THE KINETICS OF HETEROGENEOUS ORGANIC REACTIONS (II): THE REACTION BETWEEN BENZYL CHLORIDE AND SOLID SILVER NITRATE IN THE PRESENCE OF INERT DILUENTS.

By M. V. Nabar
and
T. S. Wheeler.
(From the Department of Chemistry, Royal Institute of Science, Bombay.)

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Introduction.

In a previous paper[1] the authors have shown that when benzyl chloride and solid silver nitrate react in the absence of solvents and diluents, the rate of reaction is independent of the amount of benzyl chloride, but is proportional to the surface of silver nitrate present. The course of the reaction in the presence of ether (sulphuric), chloroform and carbon tetrachloride has now been investigated; results similar to those in Part I have been obtained.

Materials Used.

Silver Nitrate.—This was of the same quality and prepared in the same way as described in the previous paper; the average particle size was the same as that of the sample (M) used before.

Benzyl Chloride.—Kahlbaum's benzyl chloride "purest" was used as before.

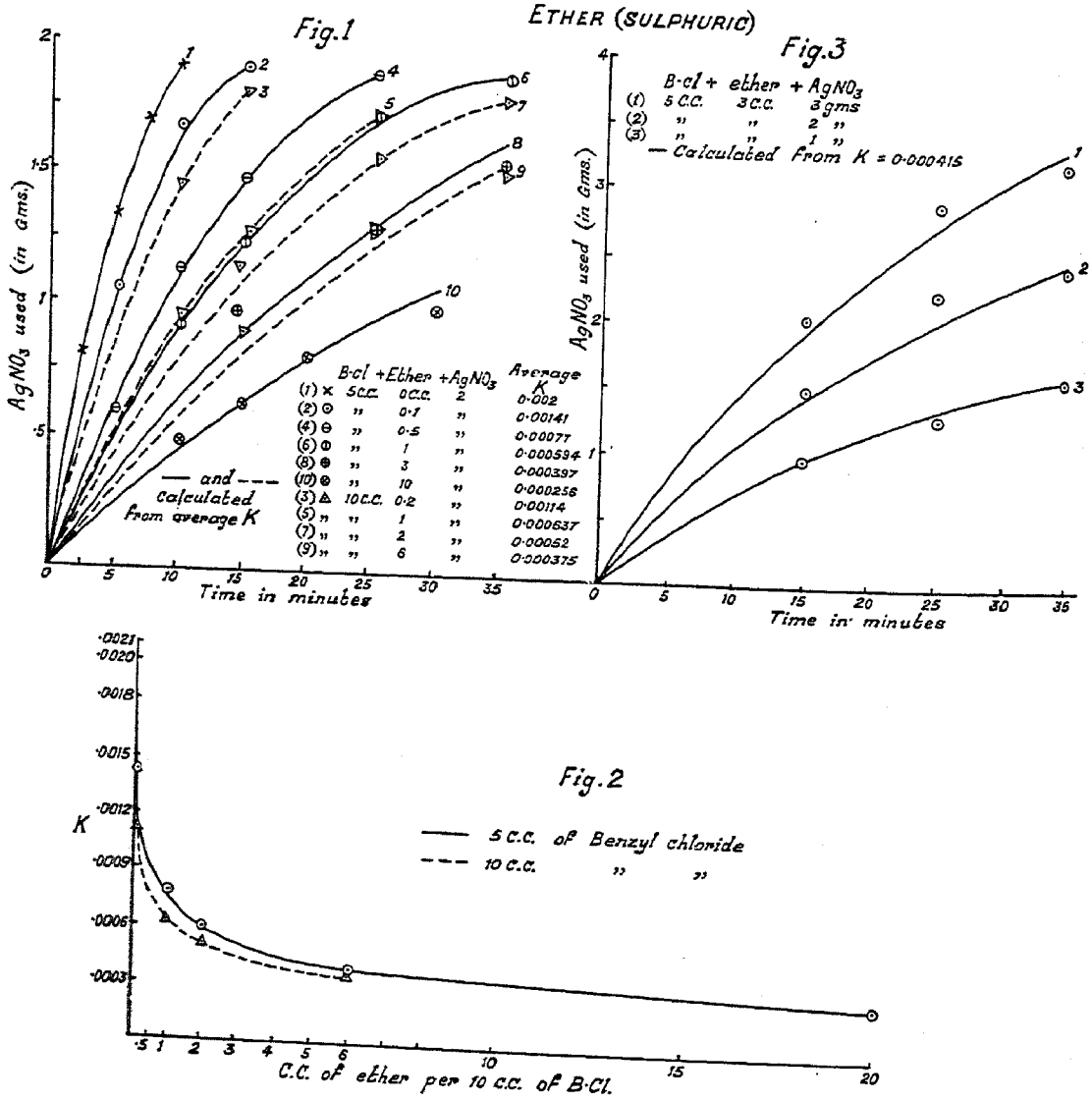
Diluents.—Kahlbaum's ethyl ether anhydrous, distilled over sodium, for analytical purposes, Merck's chloroform P.B., double distilled over phosphorous pentoxide and Merck's extra pure carbon tetrachloride, distilled over phosphorous pentoxide were used. Kahlbaum's chloroform and carbon tetrachloride gave the same type of results in check experiments.

