

### 91. The Influence of Pressure on the Rate of Formation of Cetylpyridinium Halides.

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In the preceding paper it was shown that pressures of 3000 atm. have an accelerating effect on chemical reactions in the liquid phase. In order to obtain a clearer idea of the magnitude and nature of the effects involved, it will be necessary to make a detailed quantitative study of a number of reactions of different types at different pressures and temperatures. The present paper records the first attempt at such a study.

#### EXPERIMENTAL.

*Materials.—Pyridine.* A.R. Pyridine (British Drug Houses Ltd.) was dried over solid caustic potash and distilled, the fraction of b. p. 115.0—115.5° being used.

*Cetyl bromide.* Technical quality material was employed; it contained homologues of cetyl bromide and substances containing more than one atom of bromine. The crude material was slowly distilled at 2 mm. pressure, and the fraction of b. p. 175—185° collected, dissolved in an equal volume of dry acetone, and cooled to 4°. The cetyl bromide crystallised in small, pure white plates. The crystals were filtered off at 4° and twice recrystallised. The final crop of crystals was distilled under 2 mm., and the fraction of b. p. 182—185° collected. This material contained a trace of hydrogen bromide which was removed by a current of dry air. The bromine content was, however, low (Found, in two samples: Br, 25.25, 25.45. Calc.: Br, 26.2%); this was due to the presence of cetyl alcohol and/or hexadecene but, as these substances merely act as diluents in the reaction studied, no further attempt was made to remove them.

*Cetyl chloride.* Attempts to prepare cetyl chloride from cetyl alcohol and phosphorus trichloride always gave products which, even after extensive fractional distillation, contained considerable quantities of unchanged alcohol and of hexadecene (Found: Cl, 11.21. Calc.: Cl, 13.67%).

For this reason the cetyl chloride reaction has been studied at one temperature only.

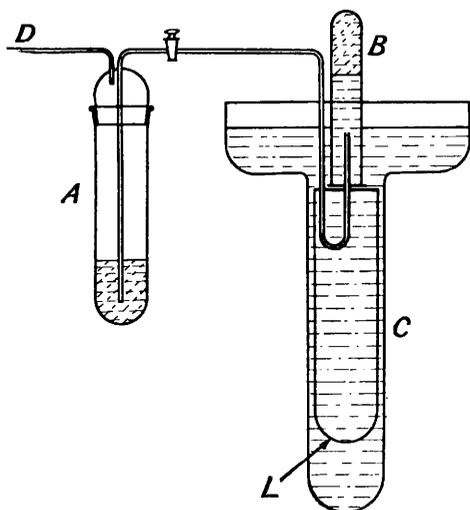
*Products.*—The cetylpyridinium bromide and chloride were obtained as pure white solids. When prepared at 40° the bromide separates from the reaction mixture in very thin transparent plates; under other conditions it separates as a transparent jelly which solidifies on standing. The chloride is soluble in the reaction mixture at 110°, but the system separates into two liquid layers on slight cooling, the lower layer solidifying on further cooling.

Cetylpyridinium hydroxide is a strong base and forms some sparingly soluble salts—an insoluble, bright yellow chromate, an orange perbromide, a white perchlorate, and a rather sparingly soluble iodide.

*Procedure.*—In both cases the reactants are miscible liquids and the products are solids, sparingly soluble in the reaction mixture. It was not possible to adopt any method which involved sampling, and a fresh sample of the reactants had to be made up for each run.

