ously excluded, there is oxidation of the sulfur dioxide with increased solution of alumina. The average of three determinations showed a solution containing 14.3% sulfur trioxide to contain 6.7% aluminum oxide.

Ferric sulfites have been described by several investigators. It is generally conceded that they are readily reduced in the presence of an excess of sulfur dioxide. The sulfur trioxide formed increases the solubility.

Ferrous hydroxide was prepared by precipitation from a hot solution of ferrous sulfate with ammonia, filtering and washing in an atmosphere of nitrogen in the device proposed by Bost.[3] Vapor pressure measurements of the suspensions in aqueous sulfur dioxide were made in the same manner as for aluminum hydroxide described above with quite similar results. One sulfite exists and addition of further quantities of sulfur dioxide produces increased pressure directly proportional to the excess sulfur dioxide.

Several samples of the solid phase were prepared. Stable in dry air, they were readily oxidized and decomposed in moist air. Analyses of the separately prepared products all gave results agreeing well with the formula of a normal salt, $FeO \cdot SO_2 \cdot 6H_2O$. Previous investigations have reported the normal sulfite as containing but 3 molecules of water of crystallization, and this is the figure reported by Henderson and Weiser[4] who prepared it in a quite different way.

It was not practicable to prepare aqueous solutions of ferrous sulfite which were entirely free of sulfates. Apparently ferrous hydroxide is somewhat more soluble in aqueous sulfur dioxide than is aluminum hydroxide.

[3] A. S. Wheeler and R. W. Bost, This Journal, **50**, 2000 (1928).

[4] W. E. Henderson and H. B. Weiser, *ibid.*, **35**, 289 (1913).

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## The Radical of Tri-*p*-tolylamine

By S. Granick and L. Michaelis

Tri-*p*-tolylamine on oxidation yields an intensely blue colored compound, according to Wieland,[1] which has been interpreted by Weitz and Schwechten[2] as a free radical. Direct evidence for this interpretation has never been given. Direct determination of molecular weight, which in comparable cases was sometimes used and often with misleading results,[3] could not even be attempted in this case because of insufficient stability of the substance. However, the method of potentiometric titration can be used for the purpose. It unequivocally confirms the structure of a singly charged cationic free radical.

The potentiometric titration was carried out in a nitrogen atmosphere at 30°, using a potassium chloride–agar bridge. The solvent used consisted of 80 parts glacial acetic acid plus 20 parts, by volume, of water. Fifty cc. of a $1.5 \times 10^{-4}$ *M* solution of tri-*p*-tolylamine in this solvent was titrated with a $3 \times 10^{-3}$ *M* solution of lead tetraacetate in the same solvent. A blue color appeared and progressively increased in intensity with the addition of more oxidant. The potentials during the titration were rapidly established and were, although not perfectly stable, yet sufficiently so to yield an interpretable titration curve. As regards the stability of the potentials, the following experiment is characteristic: When the amine is mixed with about one-half equivalent of the oxidizing agent, the potential is rapidly established and drifts about 3 millivolts within ten minutes toward the negative side. Since for a regular titration experiment only a few minutes are requisite to obtain the whole curve, this drift is practically negligible. The whole titration experiment is shown in Fig. 1. As can be seen,

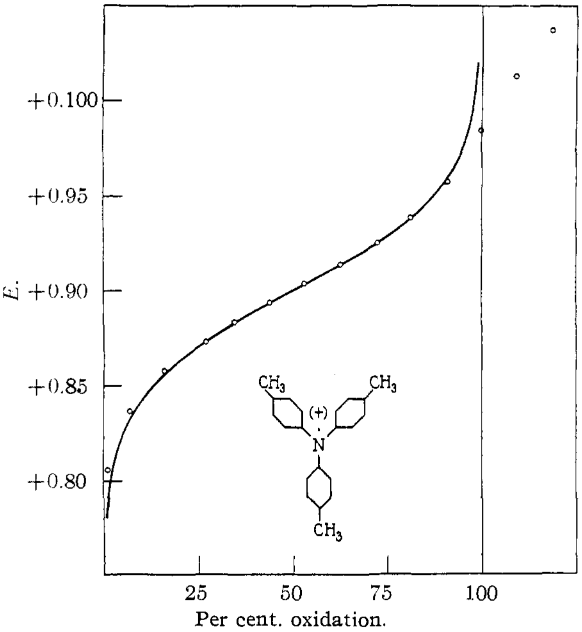

Fig. 1.

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[1] Wieland, *Ber.*, **40**, 4260 (1907).

[2] Weitz and Schwechten, *ibid.*, **59**, 2307 (1926).

