THE KINETICS OF HETEROGENEOUS ORGANIC REACTIONS: THE REACTION BETWEEN BENZYL CHLORIDE AND SOLID SILVER NITRATE.

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Introduction.

In connection with a systematic study which is being made in these laboratories on the kinetics of heterogenous organic reactions[1] we have investigated the reaction between solid silver nitrate and benzyl chloride in the absence of all solvents and diluents. No previous work of this type appears to have been carried out on the reaction. Burke and Donnan[2] (1904), Donnan and Potts[3] (1910) and Senter[4] (1910) investigated the reaction between silver nitrate and alkyl iodides in alcoholic and aqueous alcoholic solutions and have found the reaction to be complicated by the presence of the solvent.

Materials Used.

Silver Nitrate.—Experiments were carried out with Kahlbaum's "purest for analysis", Merck's "purest guaranteed reagent", and Johnson's "double crystallized" silver nitrate. It was found that all these different samples gave results agreeing within the experimental error. To obtain reproducible results, it was essential to have the particles of silver nitrate of average uniform size. This was accomplished in the following way :—

Silver nitrate was ground in a pestle and mortar in dim diffused light, and then sieved through a silk cloth of fine mesh to remove small particles, and then through a slightly bigger mesh. What passed through the second mesh was collected. The particles were examined under a microscope and the sieving repeated until they were of an average uniform size, and gave a standard rate of reaction under standard conditions. The standard reaction for medium size particles was :—

1 *J. Phys. Chem.*, 1935, **39**, 727, 901, 907.
2 *J. C. S.*, 1904, **85**, 555.
3 *J. C. S.*, 1910, **97**, 1882.
4 *J. C. S.*, 1910, **97**, 346.

Temperature	Benzyl chloride	Time of reaction	Initial silver nitrate	Silver nitrate reacting
35°C.±1°	5 c.c.	10 mts.	2 gm.	1·85±·05

The sieving cloths and the process of sieving were standardized before beginning the set of experiments.

Three different sizes of particles denoted "Small", "Medium" and "Large" were employed. No difficulty was experienced in preparing fresh samples of the sizes.

It was observed that the presence of moisture considerably inhibits the reaction (see Fig. 4). Hence the samples of silver nitrate were kept in the

	Small size S	Medium size M	Large size L
Mesh of fine sieve ..	L 0·019 cm.	L 0·028 cm.	L 0·048 cm.
	B 0·017 cm.	B 0·024 cm.	B 0·037 cm.
Mesh of coarse sieve ·	L 0·023 cm.	L 0·031 cm.	L 0·057 cm.
	B 0·017 cm.	B 0·026 cm.	B 0·049 cm.
Average weight of a particle ..	$1·216\times10^{-5}$ gm.	$4·272\times10^{-5}$ gm.	$4·145\times10^{-4}$ gm.
Number of particles per gm. ..	82402	23407	2412
Average volume of a particle ..	$2·795\times10^{-6}$c.c.	$9·82\times10^{-6}$ c.c.	$9·53\times10^{-5}$c.c.
Average dimensions of a particle ..	L 0·031 cm.	L 0·048 cm.	L 0·093 cm.
	B 0·019 cm.	B 0·03 cm.	B 0·055 cm.
	T 0·00474 cm.	T 0·00682 cm.	T 0·0186 cm.
Average surface area of a particle ..	0·00165 sq. cm.	0·00394 sq. cm.	0·0158 sq. cm.
Surface area of one gm. ..	136 sq. cm.	92·2 sq. cm.	38 sq. cm.

dark, in a desiccator over phosphorus pentoxide. At intervals the reaction velocities of these samples were checked in standard experiments.

The sizes of the meshes of different cloths, and the sizes and surface area of particles are given in the above table.

The average surface area of a particle was determined as follows :—

A fraction of a gram of the particles was weighed and the number of particles was counted. From this, the average weight of a particle and the number of particles per gram were calculated. Then about fifty particles were examined under a microscope. The shape of all these three types was observed to be cuboid. The length and breadth of each particle was measured under the microscope by means of a standard scale placed in the eye-piece. From this the average length L and the average breadth B of each particle were calculated. From the average weight of each particle, and the density of silver nitrate (4·35), the volume of each particle was determined. Hence from the knowledge of the volume and L and B, the average thickness T of each particle was calculated. The surface area was calculated from the formula $2(L \times B + L \times T + B \times T)$.

