Summary.

An examination of recently available literature on catalysis of esters at varying temperatures, together with some new experimental data on neutral salt action in ester catalysis at 0°, 25°, and 40° is shown to yield the conclusion that the ratio of the catalytic activities of undissociated molecule and hydrogen ion does not possess a considerable temperature coefficient such as was suggested by MacBain and Coleman, but, on the contrary, is independent of temperature. The importance of a consideration of the activity of the undissociated molecule in calculations of reaction constants in acid catalyses has been emphasized.

PRINCETON, N. J.

ORGANIC OXONIUM COMPOUNDS.

I. DIMETHYLPYRONEHYDROCHLORIDE.

By H. N. K. Rördam.

Received January 6, 1915.

Theoretical Part.

Since the discovery by Collie and Tickle[1] of the addition compounds of dimethylpyrone with acids, numerous investigations have been made upon this matter. That these and similar addition products of organic compounds containing oxygen are real and stable compounds and chemical individuals has been shown in researches by several authors, among many others recently by Kendall,[2] and Maas and McIntosh.[3] As to their being oxonium compounds, the question is still open. Not one single experimental fact is known, which absolutely compels us to see in them anything more than molecular compounds in which the acid is bound in the manner that the water of crystallization is in crystallized salts. If the addition compounds with acids are true oxonium compounds, they must be salts; but although many observations have been made which may suggest a salt character, only evidence, not certainty, has been won. The conductivities of these compounds as well as the depression of the freezing point of their solutions have been measured by several investigators. It was found that their solutions were conductive, and that the freezing point was more depressed than the number of dissolved mols would account for. From these measurements constants of dissociation for dimethylpyrone as a base were calculated. It is, however, evident that the results would be the same if only dissociation into components, for instance for dimethylpyronehydrochloride after the scheme:

$$C_7H_8O_2.HCl \rightleftarrows C_7H_8O_2 + HCl$$

takes place in the solutions. To prove that dimethylpyronehydrochloride is a real salt it must first be proved that, besides the above-named

---

[1] *J. Chem. Soc. Trans.*, 1899, 710.

[2] This Journal, 36, 1222.

[3] *Ibid.*, 34, 1273 and 35, 535.

hydrolytic dissociation into components, also electrolytic dissociation of the hydrolytically undissociated part takes place in solutions according to the scheme:

$$C_7H_8O_2.HCl \rightleftarrows C_7H_8O_2.H^+ + Cl^-$$

This has not yet been proved.

Nevertheless in modern textbooks the quadrivalence of oxygen is often treated as a matter of fact equal to the pentavalence of nitrogen, but this is due to a wrong estimation of some experimental results, the essentials of which I shall hereby briefly summarize, the question being about as important a matter as the supplementing of the theory of valency.

Coehn[1] has by means of migration measurements tried to demonstrate the presence of the ion

$$C_7H_8O_2.H^+$$

in solutions of dimethylpyrone into hydrochloric acid (20% HCl). He found that dimethylpyrone was carried to the cathode, but in one of the two experiments which he made, the electrode spaces were separated from the rest of the solution by parchment membranes, so that it was not excluded that electric endosmose might have taken place. Therefore Coehn made another experiment without membranes. When the electrolysis was finished, the contents of the electrode spaces were removed, and phosphotungstic acid was added, whereby dimethylpyrone is precipitated. The precipitate was not isolated or determined in any way, as was the case in the first of the two experiments; the author only reports that it could be directly seen that there was more of it in the cathode room than in the anode space. The omission of weighing the precipitate deprives this investigation of its significance, and moreover, among others, Coehn[2] himself has shown that non-electrolytes also can migrate under the influence of the electric current. For instance, cane sugar in hydrochloric acid will migrate to the cathode without the conductivity of the acid being altered more than the trifle which is due to the alteration of viscosity of the solution.

Walden's[3] investigations mainly include:

1. The depression of the freezing point in solutions of dimethylpyrone and of dimethylpyrone + hydrochloric acid in water. 2. The conductivity of picric acid in water and of picric acid + dimethylpyrone in water.

These two series of experiments showed that part of the acid (picric or hydrochloric) was linked to the dimethylpyrone, and from the results Walden calculates the constants of hydrolytic dissociation for the oxonium salt which I have put together in the following table under K^I and K^{II}.

---

[1] *Ber.*, 35, 2673.

[2] *Z. f. Elektrochemie*, 1909, 652.

