

TABLE IV

Ethane	T°	% ethane	$\frac{-x_s}{\times 10^4}$	α
Di- <i>p</i> -tolyltetraphenylethane	28	4.74	0.695	0.053 \pm 0.02
Di- <i>o</i> -tolyltetraphenylethane	30	5.85	.632	.287 \pm .02
Di- <i>p</i> -isopropylphenyltetraphenylethane	28	6.77	.680	.083 \pm .02
Di- <i>p</i> - <i>t</i> -butylphenyltetraphenylethane	29	6.09	.688	.078 \pm .02
Hexa- <i>m</i> -tolylethane	28	6.47	.594	.400 \pm .02
Hexa- <i>p</i> -ethylphenylethane	29	6.06	.670	.167 \pm .03
Hexa- <i>p</i> - <i>n</i> -propylphenylethane	29	6.81	.662	.209 \pm .03
Hexa- <i>p</i> -isopropylphenylethane	28	6.85	.660	.260 \pm .03
Hexa- <i>p</i> -isobutylphenylethane	29	7.65	.650	.269 \pm .03
Hexa- <i>p</i> - <i>s</i> -butylphenylethane	29	7.66	.635	.330 \pm .03

it is possible to calculate the equilibrium constant for the dissociation of any ethane from the equation

$$K = \frac{\alpha^2 w_0}{1 - \alpha}$$

where w_0 = initial concentration of the ethane.

Then from the equation

$$x_p = \frac{1233}{w_1} \sqrt{K^2 + 4Kw_1} - K$$

where w_1 = the concentration of the ethane, it is possible to calculate the paramagnetic susceptibility due to the free radical for any value of w_1 , and from the equation

$$x_s = \frac{X_d}{M} w_3 + 0.708 w_2 - \frac{\rho}{M} w_1$$

where w_2 = the weight fraction of the solvent, the corresponding measured susceptibility of the solution. Using the values of x_s obtained in this way,

the amount of undecomposed ethane present at any given time may be obtained from Fig. 2. When the logarithms of the concentrations so obtained are plotted against time (see Fig. 1) a series of straight lines are obtained indicating that the decomposition is apparently a first order reaction.

Summary

1. Hexa-*p*-alkylphenylethanes in which the alkyl group has a hydrogen atom on the carbon atom attached to the ring have been found to dissociate to free radicals which undergo disproportionation.

2. The degree of dissociation of ethanes in this series has been found to be much higher (17–33%) than was previously thought (2–6%).

3. Ortho- and meta-methyl substituents in hexaphenylethanes have a greater effect on the degree of dissociation than do para-methyl substituents and the ortho- and meta- derivatives give relatively stable radicals.

4. A few di-*p*-alkylphenyltetraphenylethanes have been described. They are more highly dissociated than hexaphenylethane and disproportionate less rapidly than the corresponding hexa-alkyl derivatives. In this series the *t*-butyl derivative did not undergo disproportionation.

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RECEIVED AUGUST 14, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Alleged *cis-trans* Isomerism of alpha- and beta-*p*-Azophenol

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The existence of isomeric forms of *p*-azophenol was reported in 1906 by Willstätter and Benz.² One form, designated α , was obtained by coupling *p*-hydroxybenzenediazonium chloride with phenol or preferably by the fusion of *p*-nitrophenol with potassium hydroxide, while the second form, designated β , resulted from the reduction of benzoquinoneazine with phenylhydrazine.³ An analysis of the evidence at their disposal led these investigators to the view that *cis-trans* isomerism was the most likely basis upon which to account

for the existence of isomers in this case. This interpretation also was favored by Hantzsch,⁴ who studied the absorption spectra of α - and β -azophenol and their sodium salts. Several years later, Robertson⁵ also concluded that this was a case of *cis-trans* isomerism on the basis of a difference in behavior of the two forms, which he observed on bromination and nitration. Thus, he reported that nitration of α -azophenol gave a tetranitro derivative (m. p. 230°), whereas dinitroazophenol (m. p. 240°) was obtained from β -azophenol, and that bromination produced different tetrabromo derivatives (m. p. 250–252°, m. p.

(1) Abstract of Ph.D. Thesis, 1939.

(2) Willstätter and Benz, *Ber.*, **39**, 3492 (1906).

(3) Two additional forms were described in a later publication [Willstätter and Benz, *ibid.*, **40**, 1578 (1907)], which lists the properties of all of the alleged isomers.