The reaction mixture (1 mol. of cetyl halide and 1 mol. of pyridine) was made up in a small weight pipette, *A* (Fig. 1). The reaction tube *B*, of thin-walled glass tubing closed at one end, was filled with mercury and inverted in a trough *C*, also filled with mercury. The end of the pipette was introduced into the tube under the mercury, and a known weight of the mixture blown into the tube by means of a rubber bulb attached at *D*. The tube thus filled was floated into a glass liner, *L*, immersed in the trough. The liner and tube were then removed and placed in a high-pressure vessel, which was placed in a thermostat and allowed to attain the required temperature; pressure was then applied for the required time, as described in the preceding

FIG. 1.



paper. The pressure was then released, the vessel removed from the thermostat, cooled, and opened. The glass liner and reaction tube were taken out, washed with light petroleum to remove the oil above the mercury, and placed in the mercury trough from which the reaction tube and its contents could be transferred to a flask for analysis.

The experiments with the bromide at about atmospheric pressure were carried out in sealed glass tubes. With the chloride, anomalous results were obtained by this method owing to the temperature of the experiment ( $110^\circ$ ) being close to the b. p. of the pyridine, so that an appreciable amount of pyridine entered the vapour phase. The experiments with the chloride were therefore carried out in the same manner as the high-pressure experiments, but in small bombs in which a pressure of not more than 5 atm. was maintained by means of a spring-loaded release valve.

FIG. 2.

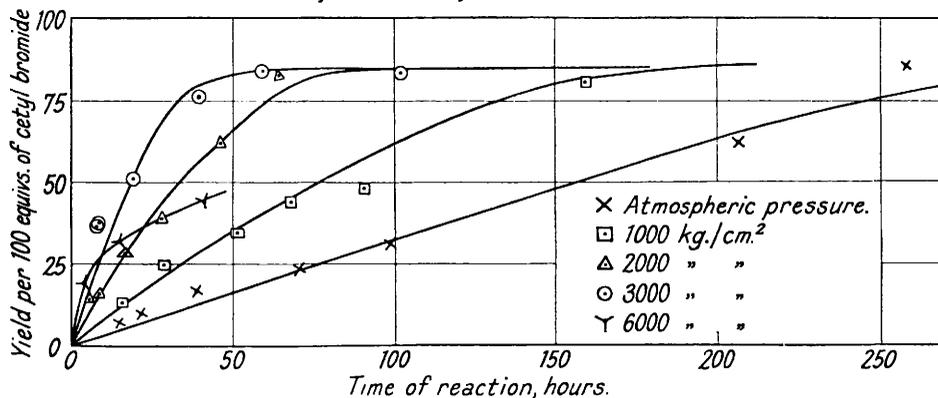
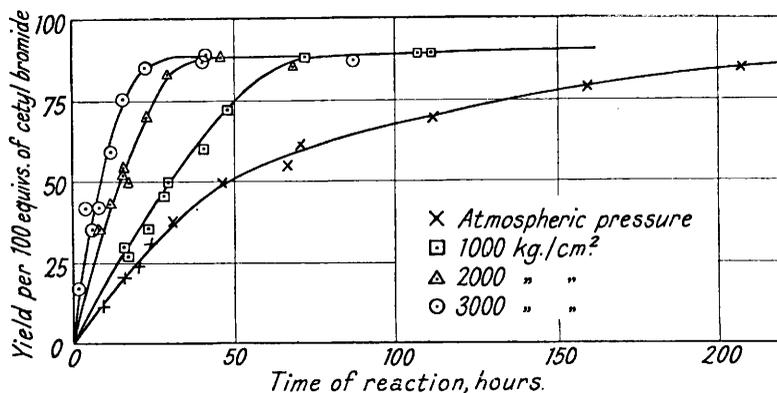
Pyridine and cetyl bromide at  $40^\circ\text{C}$ .

FIG. 3.

Pyridine and cetyl bromide at  $50^\circ\text{C}$ .

*Analytical Method.*—It was found impossible to follow the reaction either by determining the ionisable halogen ion of the product with silver nitrate, or by direct titration of the unchanged pyridine with acid, as all the indicators tried failed to give an end-point. The method finally adopted was first to separate the unchanged pyridine from the reaction mixture by steam distillation.