Benzyl Chloride.—Kahlbaum's benzyl chloride "purest" was used throughout the set of experiments. Its properties were not altered by fractionation under reduced pressure. The standard rate of reaction of a sample of benzyl chloride decreases on keeping for some weeks. The effect is marked with smaller amounts (less than one gram) of silver nitrate, where the impurity in the benzyl chloride is relatively more important. The decrease is probably due to the hygroscopic nature of benzyl chloride. Accordingly, it was preserved in small lots in amber-coloured bottles under anhydrous conditions.

Experimental Methods.

Benzyl chloride was measured by means of a burette, protected from moisture, into a small conical flask. It was confirmed that Jena-glass bottles gave the same result. A thermometer was fixed through the cork, and the flask was covered with black paper and was kept in an air thermostat adjusted to 35°± ·2°C.

When the bottle attained the required initial temperature, sieved silver nitrate previously weighed in a weighing bottle and kept in a desiccator was added and the stop-watch started. The bottle was shaken by hand to mix the reactants thoroughly—this shaking is necessary—and it was then placed on the shaker which was also fixed in the thermostat, and the latter was started. The speed of rotation of the shaker was kept constant by means of a rheostat in the circuit of the motor. It was confirmed that variation of

Control of Reaction Temperature.

The reaction is exothermic and with the larger amounts of silver nitrate the rise in temperature is marked. As the heat of combustion of benzyl nitrate has not been determined, the heat change in the reaction cannot be calculated.

After a number of experiments it was found that by starting a little below 35° C. and by adjusting a wet cloth of suitable dimensions around or at the bottom of the bottle it was usually possible to keep the average temperature of the reaction close to 35° C. The degree of the wetness of the cloth and the extent to which the bottle was covered with it for different systems was determined in preliminary experiments. It was confirmed that the reaction is not sensitive to small temperature variations.

Experimental Results and Discussion.

TABLE II.

Medium Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
1	5	2·5	35	35·7	0·60	0·40	0·0020
1	5	5	35	34	0·32	0·68	0·0020
1	5	7·5	35	37	0·164	0·836	0·0020
1	5	10	35	36	0·07	0·93	0·0019
1	10	2·5	35	36·6	0·62	0·38	0·0019
1	10	5	35	34·5	0·37	0·63	0·0018
1	10	7·5	35	35	0·19	0·81	0·0018
1	10	10	35	35·3	0·07	0·93	0·0019
1	20	2·5	35	35	0·65	0·35	0·0017
1	20	5	35	35·6	0·352	0·648	0·0019
1	20	7·5	35	35·6	0·144	0·856	0·0020
1	20	10	35	37	0·07	0·93	0·0019
2	5	2·5	34	37	1·19	0·81	0·0020
2	5	5	34	37	0·66	1·34	0·0020

TABLE II—(*Contd.*)
Medium Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
2	5	7·5	34	36·6	0·29	1·71	0·0020
2	5	10	34	38	0·10	1·90	0·0020
2	10	2·5	34	35	1·30	0·70	0·0017
2	10	5	34	36·5	0·70	1·30	0·0019
2	10	7·5	34	36	0·28	1·72	0·0021
2	10	10	34	36	0·20	1·80	0·0017
2	20	2·5	34	35·4	1·25	0·75	0·0019
2	20	5	34	36	0·70	1·30	0·0019
2	20	7·5	34	35·5	0·36	1·64	0·0019
2	20	10	34	35·3	0·20	1·80	0·0017
3	5	2·5	33	36	1·70	1·30	0·0022
3	5	5	33	36·5	0·80	2·20	0·0023
3	5	7·5	33	36·5	0·40	2·60	0·0021
3	5	10	33	37	0·26	2·74	0·0018
3	10	2·5	33	35·3	1·70	1·30	0·0022
3	10	5	33	35·5	0·86	2·14	0·0022
3	10	7·5	33	36·3	0·40	2·60	0·0021
3	10	10	33	37·5	0·25	2·75	0·0018
3	20	2·5	34	36	1·80	1·20	0·0020
3	20	5	34	36	1·00	2·00	0·0020
3	20	7·5	34	38	0·40	2·60	0·0021
3	20	10	34	37	0·25	2·75	0·0018

TABLE III.

