drawn over the box without actually igniting. Another portion of the same preparation subsequently exploded. Small fragments could, at will, be made to blow up by rubbing in a mortar.

The salt did not noticeably differ in appearance from other or ordinary samples. In considering the possible causes of the phenomena, it at once occurred to me as likely that the material contained ether, although it did not smell of it after standing for some time in the open or in a desiccator. It had been prepared by shaking an aqueous solution of nitric acid and uranyl nitrate with ether, drawing the latter off and evaporating to crystallization. A specimen of the salt which no longer had any odor of ether was moistened with a strong solution of potassium hydroxide, whereupon a very marked smell of ether was evolved. Another specimen, when dissolved in water, gave a deep blue color to Congo-red test paper, indicating presence of "free" nitric acid.

All the phenomena observed by me, except the tests mentioned, are precisely similar to those recorded by Ivanov and it is difficult to avoid the conclusion that we both had in hand essentially the same material. If it is extremely difficult to understand how uranyl nitrate could be explosive, it is quite easy to comprehend how a uranyl nitrate, $UrO_2(NO_3)_2.6H_2O$, in which the water had been replaced by ether and nitric acid of crystallization, might have a good deal of easily liberated energy. It is certain that my samples contained ether in a state of combination and it is not unreasonable to conclude that Ivanov's also did. It is not unlikely that further investigation will show that the formation of the explosive stands in an intimate relation with the concentration of nitric acid in the aqueous solution, while being shaken out with ether. I hope that this fragmentary note may stimulate some one to follow the matter up and to determin the formula of the explosive substance. LAUNCELOT W. ANDREWS.

DAVENPORT, IOWA, October, 1912.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

CATALYSIS ON THE BASIS OF WORK WITH THE IMIDO ESTERS: THE "SALT EFFECT."[1]

BY JULIUS STIEGLITZ.

Received September 6, 1912.

In the course of our studies on the action of ammonia on imido esters

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[1] Preliminary report. It had been intended to reserve the discussion herein presented until the degrees of ionization of the salts used had been redetermined with the aid of *viscosity* measurements, in order to insure the highest degree of accuracy (cf. A. A. Noyes and E. W. Washburn, THIS JOURNAL, 33, 1461). However, on receiving a courteous notification from Professor Acree that he intended to discuss part of our work at the forthcoming International Congress (without his specifying just what points would be discussed), it has been considered best, before learning the contents of the

and their salts, the conclusion was reached[1] that parallel with the action of ammonia on the positive *ion* of the imido ester, with a very high velocity coefficient, there is also a slow action on the *non-ionized* free base: both actions lead to the formation of amidines and the action on the positive ion can be accelerated by the addition of an acid, through salt and ion formation. In more recent work on the velocity of the rearrangement of acid chloramides through salt and ion formation in alkalin solutions, it was further found "that the *anions* of the salts formed certainly undergo the rearrangement but that it seems possible that *both* the anions *and* the *non-ionized* salts undergo the rearrangement simultaneously, with the probability that the *fast* reacting components in the rearrangement are the *anions*."[2]

In view of these experimental results, it has seemed desirable[3] to subject the whole series of results obtained in the decomposition of imido esters by water, which is accelerated by the addition of acid, to renewed scrutiny in order to ascertain whether a parallel action of water on the *non-ionized* imido ester *salt*, proceeding simultaneously with the main action on the imido ester *ion*, could be inferred. In referring the velocity of the action to the ion as the sole reacting component of the imido ester salt, it was necessary to assume a considerable acceleration of the action in the more concentrated salt solutions,[4] an acceleration analogous to the "salt-effect" in the inversion of sugar, the acid catalysis of esters, in the ionization of electrolytes, etc. Experiments on the effect of added neutral salts were quite in harmony with the assumptions made,[4] except

address, to put into this preliminary report a discussion of certain important questions, which have come up since the last publication on our studies in this field (THIS JOURNAL, 32, 230), although postponement to secure final experimental accuracy on all the factors involved would have been preferred by us.

