

CHEMICAL EFFECTS OF PRESSURE

PART 7.—THE RATES OF ELECTROPHILIC AROMATIC NITRATIONS IN SOLUTION

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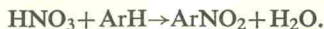
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Measurements have been made of the influence of pressure on the rates of nitration of aromatic compounds by nitric acid in inert solvents. It is found that an increase in pressure accelerates the zeroth-order nitration of toluene in acetic acid and in nitromethane by an amount corresponding to an activation volume of $-10 \text{ cm}^3/\text{mole}$. The acceleration probably arises from an increase in the stationary concentration of nitric acidium ions (H_2NO_3^+).

The first-order nitrations of p-dichlorobenzene in nitromethane and of benzene and chlorobenzene in acetic acid are all accelerated by pressure in a more marked degree than the zeroth-order reaction of toluene. Their activation volumes are about $-22 \text{ cm}^3/\text{mole}$. It is likely that, in these reactions, an increase in pressure both favours the formation of the active nitronium ions (NO_2^+) and speeds up the rate at which they attack the aromatic compounds.

This paper is the first of a series describing the influence of pressure on aromatic substitutions. The only previously reported measurements in this field are a few which Gonikberg and Gavrilova¹ made on the heterogeneous carboxylation of benzene by CO_2 in the presence of AlCl_3 . They found indications that the reaction was accelerated by an increase in pressure. But its mechanism and kinetics are obscure and the results have little fundamental value. We have, therefore, considered it worthwhile to undertake a systematic study of the effects of pressure on both the rates and products of aromatic substitutions. For the present we have restricted ourselves to simple homogeneous reactions whose mechanisms are already known at atmospheric pressure.

In this paper we describe measurements of the rate of mononitration of aromatic compounds (ArH) by an excess of nitric acid in inert solvents:



Hughes, Ingold and Reed² have made a thorough study of the rates and mechanisms of these reactions and shown that the active agent is the nitronium ion NO_2^+ formed by the decomposition of nitric acid. If the aromatic substrate is sufficiently reactive then the formation of this ion is the slowest step in the nitration, and the rate is independent of both the nature of the substrate and its concentration. In a large excess of nitric acid the kinetics are of the zeroth order and the reaction proceeds at a constant rate until all the substrate is consumed. If, on the other hand, the substrate is relatively unreactive, the rate-determining step becomes the bimolecular attack of the NO_2^+ ion on the aromatic nucleus. Under these conditions the rate of nitration depends on the nature of the substrate and is proportional to its concentration, so that the kinetics are of the first order. In our

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present work we have measured the rates of both kinds of reactions at pressures between 1 atm and 2300 atm. In a later paper we shall describe measurements of the influence of pressure on the relative yields of the different isomers formed by nitrating substituted benzene derivatives under the same conditions as applied in the present rate measurements.

Concurrently with the experiments on nitrations, we have made a less extensive study of the influence of pressure on the Friedel-Crafts benzoylation of aromatic compounds under such conditions³ that the reactions were homogeneous and obeyed simple second-order kinetics. The results of these experiments will be published later.

EXPERIMENTAL

MATERIALS

Benzene, toluene and chlorobenzene were dried and purified by conventional methods.⁴ *p*-Dichlorobenzene was purified by crystallization from alcohol. The materials were analyzed by gas chromatography and shown to be at least 99.5 % pure.

Anhydrous nitric acid was prepared by distillation from sulphuric + nitric acid mixtures, and freed from dinitrogen tetroxide (which is an inhibitor in nitrations²) by several low-temperature sublimations under vacuum. It was stored as a solid at -80°C and dispensed into the reaction mixtures as a liquid at -15°C .

Acetic acid was prepared by refluxing the reagent-grade material with potassium permanganate for 2 h and distilling it. It was then treated with pure acetic anhydride and sulphuric acid to remove water, and fractionated. Analytical grade nitromethane was dried thoroughly and fractionated.

APPARATUS

The high-pressure nitrations were carried out in a sampling vessel similar in principle to those described by Perrin⁵ and Koskikallio and Whalley.⁶ There were small differences in detail, imposed by the extremely corrosive nature of the reaction mixtures. The mixtures were held in a thin-walled polyethylene capsule which could deform to transmit the pressure of the surrounding hydraulic fluid. The capsule was connected by a polyethylene tube to the seat of a stainless steel outlet valve, so that the only metal in contact with the reaction mixture was the small area of steel at the valve seat.

A number of preliminary experiments with a thermocouple immersed in the reaction mixture showed that the heat generated by the initial compression could be counterbalanced by pre-cooling the mixture. For instance, a mixture pre-cooled to -32°C reached the desired reaction temperature of 0°C after rapid (nearly adiabatic) compression to 2000 atm. In addition to preventing over-heating, the pre-cooling had the desirable effect of quenching the reaction until the pressure was applied.

The pressure vessel was immersed in a constant temperature bath and the temperature and pressure of the mixture were kept constant during the withdrawal of each sample by simultaneously pumping more hydraulic fluid into the vessel.

METHODS OF ANALYSIS

The progress of the reactions in nitromethane was followed by titrating the unchanged nitric acid with alkali under carefully controlled conditions. But this method was unsatisfactory for the reactions in acetic acid, both because the change in total acidity was much smaller and because the end-point was less well defined. For these reactions we measured the concentration of the nitrated product by titrating it with titanous chloride solution to an electrometric end-point in the presence of sodium citrate buffer.⁷ The titanous chloride was standardized against pure nitrobenzene.

The amount of the inhibitor N_2O_4 in each sample was estimated colorimetrically as α -naphthol azo-sulphanilic acid.⁸ It was never greater than 0.002 mole/l.

RESULTS

REACTIONS IN NITROMETHANE

We made only a few measurements in nitromethane because we found that this solvent forms extremely explosive mixtures with nitric acid. Pure nitromethane can be detonated by sudden compression to 150 atm,⁹ and we found that