Large Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
1	5	5	34	35	0·678	0·322	0·0020
1	5	15	34	36	0·24	0·76	0·0020
1	5	25	34	35·7	0·096	0·904	0·0017
1	20	5	35	35	0·678	0·322	0·0020
1	20	15	35	33·5	0·274	0·726	0·0018
1	20	20	35	34	0·15	0·85	0·0019
1	20	25	35	35·2	0·096	0·904	0·0017
3	5	5	34	35	2·08	0·92	0·0018
3	5	15	34	35·5	0·678	2·322	0·0021
3	5	20	34	35	0·46	2·54	0·0018
3	5	25	34	34	0·323	2·677	0·0016
3	20	5	34	33·6	2·10	0·90	0·0018
3	20	15	34	35·5	0·654	2·346	0·0021
3	20	25	34	33·5	0·186	2·814	0·0019

Tables I, II, III, and Figs. 1, 2 and 3 give the results of the experiments. It will be seen that the rate of the reaction is independent of the initial amount of benzyl chloride. That is to say, if we take two grams of silver nitrate, it matters not as far as the rate of reaction is concerned whether we start with 5 c.c., 10 c.c. or 20 c.c. of benzyl chloride. This is a striking result, since with smaller amounts of benzyl chloride, the concentration of benzyl nitrate in the liquid reaction mixture increases rapidly. One would expect therefore the rate of reaction to fall off more quickly than with larger initial quantities of benzyl chloride.

We can explain this result by assuming that benzyl chloride is adsorbed on the surface of the silver nitrate crystals, and that the amount of adsorption does not depend greatly on the concentration of benzyl chloride in the

mixture. 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, so that during an experiment the interface between silver nitrate and silver chloride will travel inwards through the crystal at a constant linear rate.

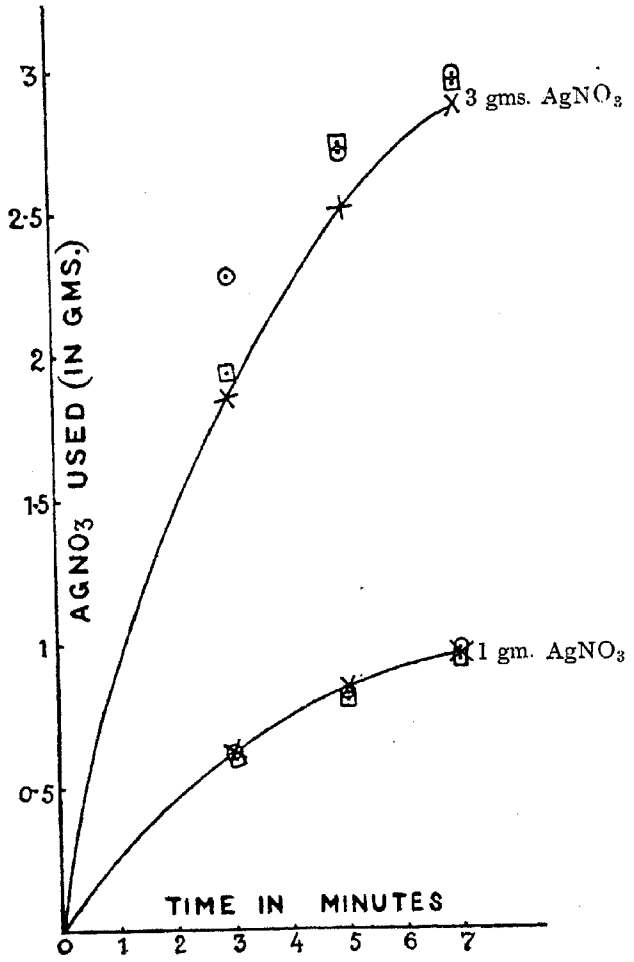

FIG. 1. Small Size $AgNO_3$ Particles.