At the conclusion of a run, the reaction tube and its contents were transferred to a flask containing about 100 ml. of water, and steam distilled until about 100 ml. of distillate had passed over, the distillate being collected in 25 ml. of *N*-hydrochloric acid. Ground-glass joints were used throughout the distillation apparatus in order to avoid the loss of pyridine by absorption on rubber or cork bungs. The resulting solution of pyridine hydrochloride was made up to 250 ml. and 25 ml. of this solution titrated with *N*/10-sodium hydroxide, a mixture of methylene-blue and methyl-orange being used as indicator (cf. Kolthoff, "Die Massanalyse," II, p. 64,

Berlin, 1927). This indicator gives a sharp colour change at  $p_H$  3.25, which corresponds to the  $p_H$  3.2 of an aqueous solution of pyridine hydrochloride. The quantity of acid neutralised by the pyridine was obtained by subtraction of this titre from that of 25 ml. of the acid against the alkali with the same indicator (*viz.*, 24.7 ml.). The method was checked on known quantities of pyridine and found satisfactory.

In order to be sure that the cetylpyridinium bromide was not hydrolysed during the steam distillation, a sample of this compound was steam distilled until 100 ml. of distillate had come over. No pyridine was detected in the distillate by the colour test with aniline and cyanogen bromide (Tallantyre, *J. Soc. Chem. Ind.*, 1930, 49, 468).

FIG. 4.  
Pyridine and cetyl bromide at 60° C.

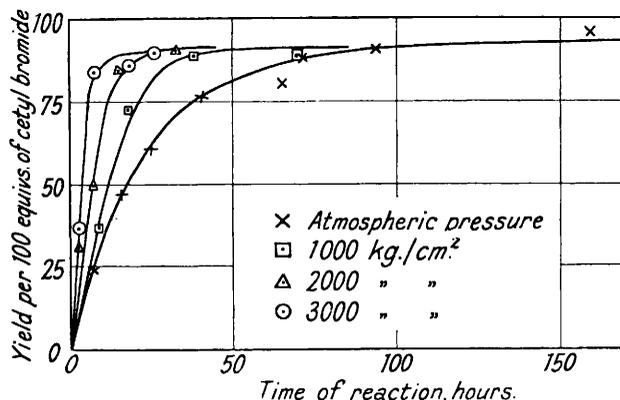
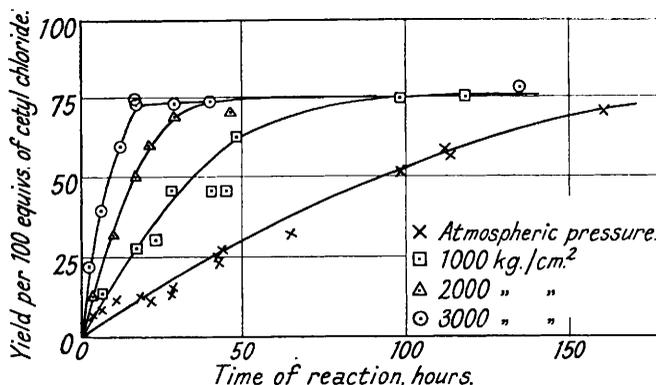


FIG. 5.  
Pyridine and cetyl chloride at 110° C.



During the analyses of the reaction mixtures, a small quantity of an insoluble oil, probably unchanged cetyl halide, passed over into the distillate, but it did not interfere with the titrations.

*Results.*—The yields of cetylpyridinium halide obtained at atmospheric pressure, 1000, 2000, 3000, and 6000 kg./cm.<sup>2</sup>\* at 40°, 50°, and 60° in the case of the bromide, and at 110° in the case of the chloride, have been plotted against time in Figs. 2—5. Smooth curves have been drawn through the points of corresponding temperatures and pressures. The accuracy of the results is disappointing. The thermostats were regulated to about 0.1°, and the temperatures of the several experiments in each series did not differ by more than a few tenths of a degree. Although each experiment was started at the given pressure, the pressure fell during

\* Most of the experiments in the preceding paper were done with gauges registering in atmospheres, but in the quantitative work now recorded more accurate gauges, calibrated in kg./cm.<sup>2</sup>, were used (1 kg./cm.<sup>2</sup> = 0.968 atm.).

its course owing to the decrease in volume of the reaction mixture, the fall amounting to 10% when the reaction approached completion.

