

Constitution of the Salts of Aminoacetophenones

By

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The authors have observed the interesting colour changes which the salts of o- and p-aminoacetophenone suffer under the influence of heat, solvents and some reagents, but not the salts of the meta compound¹. In order to inquire after the causes of such phenomena, the absorption spectra of the different salts of the three isomeric aminoacetophenones have been studied under various conditions, and it has been found that the coloured salt of each of o- and p-aminoacetophenone in alcoholic solution shows a new absorption band in the visible region at the greater concentration than the broad band which is originally noticed in each.

A close analogy in the chemical conducts is found to exist between the salts of o-aminoacetophenone and those of the para isomer, but those of the meta isomer show a character wholly different from those of the other two isomers.

When colourless p-aminoacetophenone hydrochloride is heated at 100° for several hours, it acquires a deep yellow colour which gradually fades away on standing. The colourless and coloured salts both dissolve in alcohol under the exhibition of the same colouration, while their aqueous solution are almost colourless. The yellow colour of the alcoholic solution greatly weakens by passing an excess of dry

¹ Kuhara and Ogawa first noticed a colour change of p-aminoacetophenone hydrochloride by heat,—unpublished work.

m-Aminoacetophenone, unlike the ortho and para compounds can not undergo isomeric change to the quinoid form, inferring from the constitutional point of view.

Likewise, p-dimethylaminoacetophenone can not assume the quinoid form as it carries no movable hydrogen for rearrangement. In both cases, therefore, the isomeric change, viz. the alteration in constitution would evidently not take place. o-Monomethylaminoacetophenone hydrochloride may, however, take the quinoid form as it carries a movable hydrogen, and actually undergoes the colour change.

Baly and Marsden¹ have already carried out the spectrographic investigation with regard to the aromatic amino-aldehydes and -ketones, and give from the results of experiments the following conclusions :

“ 1. The amino-aldehydes and -ketones of the aromatic series in neutral alcoholic solution exhibit one broad absorption band.

“ 2. The addition of small quantities of alcoholic hydrogen chloride to the solution causes the development of a second absorption band, the first remaining unaltered, provided that insufficient acid has been added to produce the hydrochloride.

“ 3. It is not produced at all in aqueous solution.

“ 4. The phenomenon appears to be due to the amino-group; it is possible that the nitrogen atom is caused to functionate as a quinquevalent atom, so that the residual affinity is increased in the ratio of 5 to 3.”

The experimental results by the authors almost coincide with those above-mentioned by Baly and Marsden, but the authors put forward somewhat different explanation, based upon the assumption that the coloured salts take the quinoid form as will be seen in the following statements :

1. Of the three isomeric aminoacetophenones the para shows the deepest absorption band, the ortho next and the meta compound the shallowest.

2. The coloured hydrochloride of each of the ortho and para compounds in alcoholic solution produces a new narrow absorption band toward the red at the greater concentration than the original broad band. The new bands of the two isomers resemble each other in their depth and position, and may be due to the quinoid form.

3. The aqueous solutions of the coloured salts do not exhibit

¹ Baly and Marsden: J. Chem. Soc., **93**, 2108, (1908).

the above phenomenon; this may be due to the change of the quinoid into the benzoid.

4. An excess of hydrochloric acid added to the alcoholic solutions of the coloured salts act so as to annual the characteristic new band in each case and makes general absorption much less; hence the action of hydrochloric acid seems to convert the quinoid into the benzoid form.

5. *m*-Aminoacetophenone and *p*-dimethylaminoacetophenone and their hydrochlorides do not manifest the second band; this may be due to the non-formation of the quinoid form.

EXPERIMENTAL PART.