(4) Hantzsch, *ibid.*, **43**, 2512 (1910); see also Tuck, *J. Chem. Soc.*, **95**, 1816 (1909).

(5) Robertson, *ibid.*, **103**, 1472 (1913).

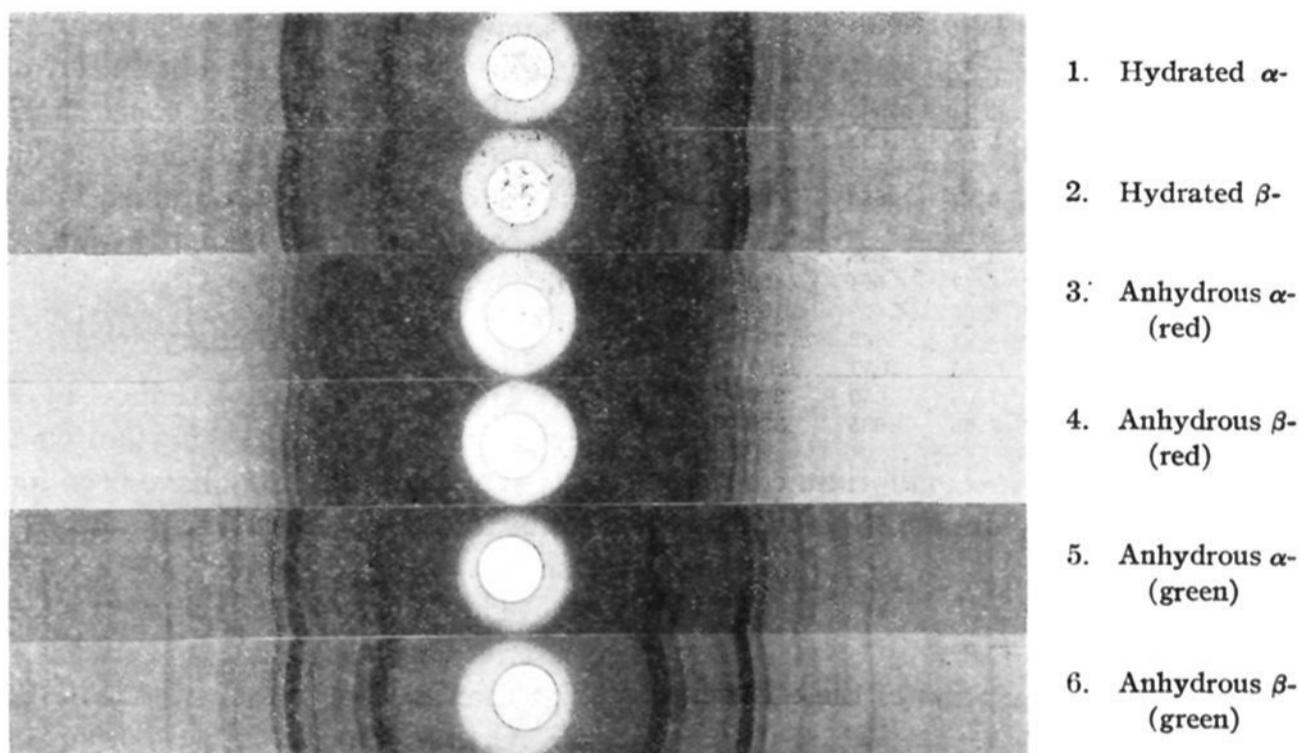


Fig. 1.—Powder photographs of *p*-azophenol.

271°) in the two cases.⁶ This difference in behavior was attributed to steric hindrance in the case of the β -azophenol, to which Robertson assigned the *cis* configuration.

An important contribution to this problem was made recently by Dostrovsky and Le Fèvre.⁷ They found that the dipole moments of α - and β -azophenol are identical, and consequently it is very improbable that the α - and β - forms are *cis-trans* isomers. Furthermore, in view of the lability of the *cis* form of azobenzene, it appeared unlikely that the *cis* form of azophenol would maintain its configuration when subjected to bromination and nitration. These considerations, together with evidence, which was accumulated in the present work, lead to the conclusion that the alleged isomers, α - and β -azophenol, are in reality identical. Hydrated *p*-azophenol upon dehydration gives the anhydrous compound, which exists in two solid modifications, brick-red and green. The transformation of the brick-red metastable form to the green form is subject to various influences (*e. g.*, impurities) which were not investigated. That the so-called α -azophenol is identical with the azophenol designated as the β -form and produced by the reduction of quinoneazine becomes evident from the following studies.

