[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Electrochemical Preparation of the Tolylhydrazines

BY E. W. COOK AND W. G. FRANCE

The present investigation is concerned with the effect of the position of the methyl group in ortho-, meta- and para-tolyldiazonium chlorides on their electrolytic reduction and with the optimum conditions for the electrochemical preparation of the three tolylhydrazines.

The diazonium salts were carefully prepared and reduced in a cell similar to that previously described by the authors.(1) The anolyte was a 0.4 *N* hydrochloric acid solution and the catholyte an aqueous hydrochloric acid solution of the diazonium salt. A temperature of 5–6° was maintained throughout the electrolysis. Applied voltages of 5–8 volts with corresponding currents of 2–7 amperes were employed.

Of the cathodes used, mercury alone gave satisfactory yields of the hydrazines. The maximum current yields were 74.9, 58.5 and 35.6%, respectively, for ortho, para and meta chloride, respectively. In all cases the material yields were approximately 90% of the current yields. In the accompanying figure which expresses these results graphically the current yields are plotted as functions of the current density. The peaks of these curves represent the optimum conditions for the reductions and as would be expected occur at lower values for the more readily reduced compound. It is therefore clearly evident that the position of the methyl group exerts a marked influence on the ease of reduction.

The results for the *m*-tolyl reduction were almost the same as those obtained by Lowy and McClure(2) for phenyldiazonium chloride. Apparently therefore the methyl group in the meta position has but little influence on the ease of reduction of the diazonium group.

Using cathodes of cadmium, tin and lead at current densities of 4.5 amp. per sq. decimeter, there were obtained, respectively, with the para isomer, 4.7, 3.8, 0; with the meta isomer, 6.8, 6.0, 4.0; and with the ortho isomer, 7.8, 0.4, 4.4% current yields. The last value (4.4%), however, was obtained with a sulfuric acid catholyte. Using a platinum cathode and adding 1 cc. of an 80% solution of titanium trichloride to the catholyte, at a current density of 9.2 amp. per sq. decimeter, no hydrazine was produced.

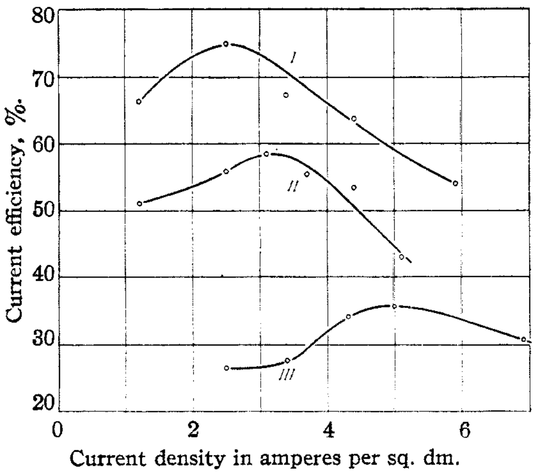

Fig. 1.—Reduction of: I, *o*-tolyldiazonium chloride; II, *p*-tolyldiazonium chloride; III, *m*-tolyldiazonium chloride, on mercury cathodes.

It is clear from the low yields obtained with cadmium, tin and lead cathodes that mercury exerts a pronounced effect on the reduction of the diazonium grouping irrespective of the hydrogen over-voltage. This effect may be due in part to differences in the catalytic activation of the depolarizer. Bancroft and George(3) suggest that in such an activation there is probably a different orientation of the depolarizer at different metals. Assuming this, one would expect the oriented adsorption of the various isomers of a given compound to be different at the same metal depending upon their polar properties. Thus with a given electrode reducible groups in the ortho, meta and para positions in an aromatic compound should exhibit variations in their ease of reducibility. Such differences in the reducibility of isomeric compounds as herein reported are frequently observed. However, if they are primarily the result of differences in the polar properties of the isomers there should be a relation between the electric moments and the order of the ease of reduction. In the present case there seems to be no such regularity. The meta isomer is the least easily reduced, whereas the electric moments of most meta

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(1) Cook and France, *J. Phys. Chem.*, **36**, 2383 (1932).

(2) Lowy and McClure, *Trans. Am. Electrochem. Soc.*, **56**, 445 (1929).

