data obtained, although still too meagre for a final decision, bear out both these consequences of the assumption made, viz. that the salt effect of sulphates is ^m much greater than of the chlorides, bromides or nitrates. The accelerating salt factor, A , calculated for one gram equivalent fully ionized salt can be calculated from equation (3) as follows:-

$$A = \frac{K_v / \alpha_1 - K_v (ion)_0}{m \alpha} \quad (5)$$

in which $K_v (ion)_0$, the velocity of decomposition of the positive ester ions with no salt effect at all is taken to be the same for the sulphate as for the hydrochlorides, etc. α_1 is the degree of ionization of the imido ester salt in the mixture, m the concentration of the added salt and α its degree of ionization in the mixture. For ethyl imido benzoate $43430 K_{v(ion)_0} = 164$, for methyl imido benzoate it is 295. Calculating A according to equation (5) we find the following:-

Footnotes)

(1) See page 3 equation 3.

(2) See page 4.

Table IV.

Sulphate of Ethyl Imido Benzoate.Sulphate of the Imido
Ester Alone.Sulphate of the Imido Ester with
Isohydric Solutions of Potassium Sulphate

m	$K_{1/2}$	A
0.0343	204	718%
0.0617	233	882%

m	$K_{1/2}$	A
0.0333	209	712%
0.0710	244	887%

Table V.

Sulphate of Methyl Imido Benzoate.Sulphate of the Imido
Ester Alone.Sulphate of the Imido Ester with
Isohydric Solutions of Potassium
Sulphate.

m	$K_{1/2}$	A
0.0354	372	737%
0.0621	424	702%

m	$K_{1/2}$	A
0.0384	390	(839)%
0.0710	443	702%

In these tables m represents the concentration in gram equivalents of the sulphate present; α is the degree of ionization of the imido ester salt and $\underline{\alpha}$ that of the potassium sulphate in the mixture for the velocity determinations used, based on the conductivity measurements and on calculations made with the aid of the principles of isohydric solutions. A is the acceleration per gram equivalent fully ionized salt and includes therefore the salt effect of both positive and negative ions.

These values can, for the present, be considered to be only approximations on account of the limited number of experiments and the difficulty in securing absolute accuracy(1). Yet it does appear from the tolerably good agreement observed for the values of Δ both for the ethyl and the methyl esters and in the absence and presence of potassium sulphate, that all the experimental facts obtained are perfectly consistent with the assumption of a much stronger salt effect for the sulphate ion than for the chloride, bromide and nitrate ions ($\Delta = 185$ for these salts). On the other hand the great difference in the values of Δ is very surprising and while it is not at all inconsistent with the fundamental hypothesis, these measurements are intended to control, yet such a difference only encourages us to persist in our critical attitude toward our own hypothesis and in the endeavor to put all of its consequences to the test of extended quantitative experimentation. The work on this problem will therefore be continued.

Footnote)

(1) For instance, relatively small errors in the value of α_1 and α strongly affects the value of Δ .

EXPERIMENTAL PART.

The Hydrobromides of Ethyl Imido Benzoate.

The hydrobromide of ethyl imido benzoate was prepared from benzonitril, ethyl alcohol and hydrogen bromide in the same way that the hydrochloride is prepared. The hydrogen bromide was prepared by the action of bromine on naphthalene in kerosene solution as described by Kastle. (1) Only a small amount of ether was used in the reacting mixture owing to the fact that hydrogen bromide is very soluble in it.

The imido ester salt was analyzed by titrating with tenth normal potassium hydroxide, phenolphthaleine being used as indicator. (2)

Analysis

- I. 0.3136 grams of salt required 13.59 c.c. tenth normal KOH.
 II. 0.2257 " " " " 9.74 " " " "
 III. 0.2049 " " " " 8.93 " " " "

Calculated for

Found.

C₉H₁₂ ON Br

HBr.	35.22	35.12	34.95	35.26
------	-------	-------	-------	-------

The degrees of ionization of the hydrobromide were determined by conductivity measurements at 0° to avoid the rapid decomposition which takes place at 25°. As is well known there is very little change in degrees of ionization of salts between 0 and 25° and the legitimacy of this method is shown by me in part II. In the table the columns have the usual significance. The value of the conductivity at infinite dilution, *Λ_∞*, was obtained by Kohlrausch's graphic method, the conductivities and (Footnotes)

(1) Am. Chem. J. 18, 105.

(2) E. E. Barnard.

the cube roots of the concentrations ^{being used on the} co-ordinates. The curve for this salt is practically rectilinear from 0.3 normal to the extreme dilution ~~###~~ used (1).

Table ~~III~~ VI.

m	Λ	α	m	Λ	α
0.3	27.30	45.12	0.1	41.97	69.36
0.5	29.47	48.70	0.03	45.05	74.45
0.4	31.38	51.88	0.05	45.95	75.95
0.333	33.05	54.32	0.02	49.70	82.15
0.3	34.00	56.20	0.01	51.82	85.83
0.2	37.34	61.71	0	60.50	100.00

The Velocity of Decomposition of the Hydrobromide of Ethyl Imido Benzoate at 25°

The velocity of decomposition of this salt at 25° was measured in the usual way. (2) In the tables the line headed t contains the time in minutes from the time the first titration was made; the line headed y contains the number of c.c. of tenth normal potassium hydroxide used to neutralize the acid remaining combined with the imido ester in the solution at the time indicated; the line headed K_v contains 43430 times the value of the constant found according to the equation:-

$$K_v = \frac{1}{t_2 - t_1} \log \frac{c - x_1}{c - x_2}$$

$$= \frac{1}{t_2 - t_1} \log \frac{y_1}{y_2}$$

The symbol m indicates the molecular concentration used and Y the volume of the reacting solution used for each titration.

Footnotes)

(1) Miss Barnard found the same for the hydrochlorides using concentrations as low as 0.002 normal.

(2) Derby, Loc. Cit.

Ethyl Imido Benzoate.

m = 0.05 *V* = 25 Table VII. *Mean* 43430 *K_v* = 133.1

<i>t</i>	0	111	176	238	297	363	416
<i>v</i>	12.06	8.80	7.07	5.80	4.88	4.07	3.36
<i>K_v</i>	--	132.3	132.5	133.6	132.3	133.3	134.1

Table VIII.

m = 0.1 *V* = 15 *Mean* 43430 *K_v* = 127.3 *Grand Av.* = 127.9 (1)

<i>t</i>	0	116	180	242	310	366	
<i>v</i>	14.69	10.45	8.62	7.28	6.94	6.03	
<i>K_v</i>	---	127.6	128.6	126.0	126.8	127.6	

Table IX.

m = 0.2 *V* = 10 *Mean* 43430 *K_v* = 118.8

<i>t</i>	0	88	151	278	333	384	487
<i>v</i>	19.70	15.61	9.22	7.88	6.86	6.18	
<i>K_v</i>	---	117.6	118.6	118.6	119.6	119.3	119.1

Table X.

m = 0.333 *V* = 10 *Mean* 43430 *K_v* = 108.4

<i>t</i>	0	97	156	213	281	341	421
<i>v</i>	32.99	25.83	22.35	19.44	16.50	14.13	11.42
<i>K_v</i>	--	109.1	109.1	107.9	107.1	108.0	109.4

A summary of the relation of the velocity of decomposition to the concentration and the degree of ionization of the salts is given in Table I, p. 7.

In order to determine the salt effect due to the bromides as compared with the chlorides, velocities of decomposition had to be determined for the hydrobromides in mixtures with potassium and sodium bromide. It was considered advisable to determine the degree of ionization of potassium bromide at 25°; the same temperature used for the imido ester salt. In the table following the degrees of ionization are given for the various concentrations. The various columns have the usual significance.

Footnotes)

(1) In some cases the value of *K_v* was also computed by using the second and third readings as *t*. In such cases the average of all the values is given and marked Grand Av.

Table XI.

<u>Ionization of Potassium Bromide at 0°</u>					
V	N	α	V	N	α
2	69.13	81.01	64	78.27	91.72
4	71.09	83.35	128	79.59	93.28
8	73.22	85.80	256	81.17	95.12
16	75.02	87.89	512	82.02	96.12
32	76.22	89.35	∞	85.33	100.00

The curve from which the conductivity at infinite dilution was obtained in the usual way is rectilinear from N/32 to N/512, but not for stronger concentrations.

Velocity of Decomposition at 25 of the Hydrobromide of Ethyl Imido Benzoate in Mixtures with Isohydic Solutions of Bromides.

The symbols have the same meaning as in the previous tables except that m indicates the molecular concentration of the potassium bromide and m' that of the imido ester salt, each in its own isohydric solution before mixing, and V indicates the volume of the potassium bromide solution mixed with V' the volume of the imido ester salt solution.

Table ~~XIII~~. XVII.