[1] THIS JOURNAL, 32, 230. Cf. a previous study of a similar case by Acree and Johnson, *Am. Chem. J.*, 38, 308; 39, 300.

[2] Dissertation of H. L. Trumbull, University of Chicago, 1911. See also Stieglitz, *Report of the Congress of Arts and Science*, St. Louis, 1904, IV, 276; *Am. Chem. J.*, 39, 29 (1908); etc. For the effects of the non-ionized salts see also Acree, *Ibid.*, 38, 258 (1907).

[3] The following footnote by Stieglitz to the dissertation of L. S. Weatherby, written in the summer of 1911, defines our program: "With the extensive data now at hand on the effect of different classes of salts in the catalysis of imido esters, it is proposed to analyze the data critically in regard to various hypotheses concerning the nature of the 'salt-effect.' It is also hoped that the data will make it possible to determin whether the *cations* of ester salts should alone be considered the active components or whether the alternative possibility, that both *the cation and the non-ionized ester salt molecules* must be considered to show approximately the same degree of reactivity. Hitherto the evidence has favored the view that the cations are the important reacting component, but the final answer to the problem will depend to a large extent on the solution of the problem of the 'salt-effect.' "

[4] See the literature references, THIS JOURNAL, 32, 221, etc.

that in the case of *sulfates* abnormally high salt-effects were indicated,[1] an abnormality, however, which probably has found its satisfactory explanation in the recent investigation on the calculations of the degrees of ionization of salts of dibasic acids.[2] However, this abnormality led us to be particularly cautious in regard to the very complex question of the salt-effect.[3]

Acree,[4] in a series of important investigations (1907–1912), first advanced and elaborated the theory that accelerations beyond the theoretical effect of a catalyzing agent could be due to a parallel decomposition of *ions and non-ionized* molecules formed and that accelerations occur in which the reacting component formed by a catalytic agent are salt molecules and not their ions. His experimental results accord excellently with his views. Bredig[5] later reached similar conclusions and Lapworth[6] still later has pointed out that abnormal accelerations and the salt-effect are open to the same kind of interpretation.

For the reasons stated, the following analysis of some of our results seems of importance, particularly also since any conclusions reached in the case of the imido esters will almost certainly apply to the ordinary catalysis of esters.

If the velocity coefficient of the decomposition of an imido ester salt by water is calculated according to the equation,[7]

$$(1)\quad dx/dt = K_v\,(1-x) \text{ and } (2)\quad K_v = \{1/(t_2-t_1)\}\,ln\,(1-x_1)/(1-x_2),$$

water being considered of constant concentration in the dilute solutions used, the constants show decidedly *decreasing* values with increasing concentration. Referred to the ester ion as the reacting component, α representing the degree of ionization of the salt in a given solution, the velocity coefficient, $K_{ion} = K_v/\alpha$ and K_{ion} shows decidedly rising values with increasing concentrations; the increase was satisfactorily interpreted as due to a "salt-effect," as explained above. The observed velocities may, however, be also considered the net result of two parallel reactions, the action of water on the ester ion, with a velocity coefficient K'_{ion} and the action of water on the non-ionized salt molecules with a velocity coefficient K_{mol}. If the velocity of decomposition of the ion were the greater, which is to be expected in view of the results obtained with imido esters and ammonia, then the decreasing net velocities with

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[1] Dissertation of W. Hickman, University of Chicago, 1910.

[2] Harkins, THIS JOURNAL, 33, 1827 (1911).

[3] *Ibid.*, 32, 223.

[4] *Am. Chem. J.*, 38, 258 (1907); 39, 300; 41, 465; 43, 358, 505; *Ber.*, 41, 3199; and subsequent articles.

[5] *Ber.*, 41, 755 (1908).

[6] *J. Chem. Soc.*, (*London*) 93, 2197 (1908).

