

THE INFLUENCE OF PRESSURE ON THE KINETICS AND ORIENTATION OF FRIEDEL-CRAFTS BENZOYLATIONS

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Summary

It has been found that the second-order rate constant for the benzylation of benzene, catalysed by aluminium chloride in benzoyl chloride solution at 29.6°, is doubled when the pressure is raised from 1 atm to 1500 atm.

The same change of pressure has no measurable effect on the orientation of benzoyl substitution in toluene.

INTRODUCTION

This paper is one of a series concerned with the effects of hydrostatic pressure on electrophilic aromatic substitutions.

The previous two papers^{1,2} have dealt with kinetic and orientational effects, respectively, in nitration reactions. In the present work we have made similar measurements on a representative type of Friedel-Crafts reaction. We selected the benzylation of an aromatic compound, catalysed by aluminium chloride in benzoyl chloride solution, because this reaction is amongst the few that are homogeneous and obey simple kinetic laws.^{3,4}

EXPERIMENTAL

(a) Materials

Brown and Jensen³ have found that it is essential to use extremely pure and dry chemicals to secure reliable kinetic data on Friedel-Crafts acylations. We therefore followed their procedures for purifying benzoyl chloride and aluminium chloride, and obtained products whose mixtures remained clear and colourless for many days.

The benzene and toluene were the best available commercial products, further purified by careful drying and fractionation.

The *ortho*-, *meta*-, and *para*-methylbenzophenones, used to standardize the isomer analyses, were synthesized from the corresponding toluic acids by converting these to the acid chlorides and condensing the chlorides with benzene by Friedel-Crafts reactions.

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¹ Coillet, D. W., and Hamann, S. D., *Trans. Faraday Soc.*, 1961, **57**, 2231.

² Coillet, D. W., and Hamann, S. D., *Nature*, 1963, **200**, 166.

³ Brown, H. C., and Jensen, F. R., *J. Am. Chem. Soc.*, 1958, **80**, 2291.

⁴ Jensen, F. R., and Goldman, G., in "Friedel-Crafts and Related Reactions." (Ed. G. A. Olah.) Vol. III, Part 2, p. 1003. (Interscience: New York 1964.)

(b) *Kinetic Procedure**Reactions at Atmospheric Pressure*

The reactions at atmospheric pressure were carried out in a glass flask fitted with a ground glass stopper and having a side arm just below the stopper. The side arm was connected to a supply of dry nitrogen at a pressure slightly above atmospheric, so that when the stopper was removed dry nitrogen flowed out of the mouth of the flask.

A standard solution of aluminium chloride in benzoyl chloride, prepared in the manner described by Brown and Jensen,³ was introduced into the flask and diluted to the required strength with benzoyl chloride. In these and in all other manipulations the liquids were transferred over as short distances as possible in pipettes that had previously been flushed with dry nitrogen. The solution was placed in a constant temperature bath at 29.6°, and the reaction started by adding benzene from a weight pipette. At suitable intervals, samples of the mixture were removed by a micropipette and analysed to determine the amount of benzophenone that had been formed.

Our method of analysis differed from that of Brown and Jensen,³ which involved a rather tedious process of isolating and weighing the benzophenone. We made use of the fact that when benzophenone is dissolved in concentrated sulphuric acid it is quantitatively protonated to the carbonium ion species $(C_6H_5)_2C^+OH$ which has an intense optical absorption centred at 346 m μ .^{5,6} The other components of the reaction mixture were found to be transparent at that wavelength in sulphuric acid. In detail, the method was to add an aliquot (0.1–0.5 ml) of the reaction mixture to 10 ml of cold anhydrous acetic acid and then add sufficient pure sulphuric acid to bring the total volume of the solution to 100 ml at 25°. The analysis was performed by measuring the optical density of the final mixture at 346 m μ . The acetic acid served both to quench the reaction and to act as a mutual solvent for the benzophenone and sulphuric acid. It was found that the presence of up to 15% of acetic acid in the final solution had no effect on the molar extinction coefficient of the carbonium ions. The method was calibrated by examining standard solutions of recrystallized benzophenone in 90 : 10 sulphuric acid/acetic acid. The solutions obeyed Beer's Law, and the extinction coefficient at 346 m μ was 2.90×10^4 cm² mmole⁻¹.

Reactions at High Pressures

The reactions under pressure were carried out in thin polyethylene capsules surrounded by hydraulic oil contained in a suitable steel pressure vessel (see, e.g., Buchanan and Hamann⁷) in a constant temperature bath at 29.6°. The capsules were sealed by Teflon plugs which, themselves, had small removable stoppers to allow samples to be taken from time to time.

Each reaction mixture was prepared as described in the last section, except that the solution of aluminium chloride in benzoyl chloride was cooled to 0° before benzene was added. After mixing, the solution was quickly transferred to the polyethylene reaction tube, the Teflon stopper was inserted, and the reaction mixture cooled to -10°. The capsule was then placed inside the pressure vessel and the desired pressure applied as quickly as possible by a 3000 atm pump. The precooling was planned to counteract the heat generated during compression¹ and had the additional benefit of quenching the reaction until pressure was applied.

At appropriate periods, samples were taken for analysis by releasing the pressure and removing the capsule. The capsule was washed free of oil and cooled to 0°; a sample was extracted and the capsule quickly cooled to -10° before being recompressed. The times needed to begin the reaction and to take samples were always very short in comparison with the total time for a kinetic run, and since the reaction was effectively stopped during these times they were not included in the figure for the reaction time t used to calculate the rate constant.

The method of analysis was the same as in the measurements at atmospheric pressure.

⁵ Treffers, P., and Hammett, L. P., *J. Am. Chem. Soc.*, 1937, **59**, 1708.

⁶ Scheibe, G., *Chem. Ber.*, 1926, **59**, 2617.

⁷ Buchanan, J., and Hamann, S. D., *Trans. Faraday Soc.*, 1953, **49**, 1425.