I. *p*-Aminoacetophenone,



For the preparation of *p*-aminoacetophenone a method suggested by Klingel¹ was repeated by heating the equimolecular quantities of acetanilide, acetic anhydride and finely divided zinc chloride over an oil bath for 8 hours. The pasty mass thus formed was treated with hydrochloric acid in order to destroy all acetanilide, and after neutralised with caustic soda it was subjected to steam distillation to drive off all aniline. The residual brown oil, after repeated recrystallisation from hot water, gave colorless needles of *p*-aminoacetophenone melting at 105–106°. It is easily soluble in alcohol, ether or hot water; difficultly in cold water and almost insoluble in benzene or petroleum ether.

The substance was analysed with the following results:

- I. 0.1092 grm. substance gave
0.2835 grm. CO₂ and 0.0670 grm. H₂O.
- II. 0.1230 grm. substance gave
0.3194 grm. CO₂ and 0.0755 grm. H₂O.

	Calc. for NH ₂ ·C ₆ H ₄ ·CO·CH ₃	I	Found	II
C	71.08	70.78		70.81
H	6.71	6.81		6.83

¹ Klingel: Ber. D. Chem. Ges., 18, 2688, (1885).

p-Aminoacetophenone hydrochloride was prepared by passing dry hydrochloric acid gas through an ethereal solution of the base. The hydrochloride consisting of colorless needle shaped crystals thus obtained is easily soluble in water or alcohol, and insoluble in ether, benzene, chloroform or petroleum benzine. The colorless salt changes deep yellow on heating at 100° for several hours, but on standing it gradually fades assuming a pale yellow color. Both colorless and yellow salts dissolve in water, giving almost colorless solutions, but in alcohol with a distinct yellow color. It is also observed that the yellow color of the alcoholic solution much weakens by an excess of hydrogen chloride and becomes colorless at last.

The analysis of the colorless and yellow salts gave the following values of chlorine :

I.	0.3000	gram.	colorless salt	gave	0.2518	gram.	AgCl.
II.	0.2000	"	"	"	0.1638	"	"
III.	0.2600	"	yellow salt	"	0.2237	"	"
IV.	0.3051	"	"	"	0.2492	"	"

Calc. for HCl. NH ₂ .C ₆ H ₄ .CO.CH ₃ or		Found	
HCl. NH : C ₆ H ₄ : COH.CH ₃	Colorless salt		Yellow salt
Cl 20.67	I. 20.73		III. 21.27
	II. 20.26		IV. 20.21

It is almost evident that p-aminoacetophenone hydrochloride exists in two desmotropic forms, and the colored alcoholic solution would be an equilibrium mixture of the two.

By measuring the molecular weights of the differently colored salts, it is certain that such a change as polymerisation has not taken place.

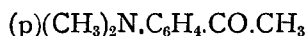
p-Aminoacetophenone sulphate was prepared by adding a drop of conc. sulphuric acid into an ethereal solution of the base. It is soluble in water or alcohol, but more difficultly than the hydrochloride, and insoluble in ether, chloroform, benzene or petroleum ether. The sulphate undergoes the similar change in color, becoming pink on heating at 100° for several hours, and these colorless and pink sulphates bear the same relation to the colorless and yellow hydrochlorides.

The pink salt was analysed with the following results :

0.3650 gm. pink salt gave 0.2331 gm. BaSO₄.

Calc. for C ₁₆ H ₂₀ N ₂ O ₂ .SO ₄	Found
SO ₄	26.08 26.28

2. *p*-Dimethylaminoacetophenone,



p-Dimethylaminoacetophenone was prepared by heating 1 part *p*-aminoacetophenone and 2 parts methyl iodide in methyl alcohol at 180–200° for 6 hours in a sealed tube. Moreover, following the method of the preparation of *m*-dimethylaminoacetophenone¹, *p*-aminoacetophenone, methyl iodide, soda and water were heated in a flask provided with a reflux condenser for several hours, and the same dimethyl compound was obtained.

It consists of platy colorless crystals melting at 105°, and easily soluble in alcohol, ether or hot water, but insoluble in cold water or petroleum ether.