$m = 0.1$ $m' = 0.1285$ $V = 150$ $V' = 100$ Mean 43430 $K_v = 130.4$

t	0	104	169	234	291	343	403
v	12.61	9.13	7.51	6.21	5.18	4.50	3.74
K_v	---	130.1	131.1	130.0	131.6	129.4	130.1

Table ~~XIV~~. XIII

$m = 0.1$ $m' = 0.1285$ $V = 60$ $V' = 90$ Mean 43430 $K_v = 128.5$

t	0	143	201	267	331	388	452
v	11.23	7.32	6.15	5.05	4.20	3.30	2.94
K_v	---	130.0	130.1	130.0	129.4	127.4	128.5

$m = 0.1$ $m' = 0.1285$ $V = 30$, $V' = 120$ Table XIV. $\text{Mean } 43430$ $K_v = 126.8$, $\text{Grand } Q_v = 127.4$ (18)

$\frac{t}{V}$	0	89	147	199	265	319	379
$\frac{V}{K}$	14.95	11.51	9.72	8.36	7.14	6.89	4.93
\underline{K}	--	127.3	127.2	126.9	126.8	126.4	127.4

$m = 0.1$ $m' = 0.1285$ $V = 30$ $V' = 120$ Table XV. $\text{Mean } 43430$ $K_v = 126.5$

$\frac{t}{V}$	0	103	182	223	235	343	400
$\frac{V}{K}$	14.97	11.14	9.35	7.73	6.52	5.36	4.72
\underline{K}	--	124.7	126.2	128.0	128.7	128.1	125.3

$m = 0.2$ $m' = 0.2923$ $V = 205$, $V' = 45$ Table XVI. $\text{Mean } 43430$ $K_v = 125.9$, $\text{Grand } Q_v = 125.2$

$\frac{t}{V}$	0	108	185	221	293	342	399
$\frac{V}{K}$	12.78	9.29	7.99	6.81	5.59	4.85	4.15
\underline{K}	---	128.3	123.6	123.8	122.6	123.1	122.4

$m = 0.2$ $m' = 0.2923$ $V = 96$, $V' = 54$ Table XVII. $\text{Mean } 43430$ $K_v = 119.8$

$\frac{t}{V}$	0	96	154	219	276	340	391
$\frac{V}{K}$	15.12	11.64	9.83	8.29	7.07	5.92	5.13
\underline{K}	--	118.3	118.6	121.4	119.6	119.8	120.1

$m = 0.2$ $m' = 0.2923$, $V = 50$, $V' = 50$ Table XVIII. $\text{Mean } 43430$ $K_v = 119.6$

$\frac{t}{V}$	0	114	173	237	300	354	447
$\frac{V}{K}$	14.23	10.36	8.79	7.42	6.24	5.36	4.17
\underline{K}	--	121.1	120.8	119.2	119.3	119.7	119.2

$m = 0.2$ $m' = 0.2923$, $V = 105$, $V' = 45$ Table XIX. $\text{Mean } 43430$ $K_v = 122.7$

$\frac{t}{V}$	0	82	141	251	313	371	436
$\frac{V}{K}$	12.77	10.08	8.52	6.28	5.29	4.51	3.75
\underline{K}	---	125.2	124.7	122.8	122.3	121.8	122.1

$m = 0.25$ $m' = 0.401$ $V = 220$, $V' = 30$ Table XX. $\text{Mean } 43430$ $K_v = 120.2$

$\frac{t}{V}$	0	147	212	271	333	393
$\frac{V}{K}$	11.57	7.74	6.33	5.48	4.34	3.84
\underline{K}	---	118.7	120.9	120.3	119.2	121.9

$m = 0.3$ $m' = 0.523$ $V = 225$ $V' = 25$ Table XXI. $\text{Mean } 43430$ $K_v = 119.2$

$\frac{t}{V}$	0	98	161	221	281	341
$\frac{V}{K}$	11.81	9.11	7.32	6.44	5.48	4.58
\underline{K}	--	(115.1)	118.2	119.2	118.6	120.6

$m = 0.333$, $m' = 0.616$, $V = 230$ $V' = 20$ Table XXII. $\text{Mean } 43430$ $K_v = 119.6$

$\frac{t}{V}$	0	108	177	227	284	340	401
$\frac{V}{K}$	11.98	8.82	7.28	6.51	5.52	4.77	3.99
\underline{K}	---	123.2	122.3	119.7	118.5	117.3	119.1

Summary.

In the table following the first column contains the volume of the imido ester salt solution; column two gives the volume of the potassium bromide solution; (These two solutions were mixed when the velocity measurement was started) column three gives the molecular concentration of the potassium bromide; column four the degree of ionization of the potassium bromide; column five the molecular concentration of the imido ester salt; column six the degree of ionization of the imido ester salt; column seven the concentration of the ionized salt; column eight the constant of velocity of decomposition as found in the foregoing tables; column nine the same value divided by the degree of ionization of the imido ester salt giving the velocity of decomposition as referred to the positive ion; Column ten gives the value as calculated from the theory according to equation (3), page 3.

Table XXIII.

<i>Vol imido salt sol.</i>	<i>Vol KBr sol</i>	<i>con KBr</i>	<i>100% KBr</i>	<i>con' imido salt</i>	<i>100% imido salt</i>	<i>Conc of ion Br</i>	<i>43430 K_u Salt found</i>	<i>43430 K_u Salt found</i>	<i>43430 K_u salt imido calculated.</i>
---	---	---	---	---	---	---	---	---	(184)
250	---	---	---	0.05	75.9	0.0379	133.4	176	175.5
100	150	0.1	86.2	0.1285	67.1	0.086	129.9	194	190
90	60	0.1	"	"	"	"	129.2	193	
120	30	0.1	"	"	"	"	127.4	190	
120	30	0.1	"	"	"	"	126.3	188	
45	205	0.2	84.3	0.292	57.7	0.166	123.2	213	213.8
54	96	0.2	"	"	"	"	119.8	208	
50	50	0.2	"	"	"	"	119.6	208	
45	105	0.2	"	"	"	"	122.7	213	
30	220	0.25	83.4	0.401	52.1	0.209	120.2	230	227
25	225	0.3	82.9	0.523	47.5	0.243	120.1	253	240
20	230	0.333	82.5	0.616	44.3	0.275	119.3	268	248

The last column marked *K_u imido calculated* was calculated by assuming a salt acceleration (1) of ^{4.75} ~~4.5~~ percent per gram molecule ionized salt, the same factor as was found by Miss Barnard for

(Footnote)

(1) Factor Δ in equation (3) page 3.

the acceleration produced by potassium, sodium and lithium chlorides. The value 134 for the hypothetical velocity of decomposition of the ester ion in the absence of any ions whatever is also taken from her tables for the hydrochloride.

Comparison of the last column with those of the column marked *K_{1/2} imido found* shows that an acceleration of 185 per cent per gram molecule ionized salt agrees very well with the experimental results, showing that potassium bromide has the same effect within the limits of experimental accuracy as has potassium chloride and that the bromide ion has therefore the same effect as the chloride ion. For the purpose of comparison, Table I. page 7 will prove of interest, giving the values found by Dr. Barnard for *K_{1/2}* in mixtures with potassium chloride side by side by those found by me for mixtures with potassium bromide of equivalent concentration.

The velocity of decomposition of the same imido ester salt in mixtures with isohydric solutions of sodium bromide was then studied. The degree of ionization of the sodium bromide in various concentrations were first determined at 25° in the same manner as was done with the potassium bromide. The following table shows the results of the work on the conductivities. The symbols have the same significance as before.

Table XXIV.

Degrees of Ionization of Sodium Bromide at 0°

V	A	100α	V	A	100α
2	53.5	73.73	64	65.02	89.85
4	58.08	77.31	128	66.82	91.85
8	58.72	80.95	256	67.33	93.15
16	60.88	83.71	512	68.78	94.82
32	62.60	86.30	∞	72.53	100.00

In the following tables on the velocity of decomposition at 25° of the hydrobromide of ethyl imido benzoate in mixtures with isohydric solutions of sodium bromide the same symbols are used with the same significance as were used in the foregoing tables.

Table XXV.

$\underline{m} = 0.1$ $\underline{m}' = 0.1209$ $\underline{V} = 150$ $\underline{V}' = 100$ Mean 43430 $\underline{K}_v = 128.5$, Grand Av. 129.2

t	0	113	179	236	297	353	416
\underline{v}	11.73	8.43	6.92	5.82	4.87	4.09	3.39
\underline{K}	---	127.0	128.0	129.0	128.5	128.3	129.6

Table XXVI.

$\underline{m} = 0.1$ $\underline{m}' = 0.1209$, $\underline{V} = 60$ $\underline{V}' = 90$ Mean 43430 $\underline{K}_v = 131.7$

t	0	127	189	251	313	369
\underline{v}	10.64	7.25	5.97	4.96	4.09	3.49
\underline{K}	---	131.2	132.8	132.0	131.4	131.2

Table XXVII.

$\underline{m} = 0.1$ $\underline{m}' = 0.1209$ $\underline{V} = 60$ $\underline{V}' = 90$ Mean 43430 $\underline{K}_v = 128.2$

t	0	92	151	202	270	329	374
\underline{v}	14.01	10.37	8.98	7.71	6.31	5.31	4.84
\underline{K}	---	128.5	127.9	128.3	128.3	128.1	128.3

Table XXVIII.

$\underline{m} = 0.2$ $\underline{m}' = 0.2726$ $\underline{V} = 205$ $\underline{V}' = 45$ Mean 43430 $\underline{K}_v = 123.7$

\underline{t}	0	104	172	229	287	348	409
\underline{v}	11.91	8.82	7.33	6.17	5.23	4.45	3.71
\underline{K}	---	125.4	122.6	124.7	123.1	122.8	123.8

Table XXIX.

$\underline{m} = 0.2$ $\underline{m}' = 0.2726$ $\underline{V} = 105$ $\underline{V}' = 45$ Mean 43430 $\underline{K}_v = 120.4$

\underline{t}	0	83	143	197	233	329	370
\underline{v}	11.75	9.29	7.87	6.82	5.80	4.72	4.18
\underline{K}	--	118.8	119.2	119.9	121.0	120.4	121.3

Table XXX.

$\underline{m} = 0.2$ $\underline{m}' = 0.2726$, $\underline{V} = 50$ $\underline{V}' = 50$, Mean 43430 $\underline{K}_v = 118.4$ Grand Av. = 118.0

\underline{t}	0	101	134	213	290	344	393
\underline{v}	13.40	10.18	8.80	7.47	6.08	5.22	4.53
\underline{K}	---	118.3	117.4	117.5	118.3	119.0	119.1

Table XXXI.

$\underline{m} = 0.25$ $\underline{m}' = 0.361$, $\underline{V} = 215$, $\underline{V}' = 35$ Mean 43430 $\underline{K}_v = 121.0$

\underline{t}	0	90	152	215	272	333	377
\underline{v}	11.28	8.73	7.37	6.23	5.24	4.43	4.04
\underline{K}	---	121.9	121.5	119.9	122.7	120.4	119.4

Table XXXII.