Experimental Methods.

The diluent used, measured by a pipette was added to the benzyl chloride before placing in the air thermostat adjusted to $35° \pm \cdot 2$ C. The experimental technique was otherwise the same as before, except that in presence of diluents, it was not found necessary to use a wet cloth to control the reaction temperature.

Experimental Results and Discussion.

Ether.—Fig. 1 shows the effect of addition of ether. It acts as a strong inhibitor, a definite result being obtained even with 0·1 c.c., with 5 c.c. of benzyl chloride. With a constant quantity of silver nitrate and the same mixtures of benzyl chloride and ether, doubling the quantity of liquid taken, slightly increases the inhibiting effect.



The equation developed in the previous paper

$$K = \frac{3}{tS}\left\{1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right\} \quad \ldots \quad (1)$$

where t = time in minutes ;
S = surface area of silver nitrate ;
X = amount of silver nitrate left ;
A = initial amount of silver nitrate ;
fits the curves moderately well.

As with sample (M) before, S was 92·2 sq. cms. throughout this set of experiments. The points show the experimental results and the lines the calculated values [equation (1)] using the values of K indicated.

Fig. 2 shows a plot of values of K for 2 gms. of silver nitrate against the quantity of ether taken per 10 c.c. of benzyl chloride. The curves for 5 c.c. and 10 c.c. of benzyl chloride lie close toegther.

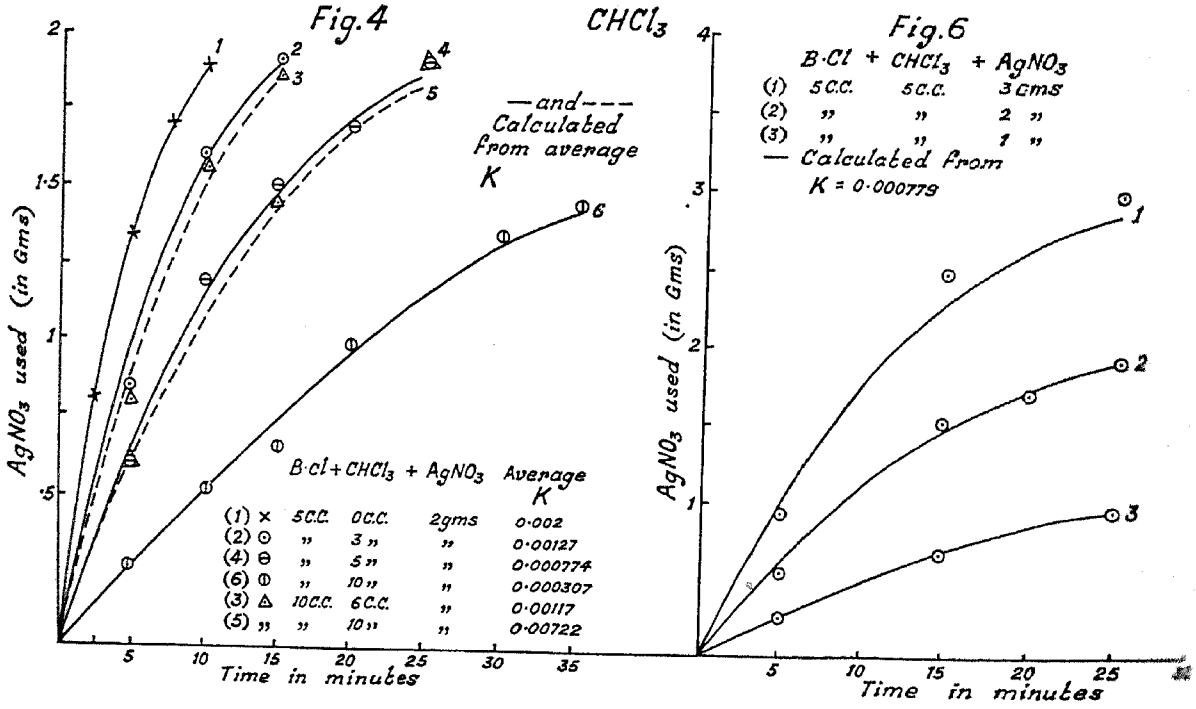
The effect of addition of ether is great initially but then falls off. This can be explained by assuming that ether is adsorbed on the surface of silver nitrate, and that saturation of this surface is attained with small quantities of ether.