I. 0.1507 gm. substance gave
0.3981 gm. CO₂ and 0.1147 gm. H₂O.

II. 0.1333 gm. substance gave
0.3570 gm. CO₂ and 0.1123 gm. H₂O.

	Calc. for (CH ₃) ₂ N.C ₆ H ₄ .CO.CH ₃	I	Found	II
C	73.58	72.07		72.99
H	8.03	8.45		8.71

p-Dimethylaminoacetophenone hydrochloride undergoes no change in color by heat.

I. 0.3020 gm. substance gave 0.2188 gm. AgCl.

II. 0.1314 " " " 0.0895 " "

	Calc. for C ₁₀ H ₁₄ NOCl	I	Found	II
Cl	17.76	17.92		17.28

It melts at 147–148° with decomposition.

p-Dimethylaminoacetophenone picrate was prepared by mixing the

¹ Rupe, Braun and Zemruski: Ber. D. Chem. Ges., **34**, 3524 (1901).

alcoholic solutions of the two components. It consists of yellow crystals melting at 124° with decomposition.

0.1200 gram. substance gave
0.2108 gram. CO_2 and 0.0455 gram. H_2O .

	Calc. for	Found
	$\text{CH}_3\text{CO.C}_6\text{H}_4\text{.N(CH}_3)_2\text{.C}_6\text{H}_2\text{(NO}_2)_3\text{.OH}$	
C	47.36	47.91
H	4.24	4.33

3. Absorption Spectra of *p*-Aminoacetophenone and its Hydrochloride¹

The following five cases have been spectrographically studied :

- (1) *p*-Aminoacetophenone in alcohol. (Fig. 1)
- (2) *p*-Aminoacetophenone hydrochloride in alcohol. (Fig. 1)
- (3) " " + excess of HCl in alcohol. (Fig. 1)
- (4) " " in water. (Fig. 2)
- (5) " " + excess of HCl in water. (Fig. 2)

They all show respectively a broad band at the vicinity of 3100. It is quite characteristic that the yellow alcoholic solution of *p*-aminoacetophenone hydrochloride develops a new small band at 2460 when the solution is more concentrated, the first broad band remaining unaltered (2), while it disappears in an excess of hydrogen chloride (3). On the other hand, the colorless or yellow salt in aqueous solution as well as in hydrochloric acid exhibits only one broad band (4) (5). It has been noted that the excess of hydrogen chloride makes the band shallower and less absorptive (3) (5).

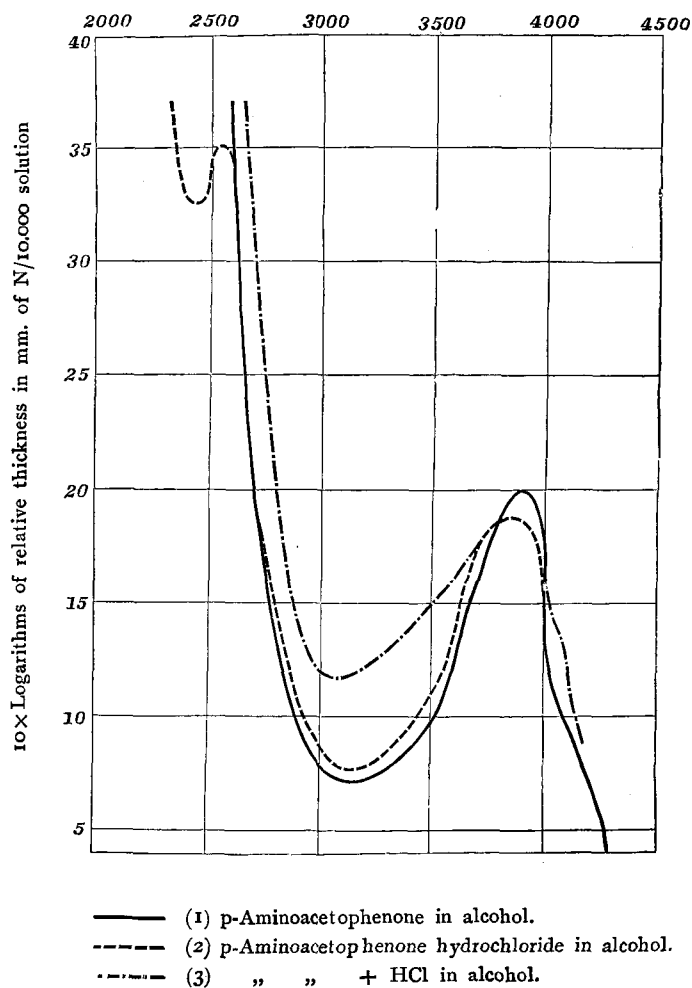
4. Absorption Spectra of *p*-Dimethylaminoacetophenone and its Hydrochloride

