

rounded end having an orifice about 1/32 in. diameter. The tube, containing approximately 2-in. length of the sulphate solution, is drawn along the edge of a blotting paper sheet cut to 4½ in. × 12 in., so as to make a band ¼–5/16 in. wide, leaving a ½-in. margin approximately; the second solution is applied in a similar manner, a little higher up, leaving a gap of about ¼ in. between it and the first band. The paper is then air-dried and cut into strips 3/16 in. wide and stored in an air-tight container with a mild drying agent (silica-gel capsule). This is desirable, as in damp weather the method is sensitive enough to react to the trace of moisture picked up from the atmosphere by the test strips.

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Determination of Reaction-rates by Conductivity Measurements

AMONG the reactions which have proved of value in the investigations of the effects of substituents on reaction-rates in solution is the one between organic chlorides and metallic iodides in acetone. This reaction, which was first investigated kinetically by Conant and Kirner¹, is suitably free from complicating side reactions, and the very low solubility of potassium chloride in acetone ensures that it goes almost to completion. It has, therefore, been extensively used in kinetic studies by Conant, Bennett and others.

Hitherto, the progress of the reaction has been followed by estimating the unreacted inorganic iodide by titration methods. Foremost among such methods is the one developed by Bennett and Berry², and based on the observation of Lang³, that the addition of an oxidizing agent, such as potassium iodate, to an acid solution of a metallic iodide in the presence of hydrogen cyanide, converts the liberated iodine into iodine cyanide, a form which does not colour starch. Unfortunately, the presence of acetone in the titration mixture makes it difficult to determine the end-point, and it is necessary to remove it before the iodide can be determined accurately. The procedure is therefore a little laborious, and when a large number of halides are examined it becomes tedious.

In these circumstances it is natural to look for a simpler method of following the course of the reaction, particularly since an extensive study is being made of the influence of two or more substituents on the reactivity of benzyl halides and related compounds. The fact that potassium chloride is precipitated, and that ions are therefore removed from solution, suggests that the reaction may be followed satisfactorily by measuring the electrical conductivity of the reaction mixture. This proves to be the case. Although the procedure used so far is capable of refinement, the publication of a similar conclusion by Evans and Hamann⁴ prompts us to report some of the results obtained. In the accompanying table the values found in an earlier investigation by a

RATE CONSTANTS FOR THE REACTION BETWEEN SUBSTITUTED BENZYL CHLORIDES AND POTASSIUM IODIDE IN ACETONE

Substituent	Volumetric (ref. 5) k_{30°	Conductometric
<i>p</i> -Cl	2.80	2.89
<i>o</i> -NO ₂	11.4*	12.1

* The reaction in this case is rapid, and therefore is determined less readily.

volumetric method are compared with the first values obtained by the conductivity method.

In these measurements the molecular ratio of organic chloride to potassium iodide is 5 : 1, but it is advisable to reduce this ratio and so minimize any risk that the organic halide might affect the determinations.

Refinements in technique are being made which should enable the rates to be determined accurately and expeditiously. With the benzyl chlorides a greater accuracy in measurement is particularly important, since variations in entropy and in activation energy may be rather small, and their significance might easily be masked by experimental errors.

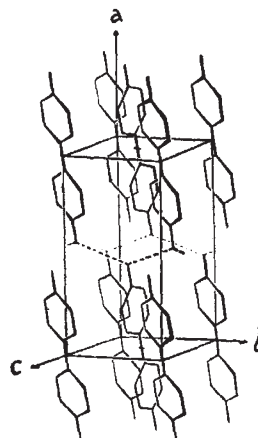
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- ¹ Conant and Kirner, *J. Amer. Chem. Soc.*, **46**, 232 (1924).
² Bennett and Berry, *J. Chem. Soc.*, 1676 (1927).
³ Lang, *Z. anorg. Chem.*, **122**, 332 (1922).
⁴ Evans and Hamann, *Trans. Farad. Soc.*, **47**, 30 (1951).
⁵ Bennett and Brynmor Jones, *J. Chem. Soc.*, 1815 (1935).

Crystal Structure of 44'-Dihydroxydiphenyl

CRYSTALS of 44'-dihydroxydiphenyl can be obtained as thin plates from alcohol-water solution or by sublimation. By optical and X-ray examination, they are found to be monoclinic with the *b*- and *c*-axes in the plane of the plate. The unit cell constants are: $a = 10.54 \pm 0.05$ Å., $b = 5.36 \pm 0.02$ Å., $c = 7.95 \pm 0.05$ Å., $\beta = 95^\circ 30' \pm 1^\circ$. The space group is $P2_1/c$, and since there are only two molecules in the unit cell (calculated from a density of 1.380 gm./c.c.) they must lie in special positions such that molecular centres of symmetry coincide with the centres of symmetry in the cell. Although there are other ways in which this condition might be satisfied, such as by free rotation about the central C—C bond, or rotation of the molecule as a whole in the crystal,



Structure of 44'-dihydroxydiphenyl