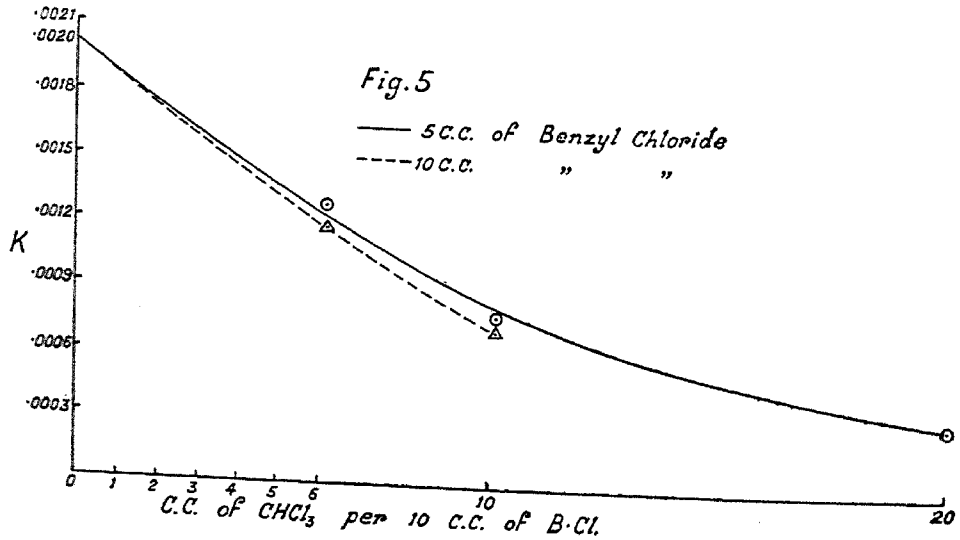
Fig. 3 shows experiments with a constant quantity of benzyl chloride and ether, with varied amounts of silver nitrate. The curves are calculated using equation (1) and as will be seen, for one value of K they pass fairly well through all the experimental points. From these results it would appear that the nature of the reaction is the same as when the diluent is absent.[2] Benzyl chloride is adsorbed on the surface of silver nitrate particles and the amount of adsorption does not depend greatly on the concentration of benzyl chloride in the mixture of benzyl chloride, ether and benzyl nitrate. There is, therefore, always a constant concentration of benzyl chloride on the silver nitrate surface, and the rate of reaction is consequently proportional to the surface of silver nitrate present. The ether while not changing the nature of the reaction causes it to proceed at a definitely slower rate, possibly because it too is adsorbed on the surface of silver nitrate.

Chloroform.—The curves (Fig. 4) with chloroform are of the same type as those obtained with ether, but the inhibition is less. Here again the lines which show the values calculated from equation (1) pass well through the experimental points.

The effect of addition of chloroform on the value of K is shown in Fig. 5. The initial effect is not so marked as with ether.

Fig. 6 shows the experiments with a constant quantity of benzyl chloride and chloroform with definite amounts of silver nitrate. The lines are calculated from equation (1) and here also they pass well through the experimental points, for one value of K.