(6) The use of an excess of bromine and rapid addition of this reagent gave the higher melting tetrabromo derivative with both forms of the azophenol. However, Hunter and Barnes [*J. Chem. Soc.*, 2051 (1928)] also reported a tetrabromo derivative, melting at 252° with decomposition.

(7) Dostrovsky and Le Fèvre, *J. Chem. Soc.*, 533 (1939).

X-Ray Diffraction Studies.—Powder photographs of eight different samples of *p*-azophenol were taken using a camera of approximately 57.4 mm. radius and FeK radiation. The history of each of the eight samples follows: (1) hydrated α -azophenol, purified chromatographically and precipitated from a potassium hydroxide solution by means of carbon dioxide; (2) hydrated β -azophenol, purified by recrystallization from alcohol and precipitation from a potassium hydroxide solution by means of carbon dioxide; (3) anhydrous brick-red modification produced by sublimation of α -azophenol; (4) anhydrous brick-red modification prepared by heating hydrated β -azophenol; (5) anhydrous green α -azophenol obtained by heating hydrated α -azophenol; (6) anhydrous green β -azophenol produced by heating relatively large crystals of the hydrated β -form; (7) hydrated α -azophenol obtained from sample 5 by rehydration; and (8) hydrated β -azophenol obtained from sample 4 by rehydration. All samples were ground in an agate mortar to 200-mesh size before mounting on or in a thin-walled glass capillary tube. The exposures in all cases except 3 and 4 were approximately four hours at 12.5 m. a. and 34 k. v. Samples 3 and 4 were sealed inside a thin-walled glass tube and required exposures of approximately twenty-four hours.

Six of the photographs are reproduced in Fig. 1. They show unequivocally that the hydrated α - and β - varieties, 1 and 2, are in reality the same substance, that the two anhydrous brick-red modi-

fications, 3 and 4, are identical but different from the hydrated or anhydrous green forms, and that the two anhydrous green varieties, 5 and 6, likewise are the same but are different in crystal structure from the anhydrous brick-red forms. Samples 7 and 8 gave patterns identical with those of 1 and 2. The X-ray photographs for each of the pairs correspond not only in the positions but also in the intensities of the lines.

Ebullioscopic Studies.—Since α - and β -azophenol decompose on melting, mixed melting point determinations are of little value as a test for identity in this case. However, a method, developed by Halford,⁸ of determining the identity of solids, by measuring the rise in boiling point on the addition of one substance to a saturated solution of the other, proved to be of considerable value. An application of this method showed that the α - and β -forms of *p*-azophenol, as usually prepared and purified, were not pure substances. The pure α -variety could be obtained by chromatographing an ethyl acetate solution, using calcium carbonate as the adsorbent. When this carefully purified α -form was added to a saturated solution of the so-called β -form in ethyl ether only a negligible rise in the boiling point was obtained. The addition of the β -form as ordinarily prepared to a solution saturated with the pure α -form was accompanied by a small rise which was of the same order of magnitude as that obtained by the addition of the β -form to a solution saturated with β -azophenol.

Polarographic Studies.—*p*-Azophenol can be oxidized to quinoneazine, and if α - and β -azophenol are in reality *cis* and *trans* forms, oxidation should take place at different potentials in the two cases. Therefore, dropping mercury electrode studies were carried out. Oxidation was first attempted in a buffer of *pH* 5.75 but it was found that the oxidation potential of *p*-azophenol at this *pH* was above that for mercury. However, both forms could be reduced at this *pH*. Identical cathodic waves were obtained for the α - and β -forms.⁹

It was possible to oxidize *p*-azophenol in a buffer of *pH* 9.2. The anodic waves were identical for the two forms.

Chemical Studies.—The chemical evidence which was cited in favor of isomerism of *p*-azophenol was reexamined. Several derivatives of

α - and β -azophenol were prepared by Willstätter and Benz,¹⁰ but only in the case of the diacetates did they find indication of any difference. Thus, it was reported that the α -azophenol diacetate melted at 198–199°, and that the melting point of β -azophenol diacetate was 192°, but that, upon repeated crystallization, the lower melting diacetate was transformed into the higher melting one. Repetition of these acetylations led only to the higher melting diacetate. Furthermore, the diacetate obtained from the β -azophenol did not depress the melting point of the diacetate derived from the so-called α -form.