$\underline{m} = .3$ $\underline{m}' = 0.463$ $\underline{V} = 323$ $\underline{V}' = 27$ Mean 43430 $\underline{K}_v = 116.1$

\underline{t}	0	97	180	251	300	360	404
\underline{v}	12.11	9.37	7.48	6.18	5.43	4.32	4.13
\underline{K}	----	114.8	116.2	116.3	113.1	113.2	115.6

Summary.

In the table the columns have the same significance as those in Table XXXIII.

Table XXXIII.

<i>cl</i>	<i>Vol</i> <i>of</i> <i>NaBr</i> <i>Salt</i> <i>Sol.</i>	<i>m</i> <i>NaBr.</i>	<i>100d</i> <i>NaBr.</i>	<i>m'</i> <i>inside</i> <i>salt</i>	<i>100d'</i> <i>inside</i> <i>salt.</i>	<i>conc.</i> <i>of</i> <i>ion.</i>	<i>43430K</i> <i>salt</i> <i>found.</i>	<i>43430K</i> <i>Salt</i> <i>& ind</i> <i>found</i>	<i>43430</i> <i>Kr Salt</i> <i>& ind</i> <i>calc.</i> (184)
R50	---	---	---	0.05	75.9	0.0379	133.4	173	173
100	150	0.1	81.9	0.1209	87.73	0.082	129.2	191	189
90	60	0.1	"	"	"	"	131.7	194	
120	30	0.1	"	"	"	"	128.2	190	
45	205	0.2	78.8	0.2723	57.88	0.155	123.4	214	212
45	105	0.2	"	"	"	"	120.4	209	
50	50	0.2	"	"	"	"	118.0	205	
35	215	0.25	77.31	0.361	53.54	0.193	121.0	226	223
27	223	0.3	76.51	0.433	49.58	0.230	113.1	234	234

The values in the last column were calculated in the same manner as explained on page 17. Comparing the values found in this last column with those in the preceding column we see that the agreement is fully as good as found for the solutions with potassium bromide.

For the purpose of comparison with the results obtained by Miss Barnard for mixtures with sodium chloride the following table has been arranged. The columns have the same significance as in Table I. page 7. The second column was calculated according to the equation:-(1)

$$K_v (\text{calculated}) = 164 (1 + 1.85 m \alpha)$$

This shows again that the influence of the bromide ion and the chloride ion are identical within the limits of experimental error.

Footnotes)

(1) Equation (3) page 3.

Table XXXIV.

<i>K Hal.</i> <u>m</u>	<i>Na Cl</i>		<i>Na Br</i>	
	<i>K_{sp}</i> <i>Found</i>	<i>K_{sp}</i> <i>Calculated.</i>	<i>K_{sp}</i> <i>Found</i>	<i>K_{sp}</i> <i>Calculated</i>
0	175	178	178	177
0.1	191.5	189	192	189
0.2	211	213	209	212
0.3	234	234	234	233

Methyl Imido Benzoate.

The hydrobromide of methyl imido benzoate was prepared from benzonitril, methyl alcohol and hydrobromic acid. It is a white solid having properties similar to those of the hydrochloride. It was analyzed in the same manner as the ethyl salt as explained on page 14. The following is the result of the analysis.

0.3133 grams of salt required 14.53 c.c. tenth normal KOH.

	Calculated for <i>C₈H₁₀NOBr</i>	Found.
HBr.	0.1173	0.1175.

The results of the conductivity measurements of this salt, which were made in the usual way at 20° are given in the following table. The columns have the usual significance.

Table XXXV.

<u>m</u>	<u><i>Λ</i></u>	<u><i>α</i></u>	<u>m</u>	<u><i>Λ</i></u>	<u><i>α</i></u>
0.4	34.12	55.95	0.05	47.73	78.31
0.3	37.12	61.00	0.02	51.13	83.83
0.2	40.31	66.09	0.01	53.18	87.18
0.1	44.60	73.11	0000	61.00	100.00

Velocity of Decomposition at 25° of the Hydrobromide of Methyl Imido Benzoate.

The symbols have the usual significance.

Table XXXVI.

$m = 0.05$ $V = 25$ Mean 43430 $K_v = 252.1$

<u>t</u>	0	50	110	155	170	200	225
<u>v</u>	12.13	9.08	8.32	4.93	4.54	3.78	3.34
<u>K</u>	---	251.4	257.4	250.5	251.0	253.2	249.0

Table XXXVII.

$m = 0.1$ $V = 10$ Mean 43430 $K_v = 243.0$ Grand $m = 241.8$

<u>t</u>	0	45	75	105	135	195	225
<u>v</u>	9.89	7.52	6.38	5.37	3.87	3.26	2.75
<u>K</u>	---	244.7	242.0	244.0	241.3	242.7	243.1

Table XXXVIII.

$m = 0.2$ $V = 5$ Mean 43430 $K_v = 230.8$

<u>t</u>	0	45	75	105	135	165	220
<u>v</u>	9.83	7.84	6.44	5.52	4.70	4.02	3.00
<u>K</u>	--	223.3	232.8	230.1	230.8	230.0	230.2

Table XXXIX.

$m = 0.333$ $V = 5$ Mean 43430 $K_v = 209.4$

<u>t</u>	0	50	81	112	140	174	204
<u>v</u>	10.33	12.54	10.93	9.35	8.26	6.93	6.05
<u>K</u>	---	218.6	208.6	211.4	207.4	210.9	208.7

A summary of the relation of the velocity of decomposition to the concentration and the degree of ionization of the salt is given in Table III. p.9.

The Nitrate of Ethyl Imido Benzoate.

The method by which the halide salts of imido esters are prepared synthetically is not practical for the formation of the nitrates owing to decomposition of the salts by water. The nitrate of ethyl imido benzoate is prepared as follows:- The pure free base is prepared from the hydrochloride of the imido ester as described by Derby (1) A weighed amount of the base is dissolved in a small amount of absolute alcohol and the solution cooled in a flask to -5° . Enough concentrated nitric acid (sp.g. 1.4) to just neutralize the amount of base used was diluted with an equal volume of absolute alcohol, both of the liquids being previously cooled to -5° . The solutions were then brought together and an excess of absolute ether at once added. The small amount of water in the nitric acid could have but a minimal effect on the imid salt at the low temperature during the few moments required for the precipitation of the imid salt. The salt is at once brought on a filter in a porcelain funnel, washed with absolute ether and placed in a vacuum desiccator over solid potassium hydroxide. It was analyzed by titration of the acid in the presence of phenolphthaleine.

Following is the result of the analysis:-

0.1615 grams salt required 7.17 c.c. tenth normal KOH.

Calculated for		Found
$C_9H_{12}N_2O_4$		
HNO ₃	0.0451	0.0450

It will be seen that the salt is obtained as readily in the pure state as those prepared by the method commonly used for the chlorides and bromides. No nitrates of imido esters seem to have been described in the literature.

Footnotes)

(1) AM. Chem. J. 39, 442.

The degrees of ionization of the nitrate were determined by the conductivity method at 0° in the usual manner.

The following table gives the results of the experiments. The various columns have the usual significance.

Table XL.

m	Λ	α	m	Λ	α
0.6	28.07	43.14	0.1	38.30	68.33
0.4	28.27	50.03	0.06	42.43	75.11
0.333	29.75	52.33	0.02	46.07	81.55
0.3	30.82	54.53	0.01	48.07	85.08
0.2	34.15	60.45	0.00	53.50	100.00

Velocity of Decomposition of the Nitrate of Ethyl Imido Benzoate.

The symbols have the same significance as in the former tables in the following tables.

Table XLI.

$m = 0.05$ $V = 25$ $\text{Mean } 43430 K_v = 132.7$ $\text{Grand Av.} = 133.4$

t	0	90	155	203	278	333	378
$\frac{t}{v}$	12.11	9.26	7.64	6.51	5.20	4.37	3.80
$\frac{t}{K}$	---	129.5	132.7	132.8	132.1	132.9	133.2

Table XLII.

$m = 0.1$ $V = 15$ $\text{Mean } 43430 K_v = 127.1$ $\text{Grand Av.} = 126.6$

t	0	92	155	211	277	332	392
$\frac{t}{v}$	14.70	11.22	9.34	7.91	6.59	5.53	4.87
$\frac{t}{K}$	---	127.6	127.2	127.5	127.9	127.0	127.0

Table XLIII.

$m = 0.2$ $V = 10$ $\text{Mean } 43430 K_v = 117.6$

t	0	81	142	202	239	321	383
$\frac{t}{v}$	19.70	15.73	13.32	11.41	9.57	8.23	7.01
$\frac{t}{K}$	---	119.8	119.7	117.4	118.6	117.3	117.2

Table XLIV.

$m = 0.333$ $V = 10$ $\text{Mean } 43430 K_v = 107.5$

t	0	79	145	202	281	339	384
$\frac{t}{v}$	32.38	27.03	22.92	19.97	13.42	14.30	12.39
$\frac{t}{K}$	---	107.7	108.1	107.2	107.4	106.7	107.7

A summary of the relation of the velocity of decomposition to the degree of ionization of the salt and the concentration is given in Table II. p. 9.

The Sulphate of Ethyl Imido Benzoate.

Several attempts were made to prepare the sulphates of the imido esters in the same manner as the nitrates were prepared. The heat formed by the action of concentrated sulphuric acid on the free base and the consequent rapid decomposition of the salt formed were eliminated by mixing the acid with absolute alcohol and adding this solution to the alcoholic solution of the free base. All the solutions were kept at the temperature of -20° and the vessels protected from the moisture of the atmosphere. Salts were obtained in this manner but they crystalized out very slowly. They were found to be exceedingly hygroscopic. It was found impractical to work with them on this account as any moisture taken in from the air rapidly decomposed them and absolutely pure salts are necessary for our purposes. It was finally necessary to give up the attempt to isolate the solid sulphate and recourse ~~was~~ had to the method of preparing the salt in aqueous solution at the moment of starting an experiment.