p-Dimethylaminoacetophenone and its hydrochloride, in alcoholic solution, exhibit only one broad band at 3000 in each case (Fig. 3). A new band is not developed when hydrochloride is dissolved in alcohol. It has been noted that these absorptions are slightly shifted toward the red as compared to those of the primary amine and its salt.

¹ Baly and Marsden: J. Chem. Soc., 93, 2108 (1908).

FIG. 1.

Oscillation frequencies



5. *o*-Aminoacetophenone,
 (o)NH₂.C₆H₄.CO.CH₃

o-Aminoacetophenone has been prepared according to Camps' method¹ by reducing *o*-nitroacetophenone with tin and hydrochloric acid. It is a pale yellow oil with a peculiar smell, which slowly

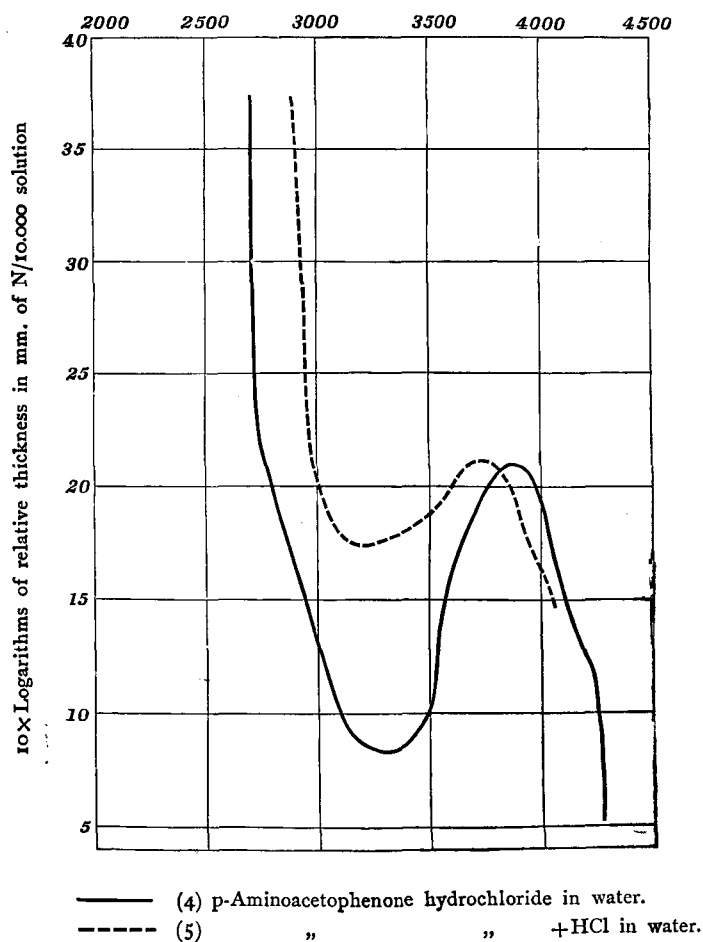
¹ Camps: Ar. Ph., 240, 6 (1902).

turns reddish when exposed to light and air. It is soluble in alcohol, ether, benzene or petroleum benzine, but almost insoluble in water.

o-Aminoacetophenone hydrochloride¹ was prepared by passing dry hydrogen chloride through an ethereal solution of the base, cooled with ice cold water. Colorless fine needles soon appeared which were quickly filtered and dried in vacuum. The salt is easily soluble in water, giving an almost colorless solution, soluble in alcohol with pale yellow color, but insoluble in ether, benzene, chloroform or petroleum benzine.