[7] See our previous papers for the development of the equations.

increasing concentrations could be due to the greater share of the slower decomposition of the non-ionized salt molecules in the more concentrated solutions, and the smaller share of the ions in consequence of the decreasing ionization of the salt in the more concentrated solutions. We would have, for dilute solutions,[1]

$$(3)\quad dx/dt = K'_{\text{ion}} \times C_{\text{ion}} + K_{\text{mol}} \times C_{\text{mol}},$$

in which the symbols have their usual significance and x is a function of C_{ion} and C_{mol}. If α is the degree of ionization of the salt and we have one mol in V liters, x representing the part of a mol decomposed in time t, then we have:

$$(4)\quad dx/dt = K'_{\text{ion}} \times \alpha(1 - x) + K_{\text{mol}}\,(1 - \alpha)\,(1 - x).$$

By comparison with equation (1) above, it is clear that

$$(5)\quad \alpha K'_{\text{ion}} + (1 - \alpha)\,K_{\text{mol}} = K_v.$$

By substituting the known degrees of ionization of the imido ester salt and the observed velocity coefficients K_v (calculated according to (2)) into this equation for any two experiments with solutions of different concentration, two equations are obtained, which can be solved for K_{mol} and K_{ion}. For the hydrochloride of ethyl imidobenzoate the values[2] $43430\ K'_{\text{ion}} = 161$ and $43430\ K_{\text{mol}} = 48.3$ may be calculated from the velocities observed for 0.05 molar and 0.2 molar solutions at 25°. These same values are then found to agree with the results obtained with 0.1 and 0.33 molar solutions. These constants would therefore satisfy the observations made *without any assumption of a salt-effect* whatever. Formerly the velocity constant $43430\ K_{\text{ion}} = 164$ was calculated for the velocity referred to the ion alone and a salt accelerating factor of about 40% per mol of salt present[3] was calculated for the "salt-effect." In other words, a parallel decomposition of the non-ionized salt molecules by water seems to agree with the data obtained quite as well as the assumption of a "salt-catalysis." Similar calculations showed the same to be true for the velocity of decomposition of the hydrobromide and the nitrate of the imido ester, the same constant $43430\ K'_{\text{ion}} = 161$ being used for all of these salts. Table I gives the data for the hydrochloride:

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[1] Cf. Acree and coworkers, *Am. Chem. J.*, 38, 258, and 43, 518, for the development of these equations.

[2] The same values for these constants have been calculated independently by Acr e and Myers and reported on at the I. C. A. C. (after the submission of this article) as well as in the *Am. Chem. J.*, 48, 352 (October). Not having had access to our exact data on the velocities of decomposition of these salts in the presence of added foreign salts (see below), with which the above values *do not agree*, Acree and Myers naturally could not detect the important "salt factor" involved in these reactions (see below) and the constants calculated by them are probably erroneous, as was pointed out by the author at the I. C. A. C.

[3] Schlesinger, *Am. Chem. J.*, 39, 731 (1908).

TABLE I.[1]

m.	α.	43430 K_v (found).	43430 K_v (calculated).
0.05	77.8	136	(136)
0.1	71.8	132	129
0.2	64.5	121	(121)
0.33	57.7	114	113

$K_{v\ (\text{found})}$ represents the value obtained from the observed data by equation (2), and $K_{v\ (\text{calculated})}$ represents the calculated value for the same constant according to equation (5), 43430 K_{ion} being taken as 161 and 43430 K_{mol} as 48.3; the bracketted values are those used for the calculation of these two constants and are, of course, no test of the validity of the relation, but the other two values, calculated, may be so considered. Nevertheless, in spite of the *mathematical* agreement shown, the interpretation is not a legitimate one for the following reason: if there were no "salt-effect" and it were a mere matter of two parallel reactions of the ester salt ions and the ester salt molecules, then the constants obtained for velocity determinations in which the ionization of the imido ester salt is suppressed by the addition of foreign salts *should be satisfied by the same constants.* That such is by no means the case is shown in Table II,[2] in which the data for the velocity of decomposition of ethyl imidobenzoate hydrochloride in the presence of potassium chloride are given: under $K_{v\ (\text{calculated})}$ are given the values calculated on the assumption that the decomposition coefficients are 43430 $K'_{\text{ion}} = 161$ and 43430 $K'_{\text{mol}} = 48.3$, respectively, for the ester ions and the ester molecules. The discrepancies between the found and observed values are very far beyond the limits of experimental error in the velocity measurements. Exactly the same kind of disagreement is found for the hydrobromides and the nitrates, and the observations for the three salts were obtained by three different investigators.