In order to test the accuracy of the method a velocity determination of the hydrochloride prepared in similar fashion from one twentieth normal hydrochloride acid and the calculated amount of ethyl imido benzoate was made side by side with a velocity determination of the sulphate. The constant of decomposition obtained from the hydrochloride agreed excellently with the constants obtained by Miss Barnard by the method of isolating the salt and making up the solution at the moment of starting a velocity determination.

The Sulphate of Ethyl Imido Benzoate.

The following table gives the results of the conductivity experiments which were carried out at 25° in the usual manner. The sulphate was prepared in solution as described at the moment of determining the conductivities. The symbols are the same as in the previous tables except that here we have the equivalent conductivities in place of the molecular conductivities and mark the first column Vol. indicating the volume in which one equivalent weight of the salt is dissolved.

Table XLV.

<u>Vol.</u>	<u>L</u>	<u>α</u>	<u>Vol.</u>	<u>L</u>	<u>α</u>
2.13	23.03	40.37	34	44.48	79.15
4.2	28.99	51.13	128	47.11	83.03
8.2	34.33	50.30	253	49.24	83.83
16	37.71	53.50	512	50.35	89.23
32	41.42	73.05	∞	53.70	100.00

Velocity of Decomposition of the Sulphate of Ethyl Imido Benzoate.

Except for the method of preparing the solutions the velocities of decomposition of the sulphate of ethyl imido benzoate were determined in the usual manner. The symbols in the following tables have the usual meaning except the symbol eq. is used and represents the equivalent solutions which are used in place of the molecular solutions.

Table XLVI.

eq. = 0.05 V = 25 Mean 43430 K_v = 139.2 Grand Av. = 140.1

<u>t</u>	0	89	151	203	233	326	410
<u>v</u>	11.87	8.97	7.37	6.14	5.06	4.13	3.14
<u>K</u>	---	133.7	137.1	139.0	139.5	139.7	140.9

Table XLVII.

eq. = 0.05 V = 25 Mean 43430 K_v = 140.0 Grand Av. = 140.7

<u>t</u>	0	95	155	220	272	323	393
<u>v</u>	11.83	8.75	7.10	5.80	4.92	4.17	3.32
<u>K</u>	---	137.9	139.3	140.8	140.1	140.2	139.4

Table XLVIII.

$eq = 0.1$ $V = 15$ Mean 43430 $K_v = 143.9$

t	0	59	120	180	240	298	381	420
v	14.21	11.37	9.55	7.83	6.43	5.30	4.28	3.50
K	---	144.9	143.8	142.9	143.5	143.7	144.4	144.9

Table XLIX.

$eq = 0.2$ $V = 10$ Mean 43430 $K_v = 141.1$

t	0	83	148	211	275	338	403
v	18.41	14.04	11.37	9.29	7.60	6.14	4.93
K	---	141.8	141.4	140.8	139.7	141.9	141.3

The unusually rapid decomposition noted here, as explained on page 12, Table IV. was investigated further by using potassium and ammonium sulphates in isohydric solutions with the imido ester sulphate in order to determine whether the increase in speed was due to the sulphate ion. In computing the isohydric solutions the degrees of ionization for the potassium sulphate were taken from Kohlrausch and Holborn. For the ammonium sulphate the same values were used as were used for the potassium sulphate.

Velocity of Decomposition of the Sulphate of Ethyl Imido Benzoate In Mixtures with Isohydric Solutions of Potassium Sulphate

Table L.

$eq = 0.05$; $eq' = 0.0571$, $V = 100$ $V' = 150$ Mean 43430 $K_v = 140.2$ $K_{v'} = 140.7$

t	0	94	149	205	268	322	379
v	8.13	5.97	5.02	4.13	3.37	2.88	2.39
K	---	137.7	139.5	140.9	141.4	140.1	139.1

Table LI.

$eq = 0.1$ $eq' = 0.1188$ $V = 150$ $V' = 100$ Mean 43430 $K_v = 145.8$

t	0	95	132	220	288	340
v	11.02	7.99	6.41	5.25	4.24	3.51
K	---	147.1	146.3	146.4	144.0	146.1

Velocity of Decomposition of the Sulphate of Ethyl Imido Benzoate in Mixtures with Isohydric Solutions of Ammonium Sulphate.

Table LII.

$eg = 0.05$ $eg' = 0.0511$ $V = 100$ $V' = 15.0$ *Mean 43430* $K_v = 141.4$

t	0	84	139	194	257	311	371
v	8.24	5.27	4.42	3.53	2.97	2.48	
K	---	139.3	141.5	140.7	142.0	142.9	140.1

Table LIII.

$eg = 0.1$ $eg' = 0.1188$ $V = 15.0$ $V' = 100$ *Mean 43430* $K_v = 148.1$

t	0	80	147	204	270	328	
v	11.24	8.33	6.93	5.37	4.31	3.77	
K	---	143.4	142.9	144.9	143.3	144.6	

A summary of the relation of the velocity of decomposition to the concentration and the degree of ionization of the imido ester salt in aqueous solution and in the presence of potassium sulphate will be found in Table IV. p.12. In the following table the action of ammonium sulphate is summarized.

Table LIV.

Sulphate of Ethyl Imido Benzoate.

Sulphate of the Imido
Ester Alone.

Sulphate of the Imido Ester with
Isohydric Solutions of Ammonium Sulphate.

nd	K_v	A	nd	K_v	A
0.0343	204	718%	0.0383	210	732%
0.0617	233	632%	0.0710	240	653%

The symbols have the same significance as in Table IV. p.12.

The Sulphate of Methyl Imido Benzoate.

Determinations were next made with the sulphate of ^mMethyl imido benzoate in precisely the same manner as was done with the ethyl ester salt.

In the following table are given the ¹results of the conductivity determinations carried out at 0°. The symbols have the same significance as those used in Table XLV.

Table LV.

<u>Vol.</u>	<u>Λ</u>	<u>α</u>	<u>Vol.</u>	<u>Λ</u>	<u>α</u>
2	23.72	40.47	64	43.45	79.23
4	30.01	51.21	128	48.97	83.57
8	34.74	59.28	256	50.98	86.97
13	39.28	67.03	∞	58.30	100.00
32	43.03	73.48			

Velocity of Decomposition at 25° of the Sulphate of Methyl Imido Benzoate.

Table LVI.

eq = 0.05 V = 25 Mean 43430 K_L = 2610

<u>t</u>	0	33	93	126	163	197
<u>v</u>	11.73	7.69	6.52	5.55	4.49	3.57
<u>K</u>	---	(279.7)	257.0	258.9	256.7	262.8

Table LVII.

eq = 0.05 V = 25 Mean 43430 K_L = 265.6

<u>t</u>	0	65	98	126	150	170
<u>v</u>	11.73	7.97	6.34	5.45	4.90	4.31
<u>K</u>	---	260.0	273.9	267.2	261.8	265.0

Table LVIII.

eq = 0.1 V = 15 Mean 43430 K_L = 260.9 Grand Av. = 264.1

<u>t</u>	0	51	81	111	141	172	191
<u>v</u>	13.43	9.89	8.26	6.93	5.83	4.77	4.19
<u>K</u>	---	262.4	261.7	258.1	257.8	262.5	265.4

Table LX.

$eq = 0.1$

$V = 15$

$Mean\ 43430\ K_v = 260.9\ Grand\ Av. = 262.0$

t	0	45	75	105	137	165	201
v	13.84	10.49	8.81	7.36	3.07	5.15	4.13
K	---	238.9	260.0	261.3	261.4	260.3	261.4

Velocity ^d Determinations were next carried out with this same salt in the presence of potassium and ammonium sulphate in isohydric mixtures. The solutions were made up and the velocities determined as in the case of the ethyl salt above. The same symbols are used in the tables.

Velocity of Decomposition of the Sulphate of Methyl Imido Benzoate in Mixtures with Isohydric Solutions of Potassium Sulphate.

Table LX.

$eq = 0.05\ eq' = 0.0565\ V = 100\ V' = 150\ Mean\ 43430\ K_v = 261.9\ Grand\ Av. = 264.6$

t	0	45	75	105	135	165	195
v	7.42	5.68	4.73	3.94	3.28	2.73	2.23
K	--	258.0	257.0	261.8	262.3	263.1	264.8

Table LXI.

$eq = 0.1\ eq' = 0.1186\ V = 150\ V' = 100\ Mean\ 43430\ K_v = 267.0\ Grand\ Av. = 265.4$

t	0	45.5	76	106	136	168	197
v	11.29	8.49	7.03	5.85	4.94	4.11	3.39
K	---	271.8	270.6	269.2	264.0	261.3	265.3

Velocity of Decomposition of the Sulphate of Methyl Imido Benzoate in Mixtures with Isohydric Solutions of Ammonium Sulphate.

Table LXII.

$eq = 0.05\ eq' = 0.0565\ V = 100\ V' = 150\ Mean\ 43430\ K_v = 263.9\ Grand\ Av. = 264.2$

t	0	50	85	110	140	177	192	241
v	8.03	5.93	4.79	4.12	3.43	2.71	2.52	1.85
K	---	233.0	264.0	263.4	263.9	266.4	262.2	264.5

Table LXIII.

$eq = 0.1\ eq' = 0.1186\ V = 150\ V' = 100\ Mean\ 43430\ K_v = 265.8$

t	0	51	81	111	142	171	210
v	11.22	8.07	6.82	5.72	4.63	3.91	3.13
K	---	(280.5)	267.0	263.3	268.7	267.7	262.0

A summary of the relation of the velocity of decomposition of this salt to the concentration and degree of ionization of the imido ester salt in aqueous solution and in the presence of potassium sulphate will be found in Table V. p.12. In the following table the action of ammonium sulphate is summarized.

Table LXIV.