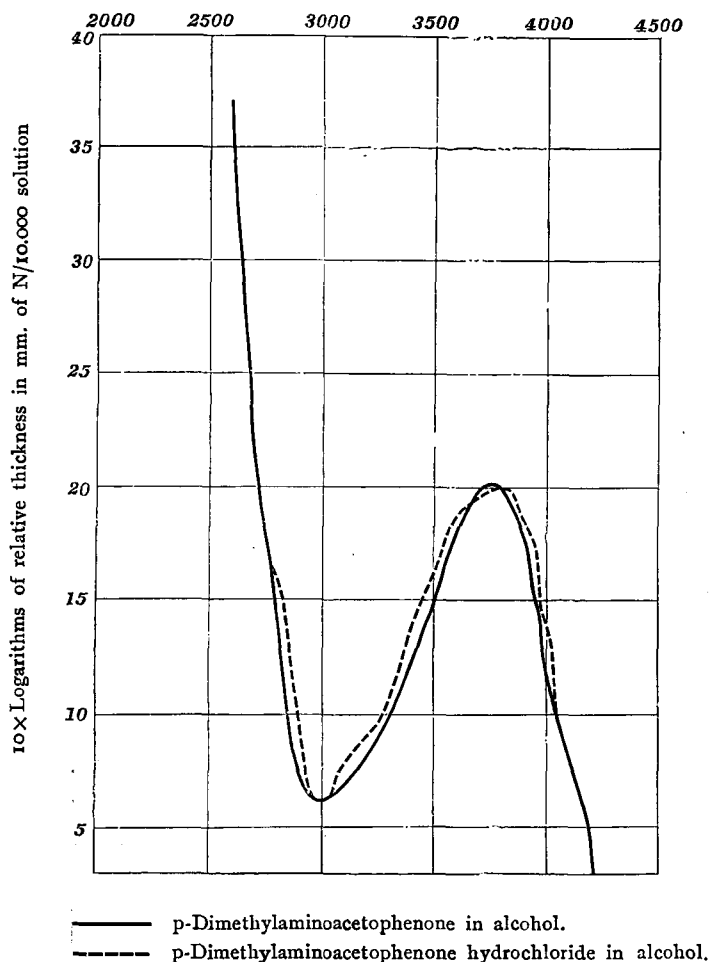
FIG. 2.

Oscillation frequencies



¹ Baeyer and Bloem: Ber. D. chem. Ges., 15, 2154 (1882).

FIG. 3.
Oscillation frequencies



When the colorless hydrochloride was heated at 100° , it slowly assumed a yellowish orange color, and after 4 hours it became bright orange, which did not seem to fade on standing. The colored salt is soluble in water or alcohol, giving orange colored solutions, the color being more intense in the latter one. An excess of hydrogen chloride weakens the color of aqueous as well as alcoholic solution of the colored salt.

I.	0.2037	gram.	colorless salt	gave	0.1681	gram.	AgCl.
II.	0.2049	"	"	"	0.1701	"	"
III.	0.1534	"	orange salt	"	0.1301	"	"
IV.	0.1320	"	"	"	0.1081	"	"

Calc. for		Found	
HCl.NH ₂ .C ₆ H ₄ .CO.CH ₃		Colorless salt	Orange salt
Cl	20.67	I. 20.36	III. 20.98
		II. 20.54	IV. 20.26

o-Aminoacetophenone sulphate¹ consists of colorless crystals, soluble in water, difficultly in alcohol, and insoluble in ether, benzene, chloroform or petroleum benzene. It does not show any change in color by the heat treatment.