(3) Bancroft and George, *ibid.*, **57**, 399 (1930).

isomers are intermediate to those of the ortho and para compounds. It would seem therefore not at all unlikely that other factors of equal or greater importance are effective in determining the ease of reducibility of the *o*-, *m*- and *p*- isomers at a given electrode.

Summary

Electrolytic reduction experiments have been made on the *o*-, *m*- and *p*-tolyldiazonium chlorides with varying current densities and using cathodes of different metals. The ease of reduction does not seem to be related to the polar properties of the compounds, although a possible correlation may be obscured by other experimental factors.

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[Contribution from the Chemical Laboratory of the University of Texas]

The Adsorption of Methylamine on Silica Gel, Alumina Gel and Charcoal;[1] The Heats of Adsorption of Ammonia and the Methylamines on Silica Gel[2]

By W. A. Felsing and Carl T. Ashby

Object of the Investigation.—The object of this investigation was the determination of the extent of adsorption of monomethylamine on coconut charcoal at 0, 30 and 40°, and the determination of the heats of adsorption of ammonia and mono-, di- and trimethylamines on silica gel at 25 and 40°. This paper is a continuation of a study by Felsing and co-workers[3] of the properties and thermodynamic constants of monomethylamine with a view to the possible use of this substance as the refrigerant in the adsorption type of refrigerating unit. Di- and trimethylamine and ammonia are included in the heat measurements because they are possible refrigerants, and also because it was thought that the heats of adsorption of the members of this series would present an interesting comparison.

Previous Investigations.—Pearce and Knudson[4] have determined the extent of adsorption of monomethylamine on coconut charcoal, and Magnus and Kieffer[5] have determined the heat of adsorption of ammonia on silica gel. The literature records no other work than these on the adsorption of the methylamines.

Experimental

The apparatus and the method used in determining the isotherms were essentially those used by Foote and Dixon[6] in their determination of the extent of adsorption of water and benzene vapors by manganese dioxide. The apparatus and the method used in the heat of adsorption determinations were very similar to those of Pearce and McKinley,[7] the construction of the adsorption vessel being exactly the same. The reservoir system, however, consisted of two large round-bottomed flasks, one being arranged so that it could be filled with mercury when high pressures were desired in the adsorption vessel.

Thermocouple.—All temperature measurements were made with a twenty-four junction copper–constantan thermocouple constructed according to the specifications of Robertson and La Mer.[8] The thermocouple was calibrated differentially as it was used. The standard arm was placed in a Dewar flask containing oil at the temperature of the surrounding box, and the other arm in a Dewar flask containing oil, a Beckmann thermometer graduated in 0.002°, a heating coil and a stirrer. After the apparatus had stood for two hours, the oil in the latter flask was stirred until the temperature remained constant, the Beckmann was read, and the voltage of the thermocouple measured. The temperature of the oil was then raised about a degree and a half and the Beckmann reading and the voltage recorded again. In this manner the values 0.00104075°/v. at 25° and 0.00102015°/v. at 40° were obtained for (dT/dE). The temperature of the oil in the standard flask was checked by letting it stand with the Beckmann thermometer in it. After an interval of an hour and a half the temperature remained constant to within 0.001° for a period of twenty minutes, though usually the change was less than that.

The thermocouple voltage was measured by means of a volt box made of No. 28 copper wire which stepped up the voltage two hundred times, the total voltage of the volt box being measured with a Leeds and Northrup Type K potentiometer.

The method of determining the water equivalent of the calorimeter and the specific heat of the light colorless mineral oil used as the calorimeter fluid was that used by Pearce and McKinley.[7]

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(1) From a thesis presented by Carl T. Ashby to the faculty of The University of Texas in 1931 in partial fulfilment of the requirements for the degree of Master of Arts.

(2) From a thesis presented by Carl T. Ashby to the faculty of The University of Texas in 1934 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(3) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); Felsing and Wohlford, This Journal, **54**, 1442 (1932); Felsing and Jessen, *ibid.*, **55**, 4418 (1933).

(4) Pearce and Knudson, *Proc. Iowa Acad. Sci.*, **34**, 197 (1927).

(5) Magnus and Kieffer, *Z. anorg. allgem. Chem.*, **179**, 215 (1929).

(6) Foote and Dixon, This Journal, **52**, 2170 (1930).

(7) Pearce and McKinley, *J. Phys. Chem.*, **32**, 360 (1927).

(8) Robertson and La Mer, *ibid.*, **35**, 1962 (1931).