The work of Robertson concerning nitration and bromination of α - and β -azophenol also was repeated. Instead of isolating the tetranitro-*p*-azophenol in the case of the α -azophenol, which according to previous work melts at 230° and is the expected product, a dinitro compound (m. p. 235–236°) was obtained from both the α -

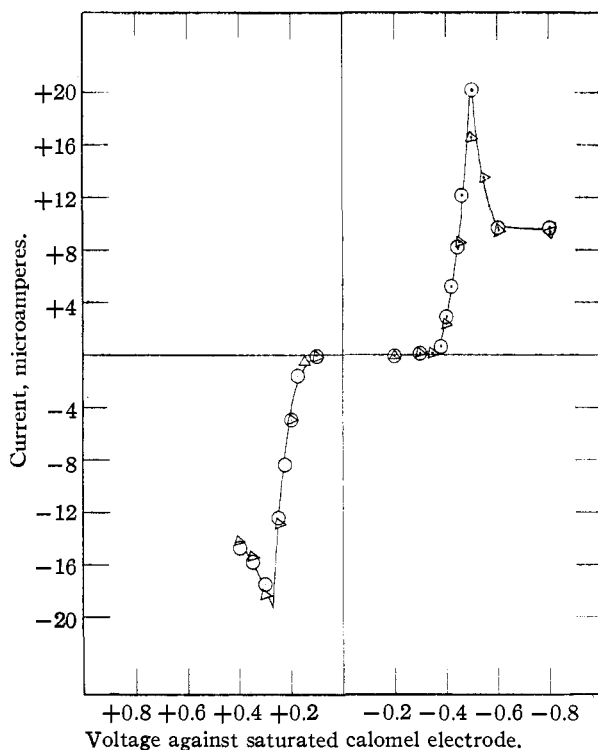


Fig. 2.—Polarographic analysis of α - and β -*p*-azophenol: ○, α , *pH* 5.75; △, β , *pH* 5.75; ○, α , *pH* 9.20; △, β , *pH* 9.20.

and β -forms. In order to produce the tetranitro compound it was necessary to use more drastic conditions and the product obtained in this way melted with decomposition at 261–262°. The α -

(8) Halford, *THIS JOURNAL*, **53**, 2640 (1931).

(9) The presence of maxima precluded an analysis of the reduction process.

(10) Willstätter and Benz, *Ber.*, **40**, 1578 (1907).

and β -azophenols upon bromination also gave only one tetrabromoazophenol, melting at 273–274° with decomposition, in spite of many attempts to obtain the lower melting isomer previously reported.

Experimental

α - and β -azophenol were prepared according to the directions of Willstätter and Benz.

Chromatographic Studies.—Anhydrous (green) α -azophenol (1 g.) was dissolved in ethyl acetate (100 ml.) and the solution passed through a column of precipitated calcium carbonate, 12 cm. long and 1.5 cm. in diameter. The α -azophenol was weakly adsorbed, but could be completely washed through with additional ethyl acetate. As the solution passed through the column a pink zone developed at the top which was not washed down by ethyl acetate. Elution of this zone with methanol gave a small amount of an oily red substance which was not investigated. The ethyl acetate solution of α -azophenol which had passed through the column yielded 0.93 g. of *p*-azophenol, which was crystallized from an aqueous ethanol solution in orange-yellow plates.

One gram of the anhydrous (brick-red) β -azophenol was chromatographed in the same manner. No pink zone was obtained. Crystallization produced β -azophenol in orange-red plates with a blue reflex.

Several mixtures of α - and β -azophenol were chromatographed using different solvents and adsorbents, but no separation was obtained. Likewise attempts to obtain *cis* and *trans* forms by irradiation according to the method which was successfully employed by Cook¹¹ were fruitless. However, irradiation of *p*-azoanisole in petroleum ether brought about deepening in the color of the solution. When this solution was passed through a column of aluminum oxide, an orange zone of rather strongly adsorbed material appeared at the top of the column. Below this the normal yellow zone of azoanisole was obtained. The orange zone gave a red solid upon elution with ether. Heated to temperatures above 50° it rapidly changed to yellow, the color of ordinary *p*-azoanisole, and melted at 162–164°, the m. p. of ordinary azoanisole. Cook reported a similar behavior in the case of *p*-benzeneazophenole.

Miscellaneous Observations.—It was noted that the method of separation of β -azophenol from solution had much to do with its appearance. Slow crystallization from an ethanol–water (1:1) solution yielded relatively large crystals which turned green rather than brick-red on heating to 120°. However, if this same material was dissolved in alcohol and rapidly precipitated by the addition of water, the small crystals so produced turned brick-red on heating to 120°, but continued heating transformed this brick-red material to a green product. The time required to bring about the change from brick-red to green varied considerably with different samples.

