316. *The Interaction of Benzoyl Chloride and Aniline in Carbon Tetrachloride and in Hexane Solution.*

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THERE are a number of reactions in solution, apparently bimolecular, which proceed at rates far smaller than the possible rate of activation of the molecules. In a previous paper (this vol., p. 258) we suggested exploring the hypothesis that reactions of this class are usually between neutral molecules, while reactions in which an ion is involved generally take place as fast as the rate of activation allows. In looking for further examples of reactions between neutral molecules in non-polar solvents, we first investigated the interaction of ammonia and methyl acetate in various solvents, but found no change in the absence of water. The ester was then replaced by acetyl chloride, and the rate was now immeasurably fast. The reaction between ammonia and benzoyl chloride in hexane was found to occur at a convenient rate, but the solutions lost ammonia very readily. Aniline was finally substituted for ammonia, and this reaction proved to be very suitable for measurement. The rate could be determined by filtering off and estimating the aniline hydrochloride formed.

EXPERIMENTAL.

The method of measurement was as follows. Standard solutions of aniline and benzoyl chloride were prepared, and stored in flasks with special externally-ground stoppers. Suitable proportions were mixed in tubes of 20, 40, or 80 c.c. capacity, which were stoppered and placed in a thermostat * controlled to 0·05°. After a known time a tube was removed and the aniline hydrochloride formed was filtered off through a fine filter-paper in a Gooch crucible and washed with solvent. The precipitate was transferred to a flask, dissolved in water to which were added the washings from the crucible and the original tube, and the chloride estimated by the Volhard method with $N/100$-silver nitrate, the whole procedure being carefully standardised. (The only detail which need be emphasised is the extreme importance of complete coagulation and separation of the silver chloride before the back titration with thiocyanate.) The quantities of reactant placed in the tubes were such that, whatever the dilution, the total equivalent of chlorine corresponded to 20 c.c. of the $N/100$-silver nitrate.

The reaction takes place quantitatively in accordance with the equation $Ph{\cdot}COCl + 2Ph{\cdot}NH_2 = Ph{\cdot}CO{\cdot}NHPh + Ph{\cdot}NH_3Cl$, no detectable amounts of by-products being formed. The benzanilide, when washed free from aniline hydrochloride with water and dried, melted sharply at 164°. The end-point of the reaction was the theoretical, in both solvents at all dilutions, and whether aniline or benzoyl chloride was in excess; *e.g.*, when 10 c.c. of $N/50$-benzoyl chloride were mixed with 10 c.c. of $N/25$-aniline, the final titre was 19·95 c.c. of $N/100$-silver nitrate (calc., 20 c.c.); with reactants respectively $N/200$ and $N/50$, the value was 19·9, and with both reactants $N/100$ it was 19·8. Numerous determinations were made.

The slow stage of the reaction is the formation of benzanilide and hydrogen chloride. The precipitation of aniline hydrochloride when hydrogen chloride and aniline are mixed in hexane solution is instantaneous and quantitative, as was shown in special experiments. 10 C.c. of $N/25$-aniline in hexane were treated with excess of a dilute solution of hydrogen chloride in hexane. The precipitate was at once filtered off, washed with hexane, and dried for some hours in a stream of air. It was then dissolved and titrated by the Volhard method. The number of c.c. of $N/100$-silver nitrate required in two cases was 40·0 and 39·7 (calc., 40·0). This experiment also justifies the analytical procedure adopted in the measurements of reaction velocity.

Before the individual results in hexane and in carbon tetrachloride solution are discussed, their reproducibility must be considered.

The carbon tetrachloride used was pure, free from sulphur compounds and elementary chlorine, and boiling over a range of not more than 0·2°. Whether used without special drying or refractionated over phosphoric oxide, it gave almost the same results. Two typical series of experiments are shown in Fig. 1, in which a is the concentration (g.-mols./l.) of benzoyl chloride, that of the aniline being double in each case.

The hexane, free from aromatic hydrocarbons, was fractionated over a range 67·1—67·9°, sometimes from phosphoric oxide and sometimes not. All samples gave results in agreement; *e.g.*, at 25·1°, for $a = 0{\cdot}0025$, in 874 minutes the percentage change in one sample of hexane was 55·3 and, after the solvent had been refractionated from phosphoric oxide, it was 56·3. The two upper curves in Fig. 1 were obtained with different specimens of benzoyl chloride and aniline, and are typical of the degree of reproducibility at this concentration. One specimen of benzoyl chloride was fractionated five times, and finally collected over 0·5° in an all-glass apparatus; the other was a twice-distilled Kahlbaum preparation boiling over the same range. The aniline

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* For experiments at low temperatures a Dewar vessel was used. It contained crushed ice and distilled water, and was stirred by a gentle current of air. Its temperature could be kept constant to about 0·01°.

was thrice distilled, after drying with potassium hydroxide, in the first instance, and in the second was redried and redistilled, finally over 0·2°.

In hexane with $N/100$-benzoyl chloride, therefore, the results are fairly well reproducible. For $N/400$, although this cannot be shown on the scale of Fig. 1, they are also satisfactory, but at an intermediate concentration of $N/200$ they tend to be erratic in the region of 30—60% change. This effect is a real one, not attributable to experimental error. The explanation will appear later.