[3] *Ber.*, 34, 4185.

	K^{I}.	K^{II}.	K^{III}.
	0.648	0.59	0.72
	0.373	0.45	0.60
	0.340	0.53	0.62
	...	0.50	0.52
Average......	0.45	0.52	0.61

These constants have been calculated under assumption of electrolytic dissociation. Thereafter also an electrolytic dissociation constant for dimethylpyrone as a base is calculated by means of the equation:

$$K_{\text{hydrolytic}} = \frac{\text{constant of electrolytic dissociation for water}}{\text{constant of electrolytic dissociation for the base}}$$

From the concordance between the values of the two series of hydrolytic constants (and consequently also electrolytic constants) found by different ways, one cannot, however, in this case deduce the correctness of the hypothesis (electrolytical dissociation), since a hydrolytic constant calculated under the assumption of dissociation into components only is of about the same amount, and the single values show as much conformity as do K^{I} and K^{II}. I have calculated this series of constants from the experiments under 2 (conductivity) and put them down in the table under K^{III}.

3. The conductivity of dimethylpyrone in liquid SO_2 was examined. The molecular conductivity was found to increase with increasing dilution, a fact that suggests the formation of a salt.

4. The conductivity of dimethylpyrone and tribromoacetic acid separately and mixed together. Separately both showed a very small conductivity, together a considerably greater. But the molecular conductivity *decreased* with increasing dilution.

Obviously there are things in these investigations which may suggest the formation of a salt in the above-mentioned cases, but none of them offers a stringent proof.

It must, however, be possible to decide absolutely the question by measuring the concentrations of H ions and of Cl ions in an aqueous solution of dimethylpyronehydrochloride. If only dissociation into components:

$$C_7H_8O_2.HCl \rightleftarrows C_7H_8O_2 + HCl$$

takes place then the H ion concentration must be equal to the Cl ion concentration, as both kinds of ions then will originate only from the acid set free by the hydrolysis. The dimethylpyronehydrochloride will in this case be a molecular compound.

If the product is a salt, then the Cl ion concentration must be greater than the H ion concentration, for besides the Cl ions which originate from the free acid:

$$C_7H_8O_2.HCl \rightleftarrows C_7H_8O_2 + H^+ + Cl^-$$

there must also be Cl ions originating from the salt:

$$C_7H_8O_2.HCl \rightleftarrows C_7H_8O_2.H^+ + Cl^-.$$

The Cl ion concentration can be determined with sufficient accuracy by measuring the potential difference between the solution and a Hg/HgCl electrode. The determination of the H ion concentration by measuring the potential difference between the solution and a H electrode had to be given up, for it turned out by experiments I made that the dimethylpyrone was decomposed by the hydrogen. But the H ion concentration can be determined in other ways. The question is only to choose a method which affords the necessary accuracy. The colorimetric method will according to Sorensen[1] only allow an accuracy of ± 0.1 in the H ion exponent ($= - \log (H^+)$). In a 0.1 *N* solution the degree of hydrolytic dissociation of dimethylpyronehydrochloride is about 0.85 according to the experiments of Walden.

If the electrolytic dissociation of hydrochloric acid is estimated to be complete into a 0.1 *N* solution, then the question will be of the determination of the difference between two H ion exponents which in the highest can be:

$$\log 0.1 - \log 0.085 = 0.07.$$

In other words, the quantity that should be determined is of about the same amount as the uncertainty of the measurement. The colorimetric method is then unfit for use in this case. A more accurate method we have in measuring the catalysis of the saponification of diazoacetic ester, but this method is unsuitable in this case, as Bredig and Ripley[2] have shown that it cannot be employed when only a trace of Cl ion is present.

While the determination of the conductivity alone cannot solve the problem, as I have shown above, determinations of the conductivity combined with determinations of the Cl ion concentration will answer the purpose.

A solution of dimethylpyronehydrochloride and a solution of hydrochloric acid, whose Cl ion concentrations electrometrically measured are equal, will have the same conductivity, if the dimethylpyronehydrochloride is only dissociated into components. If, on the contrary, also electrolytic dissociation takes place, then the molar conductivity of the dimethylpyronehydrochloride solution will be smaller than the mol. conductivity of the hydrochloric acid solution, for the Cl ion concentrations are equal in both solutions, but in the pyrone solution a part of the fast-migrating H ions are replaced by the much slower migrating dimethylpyrone ions.