The pressures were measured on calibrated Bourdon gauges. There is a relatively large uncertainty in the times of the shorter runs owing to the time required for the pressure vessel to attain the temperature of the thermostat before being subjected to pressure. The reaction proceeds at atmospheric pressure during this time, but it is difficult to apply a correction for this without a knowledge of the rate of increase of temperature of the reaction mixture.

#### DISCUSSION.

Figs. 2—5 show that, at constant temperature, pressures up to 3000 kg./cm.<sup>2</sup> have a marked influence on the velocity of the reactions. From the few experiments at 40° and 6000 kg./cm.<sup>2</sup> it is seen, however, that the increase of the reaction rate with pressure is not maintained. It is possible that, at this pressure, a part of the cetyl bromide crystallised out of the reaction mixture, and its concentration in the liquid phase therefore diminished.

From the curves it is seen that in no case was the reaction complete, even after more than 200 hours. The conversion seems to reach a limiting value which appears to be independent of the pressure but dependent on the temperature, as seen from the curves for the bromide. There are several explanations which would account for such a limiting value.

(1) The method of estimation may have given low results; blank determinations on known quantities of pyridine in the presence of cetylpyridinium halide, however, showed that it could be estimated to within 1%. (2) A portion of the halogen present may have been unreactive; this is unlikely in view of the method of purification of the cetyl bromide (see p. 396) and of the fact that the halogen content was below and not above the theoretical. (3) The reaction may proceed to an equilibrium; the cetylpyridinium halide, however, does not dissociate during steam distillation (see p. 398), and it was also found that it could be heated alone or in acetone solution to 60° for long periods without a trace of pyridine being formed (Tallantyre's test, *loc. cit.*). (4) A side reaction may occur, *e.g.*,  $C_{16}H_{33}Br + C_5H_5N \rightarrow C_{16}H_{32} + C_5H_5NHBr$ ; the pyridinium hydrobromide would be hydrolysed during the steam distillation and estimated with the unchanged pyridine, and this would explain the results.

A quantitative estimation of the effect of pressure on the rates of reaction may be obtained from a consideration of the times of reaction for equal yields at the different temperatures and pressures. The following figures, obtained from the smoothed curves, give the times (in hours) required to give a yield of 40%.

Press., kg./cm. <sup>2</sup>	1	1000	2000	3000
$C_{16}H_{33}Br$ at 40°	122	58	26	15
" 50	39	24	12·5	7·5
" 60	14	9	5·5	3·25
$C_{16}H_{33}Cl$ ,, 110	77	28	14	7·5

The effects of pressure on the rate of reaction and, in the case of the bromide, on the temperature coefficient of the reaction, are shown by comparing the reciprocals of these times with those at 1 kg./cm.<sup>2</sup> and at 40° respectively:

Press., kg./cm. <sup>2</sup>	1	1000	2000	3000
$C_{16}H_{33}Br$ at 40°	1	2·1	4·7	8·1
" 50	1	1·6	3·1	5·2
" 60	1	1·5	2·5	4·3
$C_{16}H_{33}Cl$ ,, 110	1	2·7	5·5	10·3
$C_{16}H_{33}Br$ ,, 40	1	1	1	1
" 50	3·1	2·4	2·1	2·0
" 60	8·7	6·4	4·7	4·6

The pressure effect with the bromide is seen to fall with increasing temperature.

Attempts to interpret the results by means of the ordinary reaction-velocity equations were unsuccessful, but it is doubtful whether it is legitimate to apply these equations without modification to reactions between pure liquids.

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