TABLE II.

mKCl.	100_α imid salt.	43430 K_v (found).	43430 K_v (calc.).
0.1	70.0	133.5	127
0.2	60.7	129	117
0.25	56.5	128	112
0.30	52.2	125	107
0.33	49.5	122	104
0.40	42.9	118	96.6

In view of this result, the calculated values lying considerably *below* the observed values and being the farther removed the more concentrated the salt solution is, the question was considered whether after all a "salt-catalysis" must not be considered to exhibit itself, increasing the velocities of the reactions the more, the more concentrated the salt content is.

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[1] See THIS JOURNAL, 32, 224.

[2] The data are taken from the thesis of Edith E. Barnard.

If the assumption is correct that the salt acceleration is due to the increased ionization and activity of *water* in the presence of salts,[1] then the accelerating factor would act proportionally in the same way on both the parallel reactions, and we may put:

$$(6)\quad K_v = \{\alpha K'_{\text{ion}} + (1 - \alpha)\, K_{\text{mol}}\}\,(1 + Am),$$

where m is the concentration of the salt present and A is the accelerating factor per mol of salt.[2] In this equation there are three unknowns, K'_{ion}, K_{mol} and A. By inserting into the equation the values for α, m and the observed velocity coefficient K_v (see equation 2) for three of the experimental determinations of K_v, three equations are obtained from which the unknown values may be calculated. The values thus found, from the experiments in Table III in which the values for $K_{v\,(\text{calc.})}$ are *bracketted*, are $43430\ K'_{\text{ion}} = 161$, $43430\ K_{\text{mol}} = 41.5$ and $A = 0.653$. With the aid of these values,[3] the value for K_v may be calculated according to equation (6) for the remaining experiments: these calculated values are found in the table under K_v (calc.) and it is clear that they show a satisfactory agreement with the corresponding observed value for K_v. In the estimations the "salt-acceleration" was considered to be due to the total salt present, ionized and non-ionized. It was formerly assumed that the salt-effect was primarily due to the ionized salt,[4] since non-electrolytes showed no such effect, but recent work having made it likely that the so called abnormal behavior of strong electrolytes is probably due to the non-ionized ionogen,[5] rather than to the ionized part, and the question being an unsettled one, it was thought best to use for this preliminary report, the total salt content for the basis of the calculation.[6] The mixtures examined were prepared on the basis of the isohydric principle from solutions of potassium chloride and the imido ester hydrochloride showing the same concentration of chloride-ion and therefore isohydric. The proportions used were always so adjusted that the final concentration of imido ester salt, after the mixing of the solutions, was about 0.05 molar. The imido ester salt is less ionizable than is potassium chloride and hence isohydric solutions require a greater concentration of the ester salt: at the same time, the "salt-effect" of the imido ester salt seems to be smaller than for potassium chloride:[7] considering the increased concentration of the imido ester salt to make up for this smaller effect, per mol, the concentration m, used in the calculations, was, for the simplification of the estimation, the concentration

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[1] Cf. Stieglitz, THIS JOURNAL, *loc. cit.* and references given there.

[2] Cf. *Ibid.*

[3] The values given are *preliminary* ones.

[4] Cf., however, *Am. Chem. J.*, 39, 731 (1908).