6. *m*-Aminoacetophenone,



Hitherto several methods² have been proposed for the reduction of *m*-nitroacetophenone, but we adopted Camps' method³ which affords easy manipulation and a satisfactory yield.

m-Aminoacetophenone thus obtained consists of pale yellow, odorless, shiny scales, melting at 95–96°. It is almost insoluble in cold water but fairly in hot water; soluble in alcohol or ether, difficultly in benzene, but insoluble in petroleum benzene.

m-Aminoacetophenone hydrochloride⁴ was prepared in the same way as the ortho compound. It does not show any perceptible change in color by heating at 100° for 4 hours. It has similar solubilities in various solvents as the ortho compound.

I.	0.2184	gram.	substance	gave	0.1831	gram.	AgCl.
II.	0.1932	"	"	"	0.1621	"	"
III.	0.1535	"	substance (after heating)	gave	0.1281	gram.	AgCl.

¹ Baeyer and Bloem: loc. cit.

Gevekoht: Lieb. Ann., **221**, 326 (1883).

² Engler: Ber. D. chem. Ges., **11**, 932 (1878).

Konstanecki and Tambor: Ber. D. chem. Ges., **34**, 1691 (1901).

Rupe, Braun and Zembruski: Ber. D. chem. Ges., **34**, 3522 (1901).

³ Camps: loc. cit.

Hunnius: Ber. D. chem. Ges., **10**, 2009 (1877).

Calc. for		Found	
HCl.NH ₂ .C ₆ H ₄ .CO.CH ₃			
Cl	20.67	I. 20.74	III. 20.64
		II. 20.76	

m-Aminoacetophenone sulphate also undergoes no change in color by heat.

7. Absorption Spectra of o-Aminoacetophenone and its Hydrochloride¹

The following six cases have been spectrographically examined:

- (1) o-Aminoacetophenone in alcohol. (Fig. 4)
- (2) o-Aminoacetophenone hydrochloride (colorless) in alcohol. (Fig. 4)
- (3) " " (orange) in alcohol. (Fig. 4)
- (4) " " (orange) + excess of HCl (7.7 N) in alcohol. (Fig. 4)
- (5) " " (colorless) in water. (Fig. 5)
- (6) " " (orange) in water. (Fig. 5)

They all show respectively a broad band at the vicinity of 2700. The absorption curve of the free amine (1) coincides with that of the colorless hydrochloride (2). The orange salt, in alcohol, likewise develops a new small band in the visible region (2180) at a greater concentration (3), the main band remaining unaltered as in the case of the para compound. On the other hand, the same orange salt in alcoholic hydrochloric acid (7.7 N acidity) shows much less general absorption (4), losing the second band characteristic to the colored salt. The colorless and orange salts exhibit almost identical curves in aqueous solution, having only one broad band at 2850 in each case (5) (6).