Benzyl Chloride + $AgNO_3$

⊙ 5 c.c. + 1 & 3 gms.

⊡ 20 c.c. + ,,

× Calculated from K = 0·002

This type of reaction has been found by Spencer and Topley[5] (1929), to apply to the decomposition of silver carbonate. They point out that an equation of the type deduced below applies strictly only to particles of uniform size, but is approximately true as an average result when factors such

[5] *J. C. S.*, 1929, 2633.

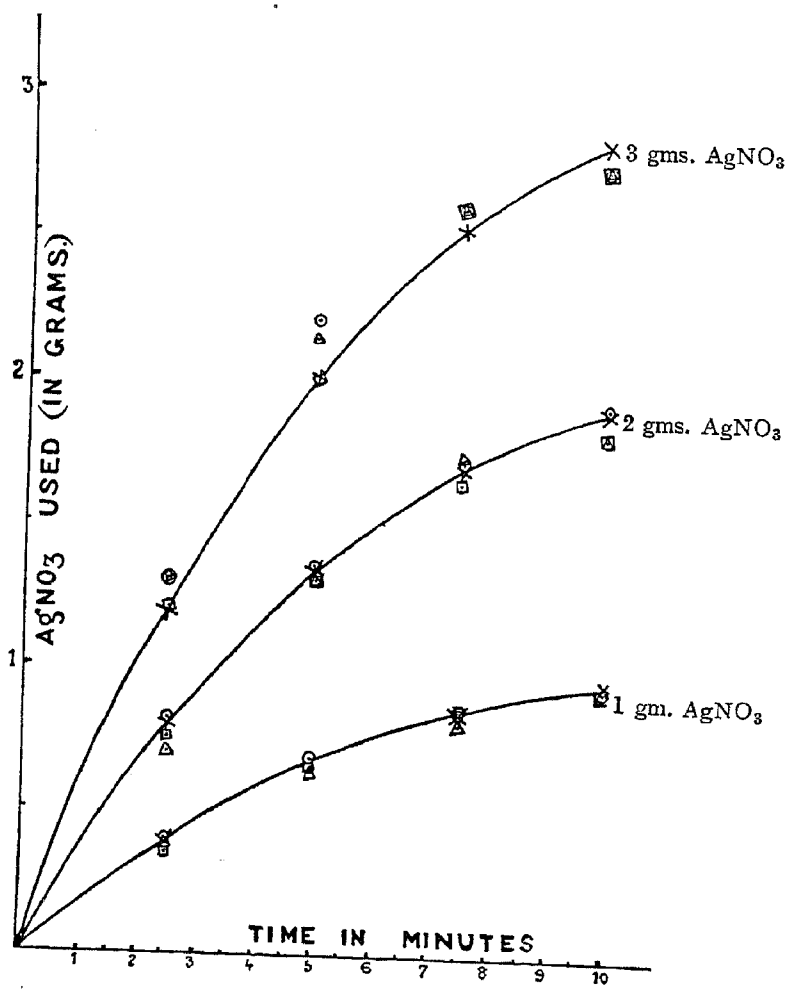

FIG. 2. Medium Size $AgNO_3$ Particles.

Benzyl Chloride	+ $AgNO_3$
⊙ 5 c.c.	+ 1, 2 & 3 gms.
◿ 10 c.c.	+ ,,
⊡ 20 c.c.	+ ,,

× Calculated from K = 0·002

as irregular shape and different reaction rates parallel to different crystal axis are averaged over the large number of particles contained in the reactive material. They also point out that reactants can be assumed to pass to and from the crystal interface by means of micro-fissures in the crystals.

With substances with large molecules such as benzyl chloride and benzyl nitrate this hypothesis is not so probable. On the other hand the silver chloride formed around the silver nitrate particles may have a loose porous form, that is to say, a continuous crystal lattice is not formed but rather an agglomeration of particles.