[5] Work by A. A. Noyes, Washburn, and J. Walker is referred to.

[6] In the final report the three possible interpretations will be considered.

[7] See below.

of the isohydric potassium chloride solution. The latter, in fact, in all but the first experiments, was present in large excess and the chief salt present. For the sake of completeness, the last two columns of the table give the values for 43430 K_v/α or 43430 K_{ion} (see p. 1690), the values calculated for the velocity referred only to the imido ester ion (column 5) and for 43430 K_v/α (calc.), the values for the same constant calculated on the assumption that the velocity of decomposition of the ion is 164/43430 (obtained graphically) and that the salt factor has the value 1.85. It is to be noted that *both* calculated columns of constants, based on the two hypotheses in question, namely that both the salt and the ion undergo decomposition by water, and that only the ion does so, agree well with the experimental facts and are thus far equally well justified. It will be also noted that the *new results give practically the same* velocity coefficient for the decomposition of the *ion*, namely 43430 K'_{ion} is 161, in place of 164, for the older 43430 K_{ion}. The chief difference in the results lies in the fact that part of the assumed salt acceleration is now ascribed to an action of the non-ionized molecules of the imido ester salt, these molecules reacting very much more slowly than the ions, but with a speed that is of importance, both theoretically and practically.[2]

Table III.[1]

mKCl.	100_α imid salt.	K_v (found).	K_v (calc.).	$K_{v/\alpha}$.	$K_{v/\alpha}$ (calc.).
0.1	70.0	133.5	(133.5)	190	190
0.2	60.7	129	(129)	213	214
0.25	56.5	128	127	227	226
0.30	52.2	125	124	240	237
0.33	49.5	122	(122)	247	245
0.40	42.9	118	117	275	261

As a further test of the latter assumptions, the velocities of decomposition of another ester, methyl imidobenzoate, in isohydric mixtures of its chloride and potassium chloride, were analyzed: if the theory is correct (see above) that the salt-effect is due in this reaction to the increased

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[1] The data are taken from the dissertation of Edith E. Barnard. The constants given are 43430 times the absolute values.

[2] Aside from the "salt-effect" the velocity coefficients of decomposition of the ion and the non-ionized salt, respectively, must be the same in solutions of the imido ester salt, without the addition of potassium chloride, as in mixtures with the latter salt. For complete analysis of the experimental data of Table I, we must assume therefore that 43430 $K'_{ion} = 161$ and 43430 K_{mol} is 41.5 (not 48.3) and that a salt acceleration manifests itself in these salt solutions, as in the mixed salt solutions. The factor A′ for the imido salt is calculated according to equation (6), with the aid of the experimental data for the 0.2 molar solution as 0.10 or 10%. The salt factor, which is specific for each kind of salt, is therefore very much smaller for this salt of an organic base than for potassium chloride, whichever hypotheses is used. With the aid of this value of A′, K_v is calculated as 135 for the 0.05 molar solution (found 136), 129 for the 0.1 molar solution (found 132), and 114 for the 0.333 molar solution (found 114). The salt factor may well be somewhat higher than that chosen, but lies between the limits of 10 and 20%.

ionization and reactivity of *water*, then the same coefficient of acceleration A should satisfy all velocity reactions of imido ester hydrochlorides at 25° in the presence of potassium chloride.[1] The coefficient 0.653 (A) was therefore used directly in the analysis of the results with methyl imidobenzoate and K'_{ion} and K_{mol} ascertained by substituting the known values for A, α and K_v into equation (6) for two of the experiments made and solving the two equations for the two unknown quantities. In this way,[2] $43430\ K'_{ion}$ was found to be 298 and $43430\ K_{mol} = 71$. Insertion of these values in the equation for the remaining experiments gave calculated values for K_v (calc.) which agreed quite satisfactorily with the observed values. It is clear, therefore, that the same acceleration factor A will do for both of these imido ester salts. At the same time, we again have quite as good agreement between observation and theory when the velocity is put proportionate to the concentration of the ion alone and the acceleration factor 1.85 is used as before.