When pure α -azophenol was precipitated in small crystals from an ethanol–water solution and then heated to 100°, it turned red, but the red material changed to a green within a few minutes. At higher temperatures the change

was so rapid that in many cases the hydrated form appeared to go directly to the anhydrous green form.

Sublimation at a pressure of 10^{-2} mm. produced the anhydrous red variety in the case of both α - and β -azophenol. The conversion of this anhydrous red to the anhydrous green modification required only a few seconds at 120°.

Ebullioscopic Studies.—Absolute ether (20 ml.) was used as the solvent in each of the following determinations: (1) boiling point elevation on saturation of ether with pure anhydrous α -azophenol, 0.384°; (2) amounts of pure α -azophenol required for saturation, 0.55 g.; (3) boiling point elevation on the addition of 0.2 g. of anhydrous α -azophenol, prepared and purified in accordance with earlier methods, to solution saturated with α -azophenol, 0.03°; (4) average boiling point elevation on the addition of 0.2 g. of anhydrous β -azophenol to solution saturated with β -azophenol, 0.038°; (5) boiling point elevation on the addition of 0.2 g. of α -azophenol, purified by chromatographing, to solution saturated with α -azophenol, 0.00°; (6) boiling point elevation on the addition of 0.7 g. of pure anhydrous α -azophenol to a solution saturated with β -azophenol, 0.01°; (7) boiling point elevation on addition of 0.42 g. of anhydrous β -azophenol to a solution saturated with anhydrous α -azophenol, 0.09°.

Polarographic Studies.¹²—The set-up used was essentially the same as that described by Kolthoff and Lingane.¹³ Measurements were made with reference to a saturated calomel electrode. The α - and β -azophenols were dissolved in the following buffer solutions: (1) a buffer of *pH* 5.75 prepared by combining 200 ml. of 0.999 *N* acetic acid, 100 ml. of 0.982 *N* sodium hydroxide and 300 ml. of absolute alcohol; (2) a buffer of *pH* 9.2 prepared by combining 80.9 ml. of 0.0982 *N* sodium hydroxide, 6.184 g. of boric acid, 209 ml. of conductivity water and 300 ml. of absolute alcohol. To this solution was added 2.5 g. of potassium nitrate to serve as an electrolyte. The molar concentrations of the azophenols were as follows:

	<i>pH</i> 5.75	<i>pH</i> 9.2
α -Azophenol	1.016×10^{-3}	1.004×10^{-3}
β -Azophenol	1.005×10^{-3}	1.017×10^{-3}

The results are shown in Fig. 2.

Nitration of α - and β -Azophenol.—Following the procedure of Robertson, anhydrous α -azophenol (1.5 g.) was dissolved in glacial acetic acid (75 ml.) by warming. The solution was then cooled until the acetic acid began to crystallize, at which time concd. nitric acid (7 ml.) was added with stirring over a period of fifteen minutes. The reaction mixture was then placed in an ice box overnight. Yellow needle-like crystals (m. p. 230–232°; 0.48 g.) separated. This crude product was extracted twice with hot ethanol and the residue crystallized twice from glacial acetic acid. The dinitro-*p*-azophenol obtained in this manner melted at 235–236°, and yielded a dinitro-dibromo-*p*-azophenol (m. p. 281–282°) on bromination.

β -Azophenol (1.5 g.), nitrated in the same manner, yielded 0.46 g. of slightly impure dinitro-*p*-azophenol, which upon purification also melted at 235–236°. A mixed melting point of the two nitration products showed no depression.

(12) The authors are indebted to Mr. Carl Miller for valuable assistance during these studies.

(13) Kolthoff and Lingane, *Chem. Rev.*, **34**, 12 (1939).

(11) Cook, *J. Chem. Soc.*, **378** (1938).

Tetranitro-*p*-azophenol (m. p. 261–262°, with dec.) was obtained by slowly adding dinitro-*p*-azophenol (1 g.) to fuming nitric acid (5 ml.), cooled in an ice-salt bath. After stirring for five minutes, the reaction mixture was poured on ice. The crude product (1 g.) was purified by crystallization from glacial acetic acid.

Anal. Calcd. for $C_{12}H_6O_{10}N_6$: C, 36.55; H, 1.52; N, 21.32. Found: C, 36.93; H, 1.73; N, 21.45.