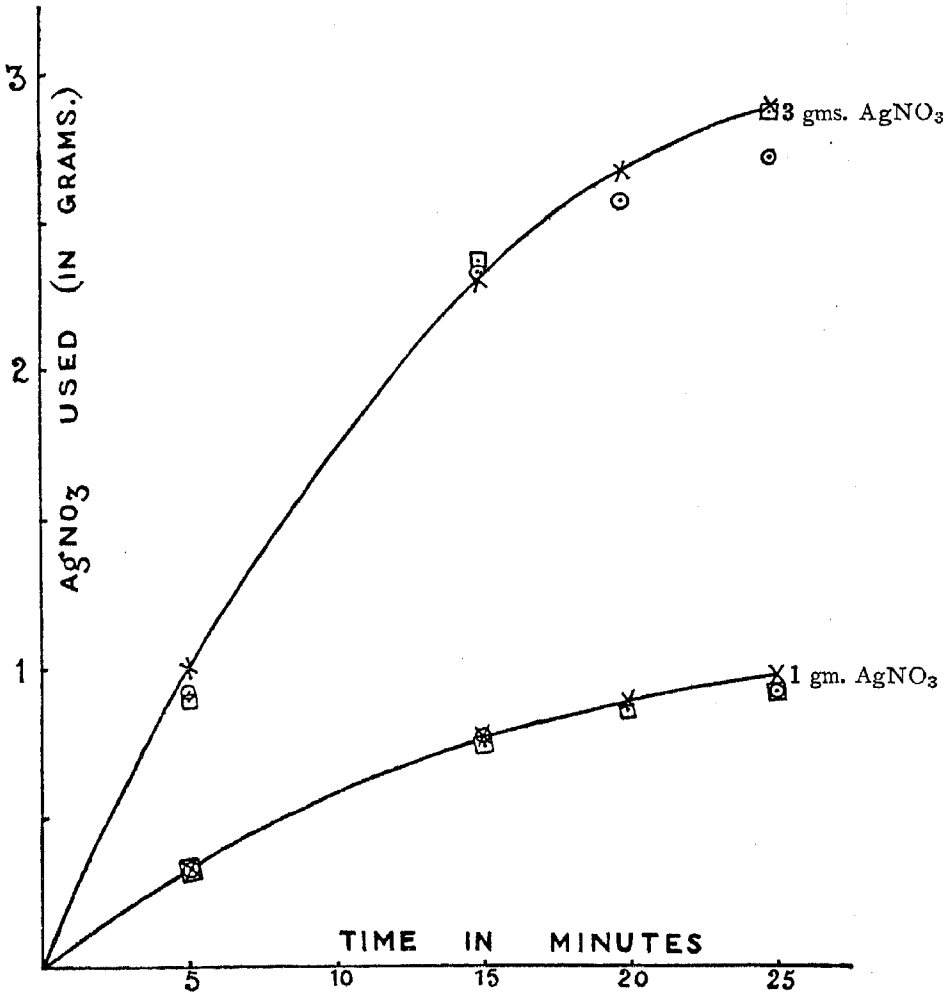

FIG. 3. Large Size $AgNO_3$ Particles.

Benzyl Chloride + $AgNO_3$
⊙ 5 c.c. + 1 & 3 gms.
⊡ 20 c.c. + ,,
× Calculated from K= 0·002

It must also be emphasised that while in many liquid phase heterogeneous reactions, the chemical effect is obscured by conditions of physical transport, yet in many other instances the chemical effect predominates. Roller[6] (1935) cites a number of reactions in which diffusion does not play a part, *e.g.*, Schmidt and Durau[7] (1924) showed that the rate of solution of glass in alkali is independent of the rate of stirring, and the concentration of alkali, but depends on the surface of the glass exposed. In our experiments the con-

[6] *J. Phys. Chem.*, 1935, 39, 221.
[7] *Z. Phys. Chem.*, 1924, 108, 128.

centration of benzyl chloride in the reacting medium is always high being never less than 60% by weight. This may tend to minimise diffusion effects, since there are always a large number of molecules near the reacting surface.