Methyl Imido Benzoate.

Sulphate of the Imido Ester Alone.			Sulphate of the Imido Ester with Isohydric Solutions of Ammonium Sulphate.		
$m\alpha$	K_{α}	A	$m\alpha$	K_{α}	A
0.0354	372	737%	0.0384	389	(830%)
0.0621	424	702%	0.0710	442	702%

The symbols have the same significance as those in Table V. p.12.

II.

Velocity of Decomposition of Imido Esters in the Presence of Hydrochloric Acid in Solutions of Increasing Concentrations.

In Schlesinger's work on the ^erelation of the decomposition of the hydrochlorides of ethyl and methyl imido benzoate to the degree of ionization of these salts, the velocity measurements were made at 25° and the degrees of ionization were based on conductivities measured at zero in order to avoid the rapid decomposition that takes place at 26°. Since these salts are not so highly ionized as salts like potassium chloride, ammonium chloride, ^{etc.} there might be an appreciable change in their ionization in the temperature interval between zero and 25°, and so in order to eliminate any uncertainty on this point and on the conclusions reached, it was thought desirable to carry out some determinations of the velocity of decomposition of these imido ester salts at zero, -- the same temperature for which the degree of ionization had been determined experimentally. The results of these determinations follow:-

The temperature was maintained at zero by means of an ice bath of forty litres capacity, well protected against absorption of heat. By drawing off the water from the bottom of this bath once each day and adding about four or five liters of ice it was found to keep a temperature so uniform that no change was observed of sufficient magnitude to be detected by a Beckmann thermometer.

The method of analysis used was the one used by Derby. (1)

Footnote)

(1) Am. Chem. J. 32, 437. (1908)

Methyl Orange and alizarin sulphonate were used as indicators.

Ethyl Imido Benzoate.

The results of the velocity determinations are given in the following tables. The first ~~column~~^{line} denotes the time in minutes from the time the first titration was made. The second ~~column~~^{line} shows, under the heading v , the number of c.c. tenth normal potassium hydroxide used to neutralize the acid remaining combined with the imido ester in the solution at the time indicated. The third line shows the value of the constant found according to the equation:

$$K_v = \frac{1}{t_2 - t_1} \log. \text{nat.} \frac{C - x_1}{C - x_2}$$

$$= \frac{1}{t_2 - t_1} \times \log. \text{nat.} \frac{V_1}{V_2}$$

The symbol m indicates the molecular concentration used and V the volume of the reacting solution used for each titration.

Ethyl Imido Benzoate.
Table LXV.

$m = 0.05$ $V = 25$ Mean 43430 $K_v = 62.8$

t	0	980	4047	5567	6893	8450	9785
v	12.33	10.77	8.91	6.54	4.57	3.64	2.93
K	---	(30.9)	62.4	62.6	62.6	62.8	63.4

Table LXVI.

$m = 0.05$ $V = 25$ Mean 43430 $K_v = 63.4$

t	0	1451	2853	4043	4285	6906	8630	9984
v	12.40	9.98	8.19	6.83	6.65	4.52	3.51	2.85
K	---	(64.8)	63.1	63.6	63.2	63.5	63.5	63.9

Table LXVII.

 $m = 0.05$ $V = 20$ Mean 43430 $K_v = 63.1$

<u>t</u>	0	1348	2883	4073	4295	5333
<u>v</u>	12.30	10.17	8.09	6.83	5.57	5.33
<u>K</u>	---	(61.3)	33.1	32.7	33.4	33.3

Table LXIX.

 $m = 0.05$ $V = 25$ Mean 43430 $K_v = 60.1$

<u>t</u>	0	1331	2811	2831	4052	4239	5333
<u>v</u>	24.70	20.28	17.13	16.34	14.09	13.33	11.82
<u>K</u>	---	(34.3)	60.3	59.9	60.2	60.3	59.7

Table LXX.

 $m = 0.1$ $V = 25$ Mean 43430 $K_v = 60.2$

<u>t</u>	0	1355	1301	2797	3015	4082	4348
<u>v</u>	19.85	16.32	16.03	13.70	13.38	11.59	11.20
<u>K</u>	---	57.0	57.2	57.3	56.8	57.2	57.2

Table LXXI.

 $m = 0.2$ $V = 10$ Mean 43430 $K_v = 57.2$

<u>t</u>	0	1359	2773	3957	4194	6814	8531
<u>v</u>	19.94	13.74	13.77	11.83	11.50	8.08	6.41
<u>K</u>	---	(55.9)	57.9	57.0	57.0	57.6	57.8

Table LXXII.

 $m = 0.333$ $V = 5$ Mean 43430 $K_v = 52.2$

<u>t</u>	0	1191	1315	4044	4239	5755	7199
<u>v</u>	14.25	12.30	12.00	8.30	8.51	7.07	6.00
<u>K</u>	----	51.2	52.7	51.8	52.4	52.9	52.2

Table LXXIII.

 $m = 0.333$ $V = 10$ Mean 43430 $K_v = 52.0$

<u>t</u>	0	910	3975	5493	6824	8373	9711	10946
<u>v</u>	33.53	30.06	21.03	17.43	14.31	12.27	10.40	8.89
<u>K</u>	---	52.3	51.0	51.7	52.0	52.1	52.4	52.6

Table LXXIV.

$m = 0.5$ $V_1 = 5$ Mean 43430 $K_v = 46.0$

<u>t</u>	0	1449	2537	2753	5381	5813	7055	8547
<u>v</u>	25.06	21.63	19.22	18.80	14.17	13.77	11.89	9.97
<u>K</u>	--	(43.5)	45.0	45.4	46.0	46.4	46.9	
<u>K</u>	--	45.0	45.4	45.2	46.0	46.0	46.6	46.8

Table LXXV.

$m = 0.5$ $V_1 = 10$ Mean 43430 $K_v = 46.0$

<u>t</u>	0	1125	4029	5563	6880	8435	9761
<u>v</u>	49.79	44.49	32.81	27.79	24.04	20.22	17.34
<u>K</u>	---	(435)	45.0	45.4	46.0	46.4	46.9

In the following table the velocity of decomposition referred to the positive ion of the ester is shown for the varying concentrations of the ethyl ester salt used. The determination of the degrees of ionization of the salt had been very carefully made by Dr. Barnard at zero and her results are used in place of the values of Schlesinger whose determinations were not so elaborate and exact as the ones carried out later by Dr. Barnard.

Column one shows the concentration of the imido salt used; column two gives the degree of ionization; column three gives the average experimental value obtained for the constant of decomposition; column four gives the value of the constant of decomposition referred to the positive ion; column five gives the theoretical values of these constants as explained below.

Table LXXVI.

<u>m</u>	100%	43430 K_v	43430 K_v found	43430 K_v calculated.
0.05	77.73	63.1	81.1	81.3
0.10	71.81	30.1	83.7	84.2
0.20	64.30	57.3	88.7	88.1
0.33	57.75	52.1	90.2	94.4
0.50	50.77	46.3	(91.2)	(99.7)

It is clear that the velocity of decomposition of the imido ester salt at zero as at 25° does decrease most decidedly with increased concentration--i.e. with decreased ionization-- falling from a value of 83.1 for 0.05 molar solution to 48.3 for 0.5 molar solution. The decrease, however, is not directly proportional to the decrease in ionization as represented by α . The values of $K_{1/2}$ show decidedly increasing values at zero as at 25°--the result of a secondary accelerating "salt effect" common to reactions(1) in which water is a decomposing agent.(2) Down to 0.33 molar solution the acceleration is proportional to the concentration of the salt ions present as shown by the last column which represents the values calculated according to equation (3), Part I. p.3 for $K_{1/2}$ on the assumption of an acceleration of 110 percent per mole ionized salt present. ($\alpha = 110\%$)(3) The hypothetical value 78.0 for the velocity of decomposition of the salt in the absence of any "salt effect" is found from the curve obtained by using the values of $C_{\infty} = m \times \alpha$ and $K_{1/2}$ on the co-ordinates.

Methyl Imido Benzoate.

The results of the experiments made with methyl imido benzoate follow:

Table LXXVII.

$m = 0.05$ $V = 25$ Mean 43430 $K_r = 123.0$

t	0	1237	2527	2831	5387	5704	6828	7100
v	11.89	8.31	5.73	2.57	2.38	1.75	1.57	
K	--	122.9	124.6	(119.4)	123.5	121.9	123.8	

Table LXXVIII.

$m = 0.05$ $V = 25$ Mean 43430 $K_r = 124.0$

t	0	1449	2846	4370	5731	6983	7388	
v	12.33	8.10	5.46	3.53	2.40	1.89	1.61	
K	--	(125.9)	124.7	124.3	124.0	123.6	123.4	

Footnotes)

- (1) E.g. the inversion of cane sugar, the saponification of esters by water in the presence of acids, the decomposition of imido esters by water etc.
 (2) Arrhenius, Zeit. Phys. Ch. 1, 126. Euler, Ibid, 32, 348. Stieglitz, Am. Chem. J. 39, 29, 136.

(3) Vide Schlesinger pp.14-16 for a more complete discussion of this point.

Table LXXIX.

 $m = 0.10$ $V = 25$ Mean 43430 $K_v = 120.5$

\underline{t}	0	1302	2787	4099	4142	6903	7227
\underline{v}	24.11	18.38	11.19	7.77	7.38	3.53	3.28
\underline{K}	---	(116.3)	119.6	120.0	120.2	120.9	121.6

Table LXXX.

 $m = 0.1$ $V = 25$ Mean 43430 $K_v = 119.7$

\underline{t}	0	1420	2828	4367	5714	6974	7372
\underline{v}	24.49	18.86	11.27	7.36	5.08	3.55	3.24
\underline{K}	----	(118.0)	119.3	120.0	119.9	120.3	119.2

Table LXXXI.