8. Absorption Spectra of m-Aminoacetophenone and its Hydrochloride

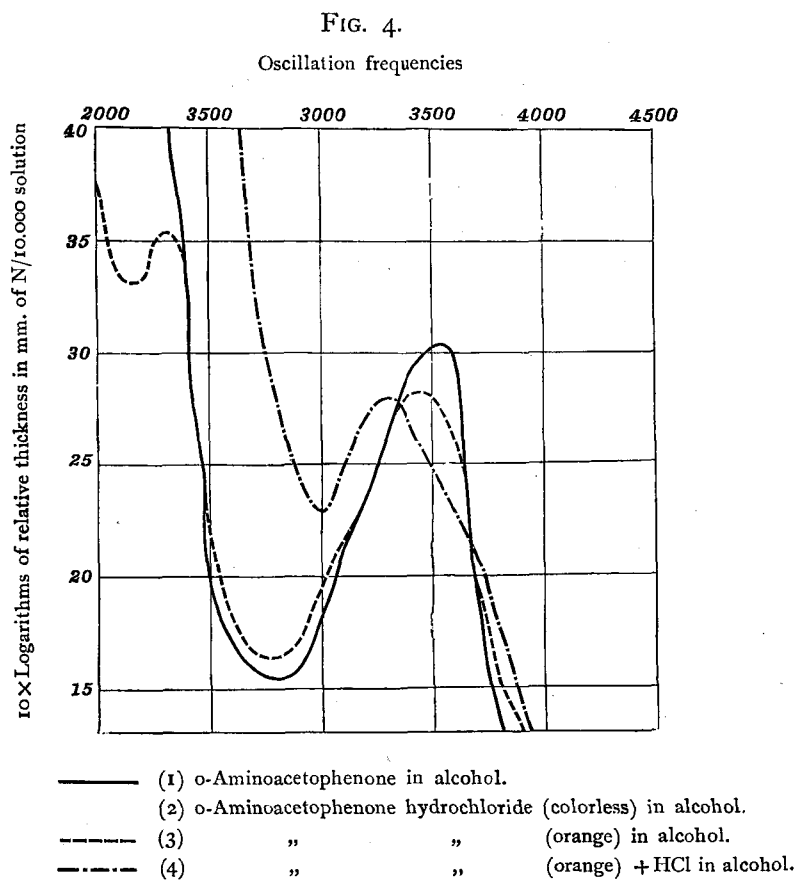
The following four cases have been examined:

- (1) m-Aminoacetophenone in alcohol. (Fig. 6)
- (2) m-Aminoacetophenone hydrochloride in alcohol. (Fig. 6)
- (3) " " (after heated at 100° for 4 hours) in alcohol. (Fig. 6)
- (4) " " in water. (Fig. 6)

¹ Baly and Marsden: loc. cit.

The general form of their absorption curves resembles those of the ortho and the para compounds, but it has been noted that the band is markedly shallower in each case.

The hydrochloride, after heated at 100° for 4 hours, in alcoholic solution (3) gives almost identical curve with that of the original salt (2), showing that no change has taken place in its constitution.



9. Alkyl Derivatives of *o*- and *p*-Aminoacetophenone

Intending to prepare the dimethyl derivative of *o*-aminoacetophenone, several experiments have been carried out, but all ended in negative results. By a prolong heating of *o*-aminoacetophenone, methyl iodide and potassium hydroxide in methyl alcohol, *o*-mono-

methylaminoacetophenone was prepared, whose hydrochloride seems to take the quinoid form by rearrangement as it assumes a deep orange color by heat.

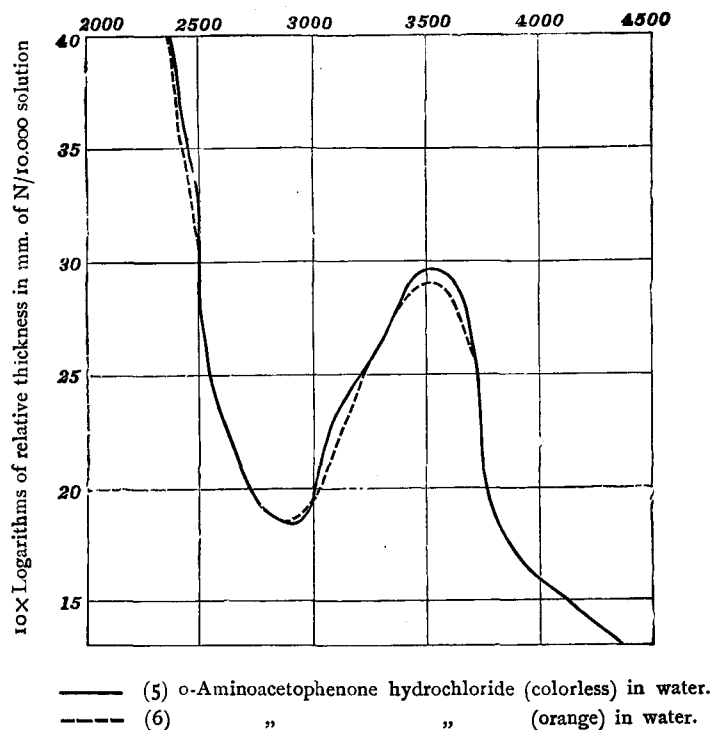
- I. 0.1037 gm. original hydrochloride gave 0.0802 gm. AgCl.
 II. 0.1080 „ heated „ „ 0.0816 „ „