The real test of the hypothesis, however, is to examine how far the corresponding kinetic equation can reproduce the experimental results.

We deduce the kinetic equation as follows :—

Let A be the intial amount of silver nitrate in gms. and let X be the amount left at a time t. Let K be the number of gms. of silver nitrate reacting per sq. cm. of silver nitrate surface per second. Let $\bar{S}$ be the surface in sq. cms. of one grm. of the silver nitrate initially used.

Now if the silver nitrate particles be taken on an average to be spheres of the calculated surface area, the surface of the X gm. remaining after time t will be equal to

$$\frac{(\bar{S}A)\,X^{\frac{2}{3}}}{A^{\frac{2}{3}}} = \bar{S}\,A^{\frac{1}{3}}X^{\frac{2}{3}}$$

Hence

$$-\frac{dX}{dt} = K\bar{S}A^{\frac{1}{3}}X^{\frac{2}{3}} \quad \ldots\ldots(1)$$

$$-dt = \frac{dX}{K\bar{S}A^{\frac{1}{3}}X^{\frac{2}{3}}} \quad \ldots\ldots(2)$$

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

$$K = \frac{3}{t\bar{S}}\left(1-\frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots(4)$$

The values of K calculated from (4) are shown in Tables I, II and III and the constancy of the values indicates the general correctness of the assumed mechanism. A more stringent test is to use (4) to calculate the experimental results.

Examination of all experimental results indicate that K has an average value of 0·002. Hence as the small size (S) of silver nitrate used has a surface area per gm. of 136 sq. cm. we have for this sample the kinetic equation

$$0{\cdot}002 = \frac{3}{t(136)}\left(1-\frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots(5)$$

For the medium size (M) with the surface area per gm. of 92·2 sq. cm. we have

$$0{\cdot}002=\frac{3}{t(92{\cdot}2)}\left(1-\frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

And for the large size (L) with the surface area per gm. of 38 sq. cm.

$$0{\cdot}002=\frac{3}{t(38)}\left(1-\frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

From (5), (6) and (7), X has been calculated for various values of t, and the results are shown by full lines in Figs. 1, 2 and 3.

It will be seen that the equation reproduces well the experimental results. The agreement is all the more striking when it is remembered that for all these three results involving three different sizes of silver nitrate only one constant K = 0·002 has been used.

It should be noted however that with quantities of silver nitrate below 1·5 gm. it was more difficult to get constant result, low rates of reaction being sometimes obtained. It is believed that this effect is due to impurity in the benzyl chloride, but it is hoped to investigate the matter further.

Effect of Speed of Shaking.

A few experiments were made to see whether the change in the speed of shaking has any effect on the velocity of reaction. The speeds employed were 180, 120 and 75 revolutions per minute of the shaker. The general experimental technique was the same as described before. The results are given in the Tables IV and V.

It will be seen from the results that change in the speed of shaking within limits has no effect on the velocity of reaction.

Effect of Water.

It has already been stated that moisture inhibits the reaction to a considerable extent. A few experiments were carried out to study quantitatively the effect of water on the rate of reaction. Distilled water was added to benzyl chloride before the reaction. Otherwise the experimental procedure was the same as before.

The systems studied were

Benzyl chloride	Silver nitrate	H_2O
5 c.c.	2 gm.	0·01 c.c.
5 ,,	2 ,,	0·05 ,,
5 ,,	2 ,,	0·10 ,,

TABLE IV.

Results with Variation in the Shaker Speed.

$AgNO_3$ initial	Benzyl chloride	Time	No. of shaker revolutions per mt.	$AgNO_3$ left gm.	$AgNO_3$ used gm.	K
1 gm.	5 c.c.	2·5 mts.	180	0·62	0·38	0·0017
			120	0·56	0·44	0·0023
			75	0·65	0·35	0·0017
1 gm.	5 c.c.	5 mts.	180	0·37	0·63	0·0018
			120	0·25	0·75	0·0024
			75	0·31	0·69	0·0021
1 gm.	5 c.c.	10 mts.	180	0·05	0·95	0·0020
			120	0·03	0·97	0·0022
			75	0·05	0·95	0·0020

TABLE V.