[3] L. Michaelis, *Chem. Rev.*, **16**, 243 (1935).

there is a fairly sharp end-point of titration just when one equivalent of oxidizing agent is used up. The drawn-out curve is the one calculated for a univalent oxidation curve (index potential, 28.6 mv.), the circles are experimental points. The potentials corresponding to more than 100% oxidation drift much more than those within the titration curve proper. The normal potential under the conditions prevailing in this experiment was +0.900 volt.

The absorption spectrum of the radical (Fig. 2) was determined with a König–Martens spectrophotometer for a solution of the amine in 80% acetic acid containing $1.5 \times 10^{-4}$ mole per liter and oxidized with 25% of the equivalent amount of lead tetraacetate. The color is not perfectly stable in time, but the fading is negligible within the period necessary for the readings.

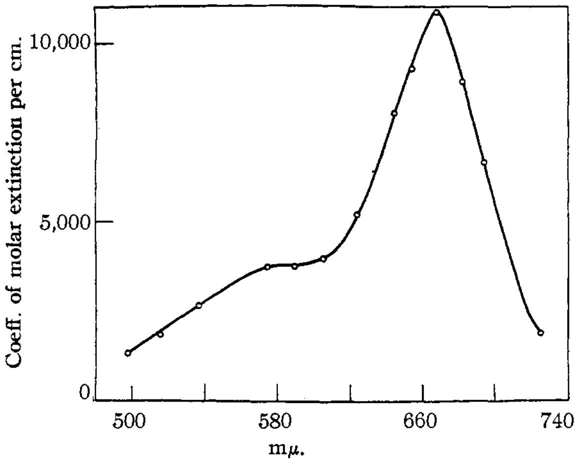

Fig. 2.

Tri-*p*-tolylamine was prepared according to Wieland[1] as a crystalline white powder, m. p. 117°. Lead tetraacetate was prepared according to J. C. Bailar.[4]

(4) "Inorganic Syntheses," Vol. I, 1939.

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## Note on the Grignard Reagent

BY MARTIN KILPATRICK AND EUGENE A. BARR, JR.

In connection with kinetic studies of the reaction of magnesium with alkyl and aryl halides it was noted that the reaction of magnesium[1,2] with bromobenzene gave a black precipitate. This precipitate has been noted in other reactions with magnesium but has not been identified. We assumed the precipitate to be colloidal magnesium, and we have confirmed this assumption by analysis. The black precipitate was washed with ether, weighed, dissolved in hydrochloric acid, precipitated as magnesium ammonium phosphate, and weighed as magnesium pyrophosphate.

| Black ppt., mg. | Magnesium found, mg. |
|---|---|
| 4.45 | 4.35 |
| 7.35 | 7.07 |

The black precipitate has been obtained with magnesium from various sources including the analyzed samples used by Kilpatrick and Rushton.[3]

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(1) Kilpatrick and Simons, *J. Org. Chem.*, **2**, 459 (1937).

(2) Gzemski and Kilpatrick, *ibid.*, **5**, 264 (1940).

(3) Kilpatrick and Rushton, *J. Phys. Chem.*, **38**, 269 (1934).

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## The Presence of Indole in "Practical" α-Methylnaphthalene

BY M. S. KHARASCH, STEPHEN S. KANE AND HERBERT C. BROWN

The presence of indole in the coal tar fraction of b. p. 220–260° has been demonstrated by Weissgerber.[1] However, to our knowledge no mention is made anywhere that "Practical" α-methylnaphthalene contains about 1–2% of indole. This product was found by us in a study of the action of oxalyl chloride on commercial α-methylnaphthalene.

### Experimental

The practical α-methylnaphthalene obtained from Eastman Kodak Co. is vacuum distilled. The original liquid is dark red with a beautiful blue fluorescence, while the distillate (b. p. 118° (17 mm.)) is light straw yellow but still shows the blue fluorescence. The red color returns on exposure to air. On addition of 2–3 cc. of oxalyl chloride to about 15 cc. of the distilled methylnaphthalene, 0.25 g. of gold yellow precipitate separates and is collected on a filter. The filtrate is distilled and a non-fluorescent, practically colorless methylnaphthalene (b. p. 118° (17 mm.)) is obtained. Exposure to light and air has no effect on the color of pure α-methylnaphthalene, but addition of a trace of indole produced a red color after a short exposure to air.

The yellow precipitate was shown to be the acid chloride of 3-indole glyoxalic acid by comparing its properties and those of its derivatives with the compounds obtained by treatment of pure indole dissolved in pure α-methylnaphthalene or benzene with oxalyl chloride. The same

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(1) Weissgerber, *Ber.*, **43**, 3520 (1910).