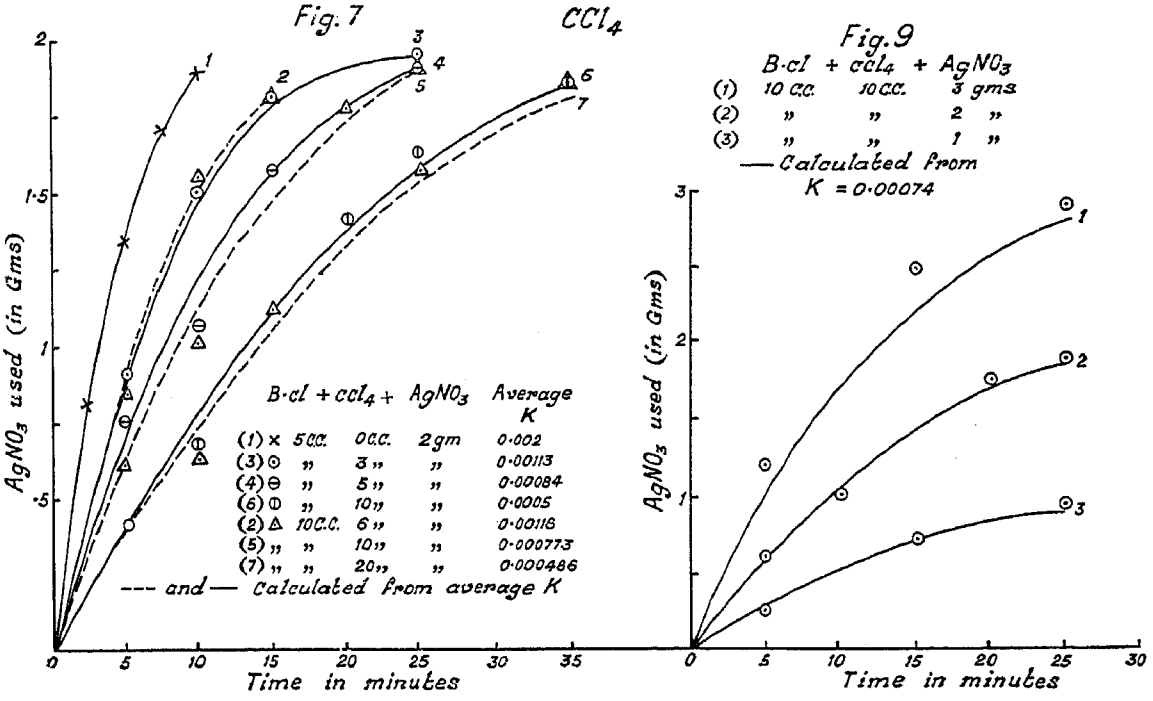


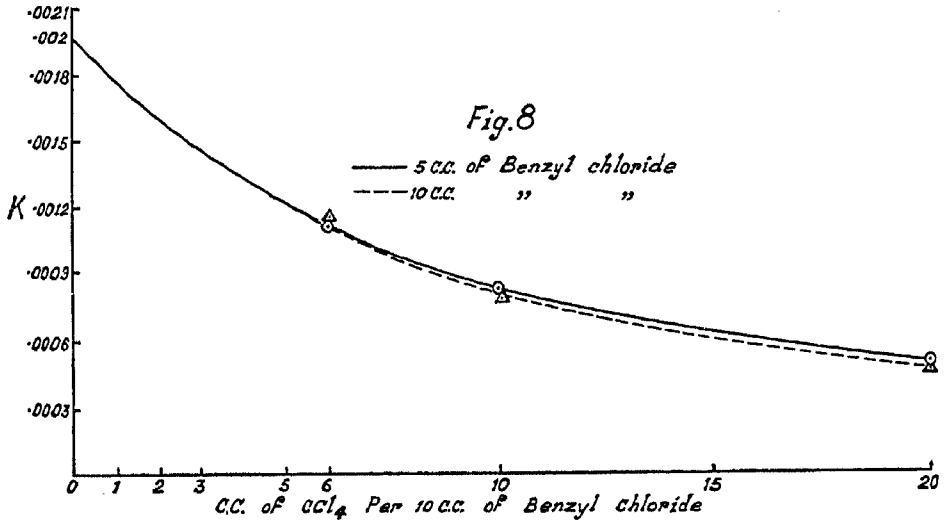


Carbon Tetrachloride.—The curves (Fig. 7) obtained with carbon tetrachloride are of the same type as obtained with ether and chloroform. Here also the inhibition is less than that with ether. The lines showing the calculated values [equation (1)] pass well through the experimental points.

The effect of the addition of carbon tetrachloride on the value of K is shown in Fig. 8.

Fig. 9 shows the experiments with a constant quantity of benzyl chloride and carbon tetrachloride with different amounts of silver nitrate.





Here again the lines calculated from equation (1) using one value of K pass through the experimental points for 1 and 2 gm. of silver nitrate ; for 3 gm. of silver nitrate the agreement is not good.

It should be understood that while the equation given above satisfies the experimental results moderately well the possibility of other interpretations of the experimental results should not be excluded.

Summary.

(1) The kinetics of the reaction between benzyl chloride and solid silver nitrate has been studied in the presence of dry ethyl ether, chloroform and carbon tetrachloride.

(2) All these diluents inhibit the reaction, the effect of ether being most marked.

(3) The rate of reaction is proportional to the surface of silver nitrate present; it is independent of the initial amount of a given mixture of benzyl chloride and diluent taken.

(4) The experimental results can be reproduced by a kinetic equation based on the assumption that the rate of reaction for a given initial mixture of benzyl chloride and diluent depends only on the surface of the silver nitrate present.

(5) The effect of the diluent may be due to the adsorption on the surface of the silver nitrate.

REFERENCES.

1. Nabar and Wheeler, *Proc. Ind. Acad. Sci.*, 1935, 2, 265.
2. See Part I, *loc. cit.*