 $m = 0.2$ $V = 10$ Mean 4345 $K_v = 114.7$

\underline{t}	0	1333	2752	2935	4073	3838	7189
\underline{v}	19.32	13.72	9.49	9.01	6.72	3.17	2.83
\underline{K}	----	114.0	114.6	114.0	114.3	115.3	115.9

Table LXXXII.

 $m = 0.333$ $V = 5$ Mean 43430 $K_v = 107.9$

\underline{t}	0	1391	2800	3890	4189	5380	8512
\underline{v}	16.37	11.38	8.21	6.23	5.78	4.33	1.88
\underline{K}	---	(118.0)	107.0	106.9	107.9	107.3	110.4

Table LXXXIII.

 $m = 0.5$ $V = 5$ Mean 43430 $K_v = 97.3$

\underline{t}	0	1390	1445	2465	2809	3907	4198	5385
\underline{v}	24.24	17.75	17.54	13.93	12.93	10.08	9.30	7.15
\underline{K}	---	96.3	96.5	96.3	96.4	97.5	98.8	98.3

Table LXXXIV.

 $m = 0.5$ $V = 10$ Mean 4343 $K_v = 97.2$

\underline{t}	0	1002	1278	2657	4183	5543	6798
\underline{v}	48.11	38.48	36.36	26.74	18.76	13.73	10.17
\underline{K}	---	96.8	95.1	96.0	97.7	98.2	99.3

Table LXIXV.

Summary of Methyl Imido Benzoate.

m	100 α	43436 K_f	43430 K_f	43430 K_f
0.			found	calculated. (154.0)
0.05	73.81	123.5	180.3	180.4
0.10	71.56	120.1	187.9	188.2
0.20	64.35	114.7	177.4	175.9
0.33	58.4	107.9	184.7	183.9
0.50	52.82	97.2	(184.9)	(198.5)

The velocity of decomposition of methyl imido benzoate in acid solution decreases like that of the ethyl salt with increasing concentrations of the salt--ie. with the decreased ionization of the salt-- from 123.5 for 0.05 molar solution to 97.2 for 0.5 molar solution at zero degrees. The accelerating "salt effect" is again evident if one consider the values of K_f in column four and the acceleration again seems proportional to the concentration of the ions present; column five being calculated according to equation (3) Part I., p.3 on the assumption of an acceleration of 110% ($A=110$) produced by a mole of ionized salt as in the case of the ethyl ester salt. Except for the highest concentration the calculated values given in the last column agree well with the found values given in column four.

These results obtained from velocities of decomposition measured at the same temperature, zero, at which the degrees of ionization of the salts had been determined confirm therefore the results obtained by Schlesinger and the conclusions based on them--a conclusion of vital importance for Stieglitz's theory of catalysis of esters and similar bodies.

Methyl Imido Para Toluylate.

The hydrochloride of methyl imido para toluylate is decomposed by water at an exceptionally slow rate. The velocity constant is less than half as large as that of the hydrochloride of the corresponding benzoate. This slow decomposition appearing favorable to exact work on the conductivity measurements used to determine the degrees of ionization of the salt, a third series of measurements were made with this salt. The results are briefly recorded in the following tables - they fully confirm those obtained with the two other imido esters.

The degrees of ionization were determined for various concentrations at zero degrees by the method used by Dr. Barnard(1) The results are given in the table following. The columns have the usual significance. The conductivity for infinite dilution was obtained graphically, the molecular conductivities being used as ordinates and the cube root of the concentrations as abscissae. For dilute solutions this curve is practically rectilinear. The molecular conductivity at infinite dilution was found to be 58.00.

The Ionization of the Hydrochloride of Methyl Imido Para Toluylate.

Table LXXXVI.

<u>m</u>	<u>Λ</u>	<u>100α</u>	<u>m</u>	<u>Λ</u>	<u>100α</u>
0.6	28.30	48.30	0.1	42.07	72.93
0.5	30.53	52.58	0.06	44.90	77.41
0.4	32.51	56.05	0.02	48.73	83.78
0.3	35.03	60.45	0.01	50.35	87.34
0.2	37.93	63.09	0.005	51.70	89.14

Footnote)

(1) Am. Chem. J.

Velocity Measurements.

In the more concentrated solutions of this salt, such a mass of methyl para toluylate separated out in the velocity determinations that were attempted at zero that I was obliged to make these determinations at 25°. The following is the summary of these determinations:-

Table LXXXVII.

$m = 0.05$ $V = 25$ Mean $43430 K_v = 118.9$

t	0	31.5	107	155	203	232	290
v	11.08	9.36	8.23	7.24	6.28	5.50	5.02
K	---	(138.9)	119.1	119.1	119.3	120.4	118.5

Table LXXXVIII.

$m = 0.1$ $V = 25$ Mean $43430 K_v = 112.2$

t	0	95	141	187.5	241	284	323
v	23.33	18.47	16.43	14.32	12.38	11.38	10.16
K	---	113.3	111.5	111.5	112.4	111.8	112.6

Table LXXXIX.

$m = 0.2$ $V = 10$ Mean $43430 K_v = 104.8$

t	0	93	144	193	243	297	
v	18.58	13.13	11.72	10.35	9.10		
K	---	105.5	104.8	103.3	103.3	104.4	

Table XC.

$m = 0.333$ $V = 10$ Mean $43430 K_v = 95.8$

t	0	127	174	222	272	322	423
v	32.79	24.74	22.38	20.18	18.04	16.12	12.35
K	----	96.5	95.2	94.8	95.5	95.3	93.6

III.

The accelerating effect produced by salts (electrolytes) in actions in which water is a reacting component, as in the catalysis of cane sugar, esters and imido esters, the influence of salts has been ascribed by chemists (1) as due at least in part to a probable increase in the ionization of the water resulting from the presence of the electrolytes. The action of water on imido ester salts producing esters and ammonium salts according to equation (1) p.2 and proceeding according to the dynamic equation (2), p.2 afforded an opportunity to test this hypothesis in the following way:-- If the salt effect is indeed an effect produced primarily by increasing the ionization of the water--just as electrolytes (e.g. sodium chloride) are known to increase the ionization (2) of other weak acids like acetic acid and formic acid-- then the accelerating effect of a given concentration of ionized salt (e.g. sodium chloride) on the velocity of decomposition of an imido ester should be the same irrespective of the imido ester used--the same for the imido esters that are decomposed rapidly as slowly. It is obvious that if the factor $(C_H \times C_{OH})$ in the dynamic equation referred to above has a definite value when no salt is present and is increased a definite amount by the addition of a definite amount of ionized salt, the effect of K_v found, ~~#####~~ when calculated on the assumption that $(C_H \times C_{OH})$ is a constant, must be to increase it in the same proportion irrespective of the original value of K_v . For example if a gram molecular weight of potassium chloride, calculated for a condition of complete ionization in solution with a fast reacting imido ester salt increases the value of K_v 185%, then we would expect that the same amount of potassium chloride under the same conditions would increase the value of K_v 185 percent for a slow reacting imido ester. The results obtained by Miss

Footnotes)

(1) See footnote (3) p.2.

(2) Arrhenius, Z. Phys. Chem., 1, 126.

Barnard (1) in the study of these imido esters showed that such an identical proportional ^{increase} does take place in the three cases studied. In such an investigation the further apart the the values for K_v are for the imido esters used, that is the greater the difference between the smallest and greatest velocity constants--the more convincing the proof would appear to be. Having found in the imido para toluylates esters that are decomposed particularly *slowly*, I made a series of determinations with the hydrochloride~~s~~ of the methyl imido para toluylate in mixtures prepared from isohydric solutions of the ester salt and potassium and sodium chloride. The isohydric solutions were computed and made up as explained by Dr. Barnard (1) and the velocities determined in the usual way. The following tables give the results of these determinations. In these tables the symbols have the usual significance.

Methyl Imido Para Toluylate with Potassium Chloride.

Table XCIII.

$m = \frac{0}{0.05}$ $m' = 0.05$ $V = 0$ $V' = 250$ Mean 43430 $K_v = 116.7$ Grand Av. = 115.6

t	0	107	148	205	253	303	363
v	12.00	8.99	6.93	6.05	5.30	4.54	
K	---	117.3	117.0	116.2	116.2	117.2	116.4

Table XCIV.

$m = 0.1$ $m' = 0.122$ $V = 150$, $V' = 100$ Mean 43430 $K_v = 113.7$ Grand Av. = 113.8

t	0	84	121	179	231	280	334
v	11.01	8.79	7.98	6.83	5.95	5.21	4.51
K	---	(118.6)	116.4	115.9	115.3	116.0	116.2

(Footnote)

(1) Am. Chem. J.

Table XCV.

$m = 0.2$ $m' = 0.266$ $V = 200$ $V' = 50$ Mean 43430 $K_v = 112.7$ Grand Av. 112.8

\underline{t}	00	98	154	203	250	294	343
\underline{v}	12.37	9.83	8.50	7.49	6.48	5.91	5.13
\underline{K}	---	112.5	112.8	112.5	(113.4)	112.7	113.3

Table XCVI.

$m = 0.25$ $m' = 0.348$ $V = 215$ $V' = 35$ Mean 43430 $K_v = 111.0$

\underline{t}	0	90	135	384	234	278	323
\underline{v}	11.45	9.11	8.11	7.14	6.30	5.67	5.01
\underline{K}	----	110.6	111.1	111.5	111.1	110.6	111.3

Table XCVII.

$m = 0.3$ $m' = 0.438$ $V = 220$ $V' = 30$ Mean 43430 $K_v = 108.5$

\underline{t}	0	94	141	194	241	283	328
\underline{v}	12.39	9.82	8.72	7.33	6.80	6.03	5.41
\underline{K}	---	107.4	108.0	107.9	107.9	109.7	110.3

Table XCVIII.

$m = 0.333$ $m' = 0.501$ $V = 225$ $V' = 25$ Mean 43430 $K_v = 108.8$

\underline{t}	0	99	172	229	284	372	
\underline{v}	10.48	8.07	6.83	5.93	5.13	4.03	
\underline{K}	---	(114.5)	108.1	108.0	108.3	110.7	

Table KCIX.