---

[1] "Ueber die Messung und Bedeutung der Wasserstoffjonenkonzentration bei biologischen Processen," S. 428.

[2] *Ber.*, 40, 4015.

This is seen most distinctly when the experimental results are plotted in a diagram. Plotting corresponding values of molecular conductivity against electrometrically measured Cl ion concentration the result will be one single curve common for the pyrone solution and the hydrochloric acid, if dissociation into components only takes place. In case of electrolytic dissociation of the non-hydrolyzed part two separate curves will result, the curve for hydrochloric acid lying higher than the other. They will unite at the point which gives the molecular conductivity of hydrochloric acid at ∞ dilution (Cl ion concentration = 0) and will separate more and more with increasing concentration.

Experimental.

Consequently my experiments included electrometric determination of Cl ion concentration and of conductivity. The solutions of dimethylpyronehydrochloride, which in the following I shall simply call D-solutions, were made by dissolving accurately weighed quantities of crystallized $C_7H_8O_2.HCl.2H_2O$.

The strength of the hydrochloric acid, of which I measured the conductivity and Cl ion concentration, was determined by adding a small excess of silver nitrate to 20 cm^3. of the acid and reducing the precipitated AgCl in hydrogen. The result was

1.1932 g. Ag

wherefrom the strength of the acid is found to be 0.4424 *N*. The other solutions were produced by dilution by means of an accurate pipet (Geissler).

To the determination of the Cl ion concentration four half-elements of the type:

$$\mathrm{Hg}\left|\begin{array}{ll}\mathrm{HgCl} & \text{D-solution} \\ \text{(solid)} & \text{or HCl solution}\end{array}\right|$$

were constructed for each dilution.

They were measured by the compensation method (Poggendorff) against a 0.1 *N* Hg, HgCl electrode, a 3.5 *N* KCl solution and a 1.75 *N* KCl solution being successively used to produce the contact between the two electrode solutions in order to eliminate the diffusion potential. During the measuring the elements were placed in a water-thermostat, the temperature of which did not alter more than 0.1°. Until the measurements were made, the syphon tubes of the electrodes dipped into small glasses holding the same solution as in the electrode spaces in order to prevent the concentration from altering by evaporation.

The results of the measurements are collected in the following Tables I and II. Under [Cl$^-$] the Cl ion concentration calculated from the potential difference. By means of Nernst's equation:

$$\pi = \frac{RT}{0.4343\epsilon}. \log\frac{c_1}{c_2},$$

which holds for the potential difference after the diffusion-potential has been eliminated, and where c_1 and c_2 mean the concentrations of Cl ions, respectively, in the D-solution (or the HCl solution) and in the 0.1 *N* KCl solution is found at 19.8°.

$$\log [\mathrm{Cl}^-] = \frac{\pi}{0.0581} + \log 0.085.$$

Table I.

(D-solutions; t = 19.8°.)

π(average of 4 elements).

Concentration of the solution.	Contact produced by 3.5 *N* KCl.	1.75 *N* KCl.	Extrapolated.	[Cl⁻].
0.3750 *N*	0.0372 Volt	0.0428 Volt	0.0316 Volt	0.2974
0.2813 *N*	0.0289	0.0342	0.0236	0.2227*x*
0.1969 *N*	0.0218	0.0263	0.0175	0.1667*x*
0.09646 *N*	0.0045	0.0079	0.0011	0.0888
0.06608 *N*	—0.0048	—0.0019	—0.0077	0.0627
0.02500 *N*	—0.0291	—0.0270	—0.0312	0.0247

Table II.

(HCl solutions; t = 19.8°.)

π(average of 4 elements).

Concentration of HCl solution.	Contact produced by 3.5 *N* KCl.	1.75 *N* KCl.	Extrapolated.	[Cl⁻].
0.4424 *N*	0.0415 Volt	0.0493 Volt	0.0336 Volt	0.3219
0.3318 *N*	0.0339	0.0412	0.0265	0.2432
0.2212 *N*	0.0236	0.0295	0.0177	0.1694*x*
0.1769 *N*	0.0172	0.0228	0.0115	0.1395*x*
0.1327 *N*	0.0110	0.0158	0.0062	0.1117*x*
0.1106 *N*	0.0074	0.0116	0.0032	0.0963
0.04430 *N*	—0.0143	—0.0121	—0.0165	0.0442
0.02210 *N*	—0.0307	—0.0287	—0.0326	0.0233

The extrapolated potential and the Cl ion concentration is shown in Figs. 1 and 2 by the curves π and [Cl⁻]. Between the points the curve has been drawn by help of a flexible ruler whereby the *x*-marked values of [Cl⁻] have been graphically corrected.