It is apparent from these results that *both the hypotheses* under discussion agree with the numerical data analyzed. The decision between the two will depend on the determination of the salt factor for a number of other reactions in which water is involved. A should be the same, if it is, indeed, a measure of the increased ionization of water, for all kinds of salt-effects produced by the same salt at the same temperature, provided the pure salt-effect can be estimated from an experimental knowledge of all the other factors of the reaction. With this object the examination of the decomposition of imido ketones is being investigated by Mr. Gooch and the salt-effects in the catalysis of ordinary esters and of cane-sugar will be analyzed. It is expected that in this way a decision may be reached as to the validity of the two hypotheses. At present, the new one just outlined appears impressive on account of the molecular velocities observed as parallel reactions in other cases, notably by Acree, making it probable that there *must be some* reactivity of the non-ionized salts. It is clear, however, that the theories of catalysis advanced on the basis of the work on the imido esters would not be invalidated, but amplified rather, by the recognition of a slow parallel reaction of non-ionized salt molecules, and it is evident that in either case the *chief* reacting component is the salt *ion* (indeed the velocity constants for the ion are found practically identical under either hypothesis) and that it is primarily now a question of the absolute value of the "salt-accelerating" factor, a *salt-acceleration* being as clearly indicated under the new hypothesis as under the older one. This salt factor, in the opinion of the writer, is due to the fact that in salt solutions we are working with *mixed solvents*, in

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[1] Stieglitz, THIS JOURNAL, *loc. cit.*

[2] These are preliminary values.

which ionization, velocities, etc., cannot be expected to be the same as in a pure solvent, as is well known to be the case for solutions in water, alcohol and a mixture of the two solvents.

CHICAGO, August 28, 1912.

THE SALTS OF ACRIDINE, PYRIDINE AND QUINOLINE.[1]

[PRELIMINARY PAPER.]

BY L. H. CONE.

Received October 7, 1912.

The salts of acridine, pyridine and quinoline are universally classified as ammonium salts, *i. e.*, as salts in which the acid radical is held in the molecule by one of the valences of a nitrogen atom. This classification is based on the resemblances of the salts of these three bases to those of the open chain amines. The resemblances are chiefly as follows: the solubility of the salts in water with more or less dissociation into ions, the formation of bases when the salts are treated with strong alkalies and, finally, theirsbitter taste. All except the last of these resemblances are based upon properties which are more or less common to all salts, and cannot therefore be used as arguments for classifying any two sets of salts under the same head. Yet a critical examination of the literature shows surprisingly little evidence, other than these resemblances, for the classification of the salts of acridine, pyridine and quinoline as ammonium salts.

Within recent years a large number of nitrogen-free organic salts have been prepared and studied. Most of them contain oxygen and sulfur, and to these have been ascribed constitutions similar to the ammonium salts, with oxygen or sulfur as the center of basicity instead of nitrogen, so that they have been called oxonium and thionium salts. Salts having only carbon and hydrogen in the cation have also been made, and as every member of this class of salts thus far prepared has a benzene ring in the quinoid state, they have become known as quino-carbonium salts (II). After the existence of the quino-carbonium salts was established, it became a logical question to ask whether many organic salts in which the center of basicity had been assumed to be either nitrogen, oxygen or sulfur might not after all be carbonium salts. The position of carbon in the periodic system leads one to expect that it may be the center of greater basicity than that of nitrogen in any of its compounds.

The first inquiries in this direction by Gomberg and Cone[2] resulted in proving that a large number of so called oxonium and thionium salts were not such at all, but were true quinocarbonium salts (V). The

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[1] Presented at the International Congress of Applied Chemistry, Organic Section, New York, Sept. 9, 1912.

[2] *Ann.*, **370**, 142 (1909); **376**, 183 (1910).