Results with Variation in the Shaker Speed.

$AgNO_3$ initial	Benzyl chloride	Time	No. of shaker revolutions per mt.	$AgNO_3$ left gm.	$AgNO_3$ used gm.	K
1 gm.	10 c.c.	2·5 mts.	180	0·60	0·40	0·0020
			120	0·62	0·38	0·0017
			75	0·58	0·42	0·0022
1 gm.	10 c.c.	5 mts.	180	0·33	0·67	0·0020
			120	0·28	0·72	0·0022
			75	0·30	0·70	0·0021
1 gm.	10 c.c.	10 mts.	180	0·07	0·93	0·0019
			120	0·04	0·96	0·0021
			75	0·09	0·91	0·0018

The results are shown graphically in Fig. 4. The effect of 0·01 c.c. of water on the reaction of 5 c.c. of benzyl chloride (0.18% by weight) is marked. This effect increases with the amount of water added.

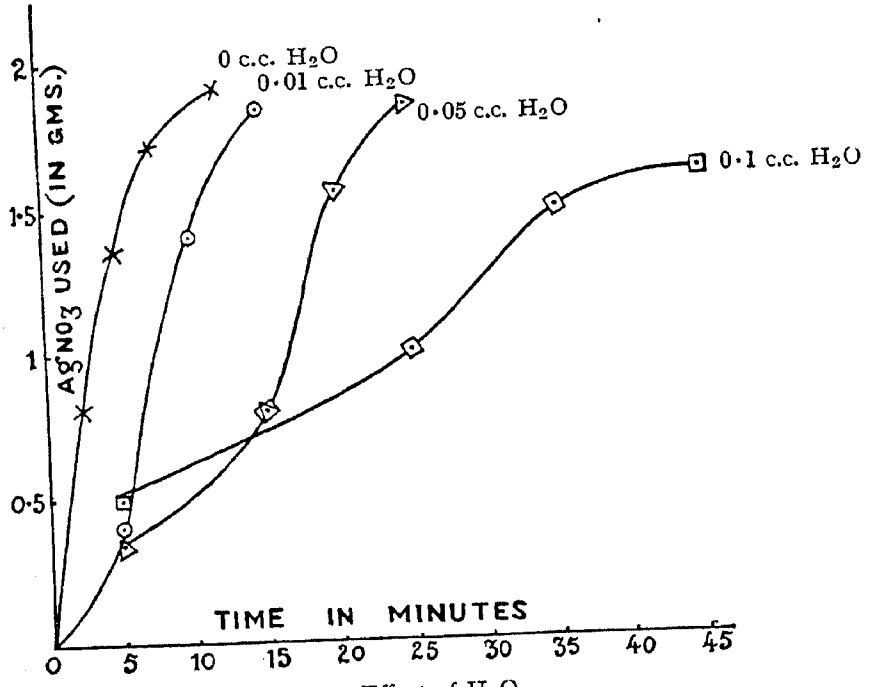

FIG. 4. Effect of H_2O.

	Benzyl Chloride	+ $AgNO_3$	+ H_2O
×	5 c.c.	+ 2 gms.	+ 0 c.c.
●	,,	+ ,,	+ 0·01 c.c.
◭	,,	+ ,,	+ 0·05 c.c.
⊡	,,	+ ,,	+ 0·1 c.c.

Summary.

(1) The kinetics of the reaction between benzyl chloride and solid silver nitrate has been studied in the absence of solvents and diluents.

(2) The reaction is independent of the amount of benzyl chloride, but is proportional to the surface of silver nitrate present.

(3) The reaction has been studied with particles of three different sizes, and it has been shown that all the experimental results can be reproduced by the kinetic equation derived on the assumption that the rate of reaction depends only on the surface of silver nitrate present.

(4) The velocity of reaction is independent of the speed of shaking.

(5) Water inhibits the reaction; the effect of 0·18% by weight of benzyl chloride taken is marked and this effect increases with the amount of water added.