The conductivity of the D-solution was measured at 18.0° and at 19.0°; in Table III the values of Λ 19.8° marked with *x* are directly measured, the others calculated by help of the temperature coefficient from the values under Λ 18.0°, which are all directly measured. For the hydrochloric acid the conductivity has been determined only at 19.8°. Between the points so determined the curve has been drawn in as good accordance as possible with the 18.0° curve, the values of which are taken from Kohlrausch and Holborn: "Leitfähigkeit der Elektrolyte."

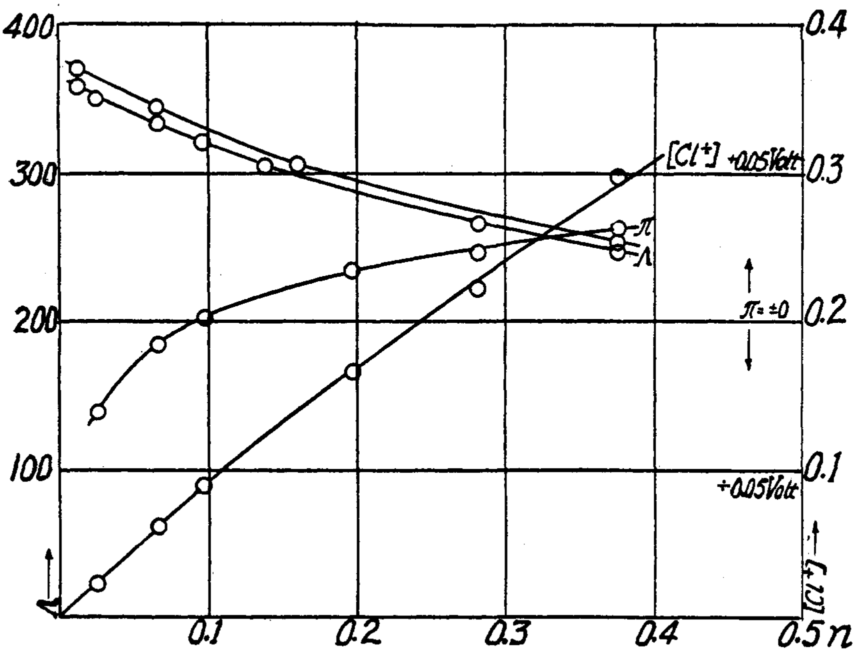


Fig. 1.—D-solution.

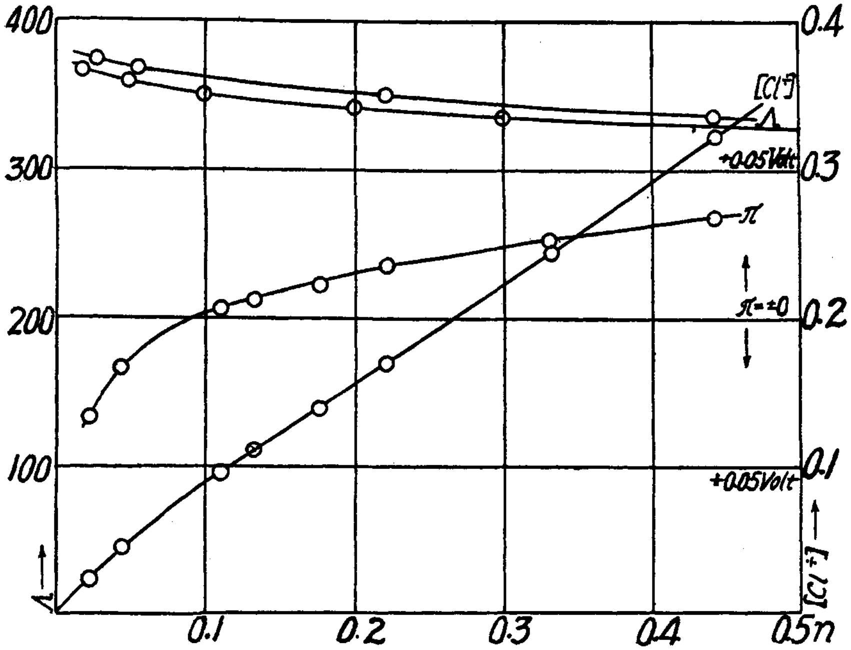


Fig. 2.—Hydrochloric acid.