$m = 0.333$ $m' = 0.501$ $V = 225$ $V' = 25$ Mean 43430 $K_v = 106.8$

\underline{t}	0	111	187	255	321	338	432
\underline{v}	10.33	7.78	6.49	5.33	4.72	4.13	3.33
\underline{K}	----	110.8	107.9	102.4	106.0	107.4	103.2

Table C.

$m = 0.4$ $m' = 0.641$ $V = 230$ $V' = 20$ Mean 43430 $K_v = 103.7$ Grand Av. = 104.0

\underline{t}	0	141	183	244	287	360	
\underline{v}	11.67	8.33	7.53	6.55	5.87	5.03	
\underline{K}	---	102.4	104.3	102.8	103.8	104.3	

In the following table is given a summary of the preceding tables. In the last column is given the theoretical value for the velocity of decomposition of the positive ester ion calculated according to equation (3), p.3. The value of $K_{v(0)}$ was obtained by the method explained by Miss Barnard.(1) It was found to be

Footnote)

(1) Am. Chem. J. ____

139. The value taken for A is 185 per cent, the same factor that was used by Miss Barnard in calculating the constants for the faster reacting bodies.

Table CI.

Methyl Imido Para Toluylate with Potassium Chloride.

<i>Vol. of imido salt sol. in 250 cc.</i>	<i>m KCl</i>	<i>100 g KCl</i>	<i>m, imido</i>	<i>100 g, imido</i>	<i>C. ion</i>	<i>43430 K₂ found</i>	<i>43430 K₂ found (139)</i>	<i>43430 K₂ found (139)</i>
250	---	----	0.050	78.88	0.038	118.7	148.5	148.8
100	0.1	85.9	0.122	70.36	0.083	113.8	181.8	181.1
50	0.2	82.1	0.233	61.85	0.165	112.8	182.7	181.4
35	0.25	81.1	0.348	58.30	0.203	110.0	188.8	191.2
30	0.3	80.3	0.438	55.00	0.241	108.5	197.3	201.0
25	0.333	79.8	0.501	53.04	0.285	107.8	203.3	207.1
20	0.4	79.0	0.645	48.97	0.318	104.0	212.4	220.3

It is evident from a comparison of the last two columns that this same increase of 185 percent per gram ion which Dr. Barnard found to hold for the faster reacting bodies, holds for the methyl imido para toluylate in isohydric solutions with potassium chloride for the varying concentrations. Owing to the greater difference of the velocities of decomposition of this ester salt and the other imido benzoates treated in the same way these results would seem to indicate that the acceleration due to the salt present in solution is entirely independent of the nature of the decomposing cation. These results, then, confirm the theory (1) that the other component, water, is the one effected by the electrolytes in solution. This must be done through the ionization of the water.

Sodium chloride was next tried to ascertain if it had the same accelerating effect as potassium chloride. Isohydric mixtures were made and the experiments carried out just as before. The results are given in the following tables.

Table CII.

$\underline{m} = 0.1$ $\underline{m}' = 0.1184$ $\underline{V} = 150$ $\underline{V}' = 100$ Mean 43430 $\underline{K}_V = 114.2$ Grand Av = 113.3

<u>t</u>	0	88	152	215	270	337	406
<u>v</u>	10.25	8.09	6.90	5.82	5.04	4.22	3.51
<u>K</u>	---	113.0	113.1	114.3	114.2	114.9	114.9

Table CIII.

$\underline{m} = 0.2$ $\underline{m}' = 0.256$ $\underline{V} = 200$ $\underline{V}' = 50$ Mean 43430 $\underline{K}_V = 112.1$ Grand Av = 110.8

<u>t</u>	0	88	154	223	287	321	389
<u>v</u>	10.99	8.09	6.90	5.82	5.04	4.22	3.51
<u>K</u>	---	(117.0)	110.8	110.8	111.5	113.2	114.7

Table CIV.

$\underline{m} = 0.25$ $\underline{m}' = 0.333$ $\underline{V} = 215$ $\underline{V}' = 35$ Mean 43430 $\underline{K}_V = 109.8$

<u>t</u>	0	152	213	233	312	334
<u>v</u>	10.98	7.69	6.59	5.73	5.10	4.50
<u>K</u>	---	101.8	102.7	105.4	108.7	108.4

Table CV.

$\underline{m} = 0.3$ $\underline{m}' = 0.415$ $\underline{V} = 220$ $\underline{V}' = 30$ Mean 43430 $\underline{K}_V = 1126$ Grand Av = 110.2

<u>t</u>	0	85	155	209	232	323	337
<u>v</u>	12.21	9.43	8.03	7.06	6.20	5.42	4.79
<u>K</u>	---	(130.3)	113.4	114.1	112.3	109.2	110.8

Table CVI.

$\underline{m} = 0.333$ $\underline{m}' = 0.473$ $\underline{V} = 225$ $\underline{V}' = 25$ Mean 43430 $\underline{K}_V = 104.6$

<u>t</u>	0	152	213	233	312	334
<u>v</u>	10.98	7.69	6.59	5.73	5.10	4.50
<u>K</u>	--	101.8	102.7	105.4	108.7	108.4

Table CVII.

$\underline{m} = 0.4$ $\underline{m}' = 0.599$ $\underline{V} = 230$ $\underline{V}' = 20$ Mean 43430 $\underline{K}_V = 104.5$ Grand Av = 103.9

<u>t</u>	0	104	180	202	239	293	373
<u>v</u>	11.41	8.71	7.41	7.02	6.42	5.53	4.37
<u>K</u>	---	(112.8)	104.2	104.4	104.5	105.8	104.0

In the following table the results are summarized in the same way as was done for the mixtures with potassium chloride. The symbols have the same significance as before.

Table CVIII.

<i>l. of. acid salt in 250cc</i>	<i>on NaCl</i>	<i>100x NaCl</i>	<i>gm' imid</i>	<i>100d' imid</i>	<i>C_{ion}</i>	<i>43430 K₂ salt found</i>	<i>43430 K₂ imid found (139)</i>	<i>43430 K₂ imid. theory (139)</i>
50	---	-----	0.050	78.6	0.0383	116.7	148	149
40	0.1	83.87	0.113	70.7	0.0837	113.3	160	160
30	0.2	79.99	0.258	32.41	0.1597	110.3	178	180
25	0.25	78.51	0.333	58.97	0.1983	110.3	187	189
20	0.3	77.25	0.415	55.83	0.232	110.6	198	199
15	0.333	76.51	0.473	53.39	0.255	105.9	197	204
10	0.4	75.19	0.599	50.18	0.301	103.9	207	216

As in the case of the velocity determinations of the isohydric potassium chloride solutions we see again from a comparison of the last two columns the same agreement between the values computed according to theory and the ones actually found by experiment. This shows not only a definite increase in the velocity of decomposition per gram ion of the electrolyte present but also that the same rate of increase is caused by the sodium as by the potassium salt, just as was found by Miss Barnard in her work on the faster reacting bodies.

SUMMARY.

The conclusions reached in these investigations may be summarized as follows:

- (1) The velocity of decomposition by water of the positive ion of an imido ester salt has been found to be the same irrespective of its origin from a chloride, bromide, ~~or~~ nitrate or sulphate.
- (2) The accelerating salt effect in the decomposition by water of the positive ion of imido ester salts has been found to be the same for bromides and nitrates ~~as~~ as for chlorides,--for instance, for potassium and sodium bromides it is the same as for potassium, sodium and lithium chlorides, viz. an acceleration of 185 per cent per gram molecule of fully ionized salt. (1)
- (3) The accelerating salt effect of sulphates (potassium or ammonium sulphate) seems to be very considerably larger, viz. about 700 per cent per gram equivalent fully ionized salt--all the experiments made agreeing with this result. But the investigations on this point can not be considered complete, as yet.
- (4) The relation of the velocity of decomposition of imido ester salts to their degrees of ionization in solutions of increasing concentration is the same at 0° as at 25°--there is a decrease of velocity with a decrease of ionization as the solutions grow more concentrated--but the increase in velocity is not proportional to the decreased ionization owing to the accelerating salt effect of the salt itself, exactly as at 25°.
- (5) The acceleration, 185 per cent, produced by one gram molecule ionized salt--e.g. potassium chloride--is the same for the decomposition of the slowest reacting imido ester and the fastest--a result in harmony with the view that the salt effect is the result of the increased ionization of water.

In conclusion, I take pleasure in acknowledging with much gratitude my appreciation of Dr. Stieglitz's direction in this work and of the patience and interest he has displayed during its progress.

The Catalysis of Imido Esters in the Presence of Acids.

Abstract of a Dissertation

Submitted to the Faculty of the
Ogden Graduate School of Science
In Candidacy for the Degree of
Doctor of Philosophy

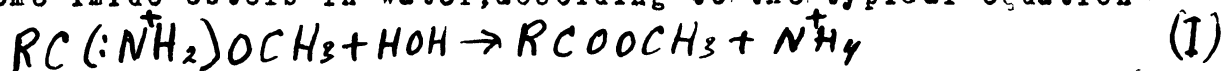
In the Department of Chemistry

By

William Weldon Hickman.

The permanent value of any theory can be insured only by the putting of the conclusions proceeding logically from its applications in different directions to the test of rigorous quantitative experimentation. In the paper under consideration some of the consequences concerning the behavior of imido esters in acid solution--the quantitative ^{study} of which has formed the basis of Stieglitz's theory of catalysis of ordinary esters, cane sugar and similar bodies--have been examined from this point of view.

It was undertaken to measure the velocity of the decomposition of the hydrobromides, nitrates and sulphates of some imido esters in water, according to the typical equation



with the object of finding whether the velocity of the decomposition of the positive ester ion--in the calculation of which the "salt effects" have been eliminated--is the same for a given imido ester, irrespective of the acid with which the ion is combined.