Calc. for $\text{HCl}(\text{CH}_3)\text{NH}.\text{C}_6\text{H}_4.\text{CO}.\text{CH}_3$		Found
Cl	19.11	I. 19.13 II. 18.79

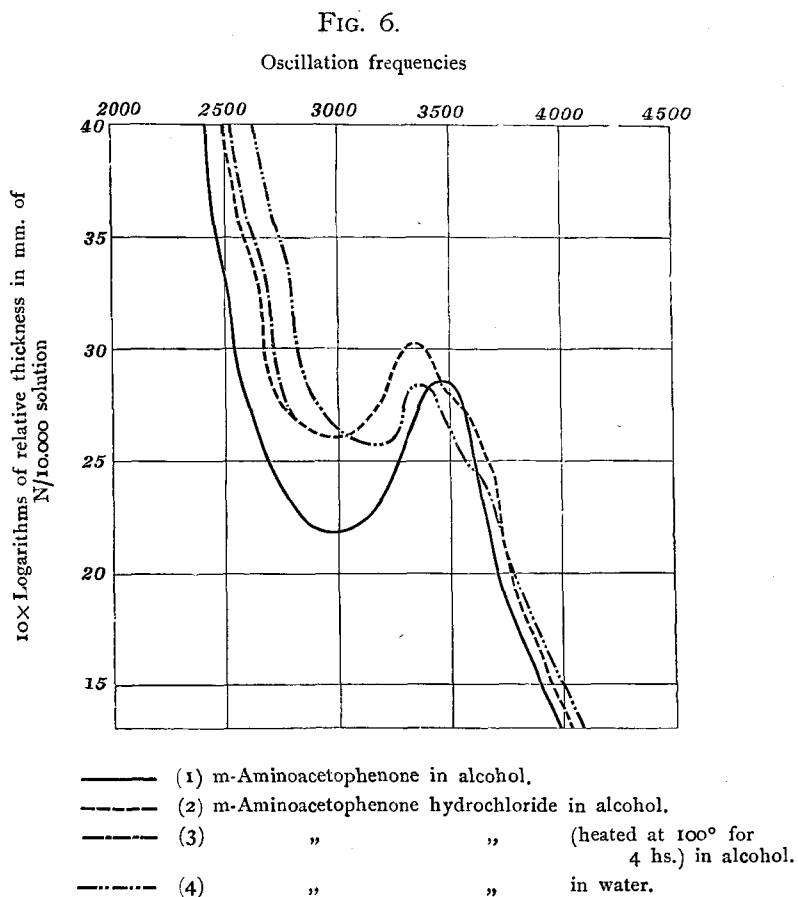
m-Dimethylaminoacetophenone was easily prepared according to Rupe, etc.¹ from m-aminoacetophenone, methyl iodide and soda in an aqueous solution. When the reaction mass was cooled, there separated out copious light brown leafy crystals, which after treatment with

FIG. 5.

Oscillation frequencies



¹ Rupe, Braun and Zemruski: loc. cit.



animal charcoal and recrystallisation from hot water, gave colorless shiny platy crystals of trimethyl-m-acetophenyl ammonium iodide $(m)N(CH_3)_3I.C_6H_4.CO.CH_3$, which melts at 195° with decomposition into m-dimethylaminoacetophenone, giving off methyl iodide. m-Dimethylaminoacetophenone hydrochloride does not undergo a change in color by heat.

0.1350 grm. substance gave 0.0961 grm. AgCl.

Calc. for $HCl.(CH_3)_2N.C_6H_4.CO.CH_3$	Found
Cl	17.76
	17.62