In Table IV the directly measured values are marked with x.

TABLE III.

D-solutions.

Conc.	Λ18.0°.	Λ19.8°.
0.3750	247.2	253.4x
0.2813	267.1	273.1
0.1969	289.8	294.5
0.1574	...	306.5x
0.1378	305.9	314.8
0.0965	321.4	331.9
0.0661	334.5	345.0x
0.0250	350.7	364.2
0.0125	358.5	370.5x

TABLE IV.

HCl solutions.

Conc.	Λ19.8°.
0.4424	335.4x
0.3318	341.8
0.2212	350.9x
0.1769	354.0
0.1327	358.3
0.1106	361.0x
0.0553	368.4x
0.0443	370.7
0.0277	374.1x
0.0221	375.7

In Figs. 1 and 2 the conductivities are shown by the curves Λ; the upper one holds for 19.8°, the lower one for 18.0°.

Finally corresponding values of Cl ion concentration and mol. conductivity are plotted together into Fig. 3, respectively, for D-solutions (curve Λ_D) and for hydrochloric acid (curve Λ_{HCl}). As deduced in the theoretical part the shape of these two resulting curves affords a stringent proof that in aqueous solutions of dimethylpyronehydrochloride electrolytical dissociation of the non-hydrolyzed part of the addition compounds takes place, so that *dimethylpyronehydrochloride is a real salt and consequently an atomistic compound.*

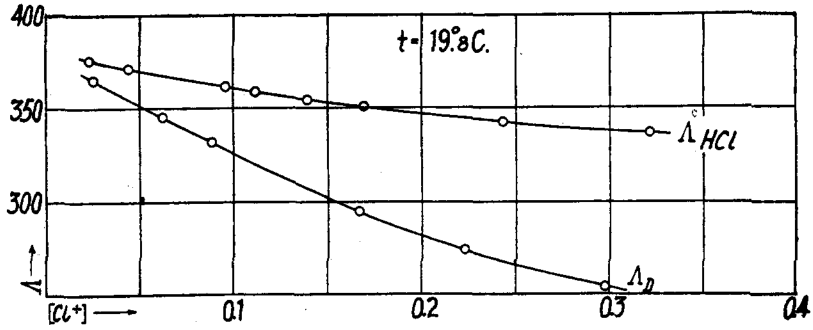


Fig. 3.

Discussion of the Results.

The equation by means of which the Cl ion concentration has been calculated from the potential only holds for diluted solutions, as it is based upon the applicability of the gas laws upon the dissolved substance. Consequently only that part of the curves which corresponds to concentrations smaller than 0.1 N gives the exact values of the Cl ion concentration.

For the higher concentrations the method of calculation employed will not give the absolutely correct values of the Cl ion concentration. Still the values can very well be used for comparison, since we must take it for granted that the same Cl ion concentration will give the same potential difference against a Hg/HgCl electrode, even if the relation between these two quantities is not expressed by the Nernst equation.

The experimental error in the determination of the molecular conductivity is about ±0.5%. The alterations which might arise in the viscosity or possibly in the dielectric constant of the solvent by the presence of dimethylpyrone have been estimated to be of no importance in this case. The experimental error in the determination of the potential difference arises mainly from the elimination of the diffusion potential. Even in concentrations below 0.1 *N* it ought to be estimated as at least ±0.5 millivolt, which gives an error in $[Cl^-]$ of about ±2%, but it can increase to double the amount, if special precautions are not taken. From the diagram it is evident that errors of this amount will not alter the shape or the reciprocal situation of the curves.

The determination of the potential difference is in itself uncertain for concentrations over 0.1 *N*, for the elimination of the diffusion potential will here involve an increasing error, but at the same time the differences between the corresponding conductivities increase so strongly, as may be seen in Fig. 3, that the reciprocal situation of the curves doubtless is correct also for this part.

As the salt character of the addition compound has hereby been proved, the calculation of a base constant for dimethylpyrone is now legitimate. Walden[1] from his conductivity measurements of the picrate calculated:

$$K_b = 2.4 \times 10^{-14}$$

by means of Bredig's table over the range between the molecular conductivity of a salt at ∞-dilution and the molecular conductivity at lesser degrees of dilution. He ascribed to the dimethylpyrone ion the velocity of migration: 35 = the velocity of migration of organic bases of similar constitution (tertiary, cyclic, containing 18 atoms).