If the reacting component is the positive ester ion then the velocity of decomposition would be the same irrespective of the origin of the ion. If various salts could be used without exhibiting the disturbing influence of an accelerating "salt effect", one could say that all the various salts must show the same velocity constants referred to the concentration of the positive ester ions. But the fact that there is a secondary accelerating factor, the "salt effect", must be taken into consideration. If the accelerating "salt effect", caused by the

salts of different anions, e.g. Cl and Br, should prove to be the same, the velocity constant obtained for the different salts would still remain the same. The amount of this salt effect could be determined by the study of the imido ester salts, not only in aqueous solution, but also in the presence of added salts of the acid under consideration.

As a matter of experiment, careful determination of the degrees of ionization by conductivity measurements and velocity determinations made with the hydrobromides in the presence of potassium and sodium bromide showed them to have the same accelerating effect as sodium and potassium chloride. This conclusion is born out by the facts presented in the following table, in which the results of the velocity determinations of Miss Barnard's work on the hydrochloride of ethyl imido benzoate in the presence of potassium chloride are compared with the results of my determinations with the hydrobromides of the same salts.

Table I.

K Hal.	KCl		KBr		
m	43430	K_v/α_1	43430	K_v/α_1	
	Found	Calculated	Found	Calculated	
0.	176	176	176	177	
0.1	191	190	191	190	
0.2	213	214	209	215	
0.25	227	226	230	227	
0.333	247	245	(268)	247	

In the table column 1 gives the concentration of the potassium salt used, columns 2 and 4 contain the values found for the velocity constant referred to the concentration of the positive ester ion in the hydrochloride and hydrobromide respectively, $K_{ion} = K_v/\alpha_1$ when α_1 is the degree of ionization of the imido ester salt and

$$K_v = \frac{1}{t_2 - t_1} \times \text{Log. nat.} \frac{C - x_1}{C - x_2} \quad (II)$$

$C - x_1$, $C - x_2$, etc. represent the concentrations of the imido ester salt at the times t_1 , t_2 , etc., columns 3 and 5 are calculated on the basis of the fundamental equation

$$\underline{K_v(\text{ion}) \text{ observed}} = \underline{K_v \text{ ion.}} (1 + A \times m \times \alpha) \quad (\text{III})$$

in which $K_v \text{ ion observed}$ is the observed velocity constant referred to the concentration of the positive ester ion, and $K_v \text{ ion.}$ is the velocity constant for the decomposition of the positive ester ion in the absence of all electrolytes. A is the acceleration produced by the salt effect by one gram molecule of fully ionized salt present and α is its degree of ionization. The accelerating factor, A , was taken as 185% both for the hydrochloride and the hydrobromide.

It is quite evident from the table that the two salts, potassium chloride and bromide, have the same effect on K_v/α , the velocity of the reaction referred to the concentration of the positive ester ion. That being the case, if the reacting component in the decomposition of imido esters by water is the positive ion of the ester, solutions of an imido ester hydrochloride, hydrobromide and nitrate, of the same degree of ionization, should show the same velocity constants, $K_v \text{ ion observed}$ or K_v/α , the secondary salt effect being the same for all of them. That such is the case is shown by the following tables.

In the first column is found the molecular concentrations of the imido ester salt used; in the second column headed α are given the percentages of ionization of each salt ~~for~~ the indicated concentrations; in the column headed K_v are given the constants of decomposition as computed from the equation (I); in the columns headed K_v/α are given the constants of decomposition as referred to the concentration of the positive ions.

Table II.

Ethyl Imido Benzoate.

m	Hydrochlorides			Hydrobromides			Nitrates		
	<u>α</u>	<u>K_v</u>	<u>K_v/α</u>	<u>α</u>	<u>K_v</u>	<u>K_v/α</u>	<u>α</u>	<u>K_v</u>	<u>K_v/α</u>
0.05	77.8	136	175	75.88	133	175	75.11	133	177
0.1	71.8	132	184.5	69.38	128	184	68.33	127	186
0.2	64.6	121	188	61.71	119	193	60.45	118	195
0.333	57.7	114	198	54.70	108	198	52.66	107	201

A comparison of the values under K_v/α for equi-molar solutions shows a very close agreement as the theory predicted. The differences are all within the experimental error. Other

experiments in which methyl imido benzoate was used in place of the ethyl salt gave the same satisfactory results.

After the investigation of the hydrobromides and nitrates our attention was turned to the sulphates of the ethyl and methyl imido benzoates. The work on these salts was handicapped by the fact that the solid salts could not be isolated in a pure condition. They are so sensitive to moisture that it was necessary to prepare the salts in aqueous solution at the time of beginning each experiment. We found by conductivity measurements that the sulphates of the imido esters, like other sulphates, are less ionized in equivalent solutions than are the salts of monobasic acids. But all our determinations showed uniformly a greater speed of reaction for the sulphates than for the hydrochlorides, hydrobromides and nitrates in equivalent solution.

This led to the suspicion that the accelerating salt effect of the salts of the sulphate ion might be greater than for the salts of the univalent ions used. This was tested by bringing into the solution extra sulphate ions by means of isohydric mixtures of potassium sulphate. It was found that the salt effect of a sulphate was actually much greater than that of the univalent salts used above.

Note:

(Following p 4)

Note: After the completion of the work reported on in the dissertation of which this is an abstract, Stieglitz studied the question as to whether the experimental results obtained could be interpreted, not as due to a decomposition of the ester-ion accelerated by a salt factor, presumably acting on the ionisation of water, as outlined above, but as due to parallel reactions of decomposition of the ester-ion and of the non-ionised ester salts. [Journal of the American Chemical Society, 34, 1687 (1912)]. Agree, Bredig, and Lapworth had advanced the theory that accelerations beyond the theoretical effect of a catalysing agent could be due to parallel decompositions of ions and non-ionised molecules. The calculations of Professor Stieglitz showed that the assumption of such parallel reactions together with a smaller but definite self-effect, would satisfy the numerical data obtained by experiment as well as the theory given in this abstract. The still more recent view which is rapidly gaining adherence, that salts are 100% ionized, if true, makes parallel decompositions of ions and non-ionised salt molecules obviously impossible; it would lead to a third theory, that we are dealing solely with decompositions of ions, as assumed in this paper, and that ionisation is not decreased by increase in concentration, but the chemical activity of the components, ~~salt ions and water~~, is decreased--as are the conductivity and related properties of salt solutions.

Experimental Part

I. The imido ester salts used were prepared in our laboratory and analyzed by means of titration against tenth normal potassium hydroxide, phenolphthalein being used as indicator.

The degree of ionization of the imido ester salts was determined at various concentrations at zero degrees in order to avoid the rapid decomposition which takes place at 25 degrees. This was done by conductivity measurements. While part of the velocity experiments were performed at 25 degrees it was assumed that there would be but little change in ionization from that at zero degrees. This was later justified experimentally as shown in part II. below.

Velocity determinations were made with the following salts:--the hydrobromides of ethyl imido benzoate and of methyl imido benzoate; the nitrate of ethyl imido benzoate; the sulphates of ethyl imido benzoate and methyl imido benzoate.

II. In this part of the investigation velocity determinations were made at 0°--the same temperature at which the degree of ionization at various concentrations had been determined. This would eliminate the chance of error in our conclusions due to the possibility of a change in ionization of the salts used between the temperatures of 0° and 25°.

The hydrochlorides of ethyl imido benzoate and methyl imido benzoate were used in these velocity experiments. The degrees of ionization determined with great care at 0° by Miss Barnard were used.

It was clear that the velocity of decomposition of the imido ester salts at 0° does decrease most decidedly with increased concentration, i.e. with increased ionization. The decrease, however, was not proportional to the decrease in ionization. The values K_v/α showed increasing values at 0° as at 25°--the result of the secondary accelerating salt effect.

Referring the velocity of decomposition to the ester ion alone. (See the note on p.4)

In order to secure a salt whose velocity of decomposition was very slow and thus make possible more accurate measurements in velocity determinations we prepared the hydrochloride of methyl imido para-toluyate. Velocity measurements were made at 25° as the decomposition proceeded too slowly at 0° for practical purposes. The results were much the same as with the preceding salts excepting that the salt effect is smaller.

III. A very slow reacting imido ester salt having been found in the chloride of methyl imido para-toluyate, it was determined to find out the effect upon the velocity of decomposition of definite additional amounts of potassium chloride solution in isohydric mixtures. If the effect of adding the salt is to increase the ionization of the water, then the velocity of decomposition of any imido ester salt should be affected in the same degree, no matter whether it was a slow reacting or fast reacting compound. Miss Barnard had shown that such a proportional increase does take place in the faster reacting compounds. The result of these determinations showed that the same increase found by Miss Barnard held for this slower reacting salt with potassium chloride for the varying concentrations. Sodium chloride solutions were then used in place of potassium chloride and with the same result.

These results seem to confirm the theory that the other component, water, is the one affected by electrolytes in solution, and that this must be done thru the ionization of water

Summary.

- (1) The velocity of decomposition by water of the positive ion of an imido ester salt has been found to be the same irrespective of its origin from a chloride, bromide, nitrate or sulphate.
- (2) The accelerating salt effect in the decomposition by water of the positive ion of imido ester salts has been found to be the same for chlorides, bromides and nitrates.
- (3) The accelerating salt effect of sulphates seems to be very considerably larger. Further experimentation is desired.

(4) The relation of the velocity of decomposition of imido ester salts to their degree of ionization in solutions of increasing concentration is the same at 0° as at 25° but the decrease in velocity is not proportional to the decrease in ionization owing to the accelerating salt effect of the salt itself, exactly as at 25°.

(5) The acceleration produced by one gram molecule of ionized salt--e.g. potassium chloride--is the same for the decomposition of the slowest reacting imido ester and the fastest--a result in harmony with the view that the salt effect is the result of the increased ionization of water.