Tetrabromoazophenol (m. p. 273–274°) was obtained in equal yield from both α - and β -azophenol. To a solution of the monohydrate of *p*-azophenol (2 g.) and sodium acetate (3 g.) in glacial acetic acid (130 ml.) was added a solution of bromine (3 g.) in glacial acetic acid (50 ml.). Mechanical stirring was employed during the period (twenty-five minutes) that bromine was added and for thirty minutes thereafter. A dark green precipitate (1.3 g.) was filtered off. After four crystallizations from glacial acetic acid, the tetrabromo derivative melted at 273–274°.

Anal. Calcd. for $C_{12}H_6O_2N_2Br_4$: C, 27.20; H, 1.14. Found: C, 27.04; H, 0.87.

The diacetate (m. p. 263–264°) was prepared in the usual way.

Anal. Calcd. for $C_{16}H_{10}O_4N_2Br_4$: C, 31.27; H, 1.63. Found: C, 31.32; H, 1.73.

The dibenzoate (m. p. 297–298°) was obtained by benzoylation in pyridine with benzoyl chloride.

Anal. Calcd. for $C_{28}H_{14}O_4N_2Br_4$: C, 42.28; H, 1.90. Found: C, 42.12; H, 2.37.

Summary

The recorded evidence for *cis-trans* isomerism in the case of *p*-azophenol has been reexamined and new findings have been introduced with the result that it may now be concluded that the so-called α - and β -forms of *p*-azophenol are not *cis-trans* isomers. The anhydrous *p*-azophenol does exist in two solid modifications, however.

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RECEIVED AUGUST 8, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Effect of Nuclear and Side Chain Substitution on the Oxonium Ion Catalyzed Iodination of Acetophenone Derivatives

BY LOIS ZUCKER¹ AND LOUIS P. HAMMETT

Nathan and Watson,^{2a} and Evans,^{2b} measured the rates of bromination of a number of acetophenone derivatives in acetic acid-water solutions containing hydrochloric acid, and found the effect on the rate of substitution of a methyl group for hydrogen in the side chain much greater than the effect of substitution in the ring. Since the reaction is subject to general acid catalysis,³ the specific bromination rate in a given medium is the sum of a series of specific catalytic bromination rates, one for each catalyst present, and the effect of a given substitution cannot be expected to be the same for different catalysts. This makes the observed rate in this medium an unnecessarily complicated function of the structure of the ketone,⁴ since undissociated acetic acid, hydrogen ion solvated with water (oxonium ion), and hydrogen ion solvated with acetic acid are possible catalysts. A more easily interpretable catalytic system is found in a not too concentrated aqueous solution of a strong monobasic acid, which can

contain only one effective catalyst, oxonium ion. Accordingly, we have measured the rates of iodination (equal to the rates of enolization) of some of these ketones, together with that of 2,4,6-trimethylacetophenone (not on the previous list), in 1.388 molar aqueous perchloric acid solution, using a colorimetric technique.

Experimental

Apparatus.—The iodinating solution was contained in a closed glass cell shown in Fig. 1, closure being made with a very well fitting ground glass joint, of which the colorimeter plunger forms the stopper. Error introduced by this closure, as far as optical alignment and effective depth of layer are concerned, was within the ordinary precision of matching, ± 0.17 mm. under the conditions of a kinetic run. A really well fitting glass joint is also necessary to retain iodine in an aqueous solution containing no iodide over a period of many hours. The double lines indicate brass, the single lines glass. The cell stood directly on a plane glass disk (removable for cleaning) which formed part of the bottom of a flattened cylindrical brass water jacket, of 80 cc. capacity with the cell mounted, which in turn was fastened to the colorimeter platform with a lock nut. Water was circulated from a large thermostat through insulated tubing and the likewise well insulated jacket at the rate of 5 cc. per sec. Temperature in the cell could be maintained at $25.00 \pm 0.01^\circ$, as checked by thermocouple, even when room temperature was as low as 17° .

(1) Part of a thesis submitted by Lois Zucker in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) (a) Nathan and Watson, *J. Chem. Soc.*, 217 (1933); (b) Evans, *ibid.*, 785 (1936); see also (c) Evans, Morgan and Watson, *ibid.*, 1167 (1935).

(3) Zucker and Hammett, *THIS JOURNAL*, 61, 2785 (1939).

(4) Hammett, *Trans. Faraday Soc.*, 34, 156 (1938).