Without help of Bredig's table[2] the dissociation constant can be calculated in the following way, when the Cl ion concentration is known both for D-solution and for HCl solutions.

By comparing the molecular conductivities of a D-solution and a HCl solution, both with the same Cl ion concentration, it is evident that the ratio of the difference δ between these two conductivities and the difference which would arise, if all H ion was linked under formation of dimethylpyrone ion is

---

[1] *Loc. cit.*

[2] *Z. physik. Chem.*, 13, 191 (1894).

$$= \frac{\delta}{\gamma(\Lambda_H - \Lambda_D)} = \text{the degree of association}$$

= 1 — the degree of hydrolysis. Then the degree of hydrolysis is:

$$\alpha = 1 - \frac{\delta}{\gamma(\Lambda_H - \Lambda_D)} = \frac{\gamma(\Lambda^H - \Lambda_D) - \delta}{\gamma(\Lambda_H - \Lambda_D)}$$

wherein Λ_H means the velocity of migration of H ion, Λ_D the velocity of migration of dimethylpyrone ion which, like Walden, I estimate to 35—γ is the degree of dissociation of the hydrochloric acid and it is supposed that a non-hydrolyzed dimethylpyronehydrochloride solution would have the same degree of dissociation, a supposition which can involve no remarkable error.

By this the following values are calculated:

Strength of the solution.	α.	Constant of hydrolysis.
0.100	0.88	0.63
0.0661	0.92	0.68
0.0250	0.96	0.59
	Average,	0.63

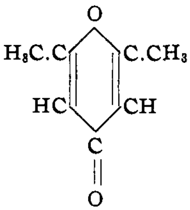
from which the constant of dissociation for dimethylpyrone as a base is found:

$$K_b = 1.9 \times 10^{-14}$$

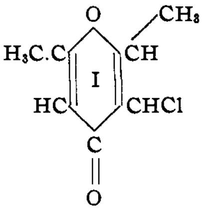
of about the same amount as the constant calculated by Walden.

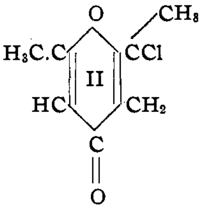
After this there can be no serious doubt about the configuration formula of the dimethylpyronehydrochloride.

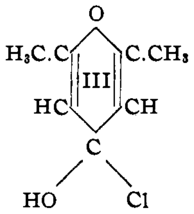
The configuration of dimethylpyrone itself is:

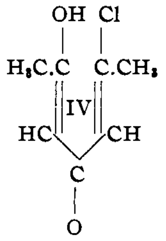


The possibilities for the formation of an addition compound with one molecule HCl, excluding the oxonium formula, are:

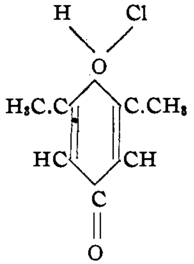

I


II





All of them have been discussed and some of them defended, but surely not one of them can account for electrolytic dissociation, so that the oxonium formula must be correct:



I am going to extend these investigations to the addition compounds of ethers with acids. The simple structure of the ethers will entail that the structure of the addition compounds is quite doubtless, if they turn out to be salts like dimethylpyronehydrochloride.

Polytechnical High School.
Copenhagen, Denmark.

THE PRODUCTION OF CHLOROPICRIN BY THE ACTION OF AQUA REGIA ON ORGANIC COMPOUNDS.

[PRELIMINARY PAPER.]

By Rasik Lal Datta and Nihar Ranjan Chatterjee.

Received January 12, 1915.

Aqua regia has been found to be a chlorinating[1] as well as an oxidizing agent.[2] It has now been found that it sometimes acts destructively, leading to the rupture of organic substances subjected to its action, with the production of chloropicrin. The transformation into chloropicrin is quantitative in some cases, in others it takes place to a limited extent while in some cases it does not take place at all. The action of aqua regia on the following substances has been studied.

Acetone.—Aqua regia decomposes acetone almost quantitatively into chloropicrin and the reaction can therefore be employed as the best method

---

[1] Datta and Fernandes, This Journal, 36, 1007 (1914).

[2] Datta, *Ibid.*, 36, 1011 (1914).