The Reaction in Carbon Tetrachloride Solution.—Table I shows the course of the reaction and the influence of dilution. For given initial concentrations, the course is almost bimolecular,

Fig. 1.

Rate of interaction of benzoyl chloride and aniline at 25·1°.

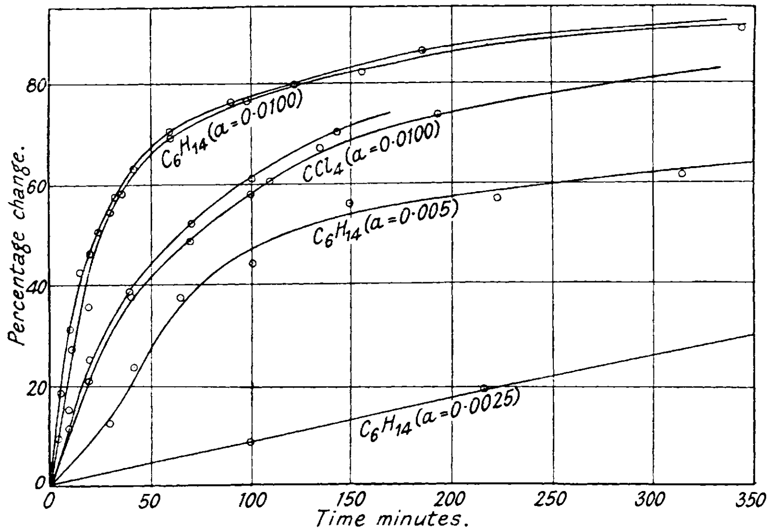


TABLE I.

Interaction of benzoyl chloride and aniline in carbon tetrachloride solution at 25·1°.

Initial concentrations (g.-mol./l.) of benzoyl chloride and of aniline = a and b respectively; k is the bimolecular velocity constant in l./g.-mol./sec.; t = time in *minutes*; x' = change, %.

$$k = \frac{1}{2 \times 60t}\left(\frac{1}{100 - x'} - \frac{1}{100}\right) \times \frac{100}{a}.$$

a = 0·0100, b = 0·0200.			a = 0·0050, b = 0·0100.			a = 0·0025, b = 0·0050.		
x'.	t.	$k \times 10^3$.	x'.	t.	$k \times 10^3$.	x'.	t.	$k \times 10^3$.
10	9	10·3	10	20	9·26	10	56	6·61
20	19	11·0	20	44	9·47	20	126	6·62
30	31	11·5	30	77	9·28	30	208	6·87
40	47·5	11·7	40	124	8·97	40	306	7·26
50	71	11·7	50	190	8·77	50	470	7·09
60	104	12·0	60	276	9·06	60	700	7·15
70	154	12·6	70	400	9·72	70	1100	7·07
80	254	13·1	80	608	10·96			
90	389	10·3						

but the constant tends to fluctuate. The variations are not due to accidental errors, since the values in the table are taken from smoothed curves. With increasing dilution the bimolecular constants fall considerably.

Since in each case $b = 2a$, the constants are derived from the formula $dx/dt = k(a - x)(2a - 2x)$: two molecules of aniline are removed for each molecule of benzoyl chloride. A few experiments were made which showed that, with a doubled concentration of either one or the other reactant, points were obtained lying on the same curve; the significance of this result is discussed in the next section.

Table II shows the influence of temperature, allowance being made as far as possible for the

TABLE II.

Interaction of benzoyl chloride and aniline in carbon tetrachloride solution at various temperatures.

The initial concentrations are benzoyl chloride, 0·0100; aniline, 0·0200; k_x is the value of k, a bimolecular velocity constant, when the percentage change is x.

Temp.	$100k_0$.	$100k_{20}$.	$100k_{40}$.	$100k_{60}$.
56·25°	3·16	3·78	3·71	4·22
42·1	1·99	2·27	2·31	2·55
25·1	1·04	1·10	1·17	1·20
0·07	0·56	0·69	0·83	0·84

E_0 = 7000 cal., E_{20} = 7600 cal., E_{40} = 7200 cal., E_{60} = 7900 cal.

drift in the constants. The values for the three highest temperatures conform to an Arrhenius equation, from which the heats of activation given in the table are calculated. The constant for 0·07° is higher than corresponds to the equation.

These results could be summarised by the statement that the reaction in carbon tetrachloride solution is bimolecular, the constant decreasing in an anomalous way with increasing dilution, and the energy of activation, between 7000 and 8000 calories, being abnormally small for a reaction proceeding at the observed rate.

TABLE III.

Influence of glass surface (p = packed, u = unpacked tube).

Temp. 25·1°. Initial concentrations : benzoyl chloride = 0·0025, aniline = 0·005.

Solvent.	Time.	% Changed.	Solvent.	Time.	% Changed.
Hexane	470	36·3 *p*	CCl_4	460	57·8 *p*
	461	37·8 *u*		444	53·3 *u*
	649	49·8 *p*		670	67·3 *p*
	655	46·0 *u*		670	62·8 *u*

The anomalies are best discussed after consideration of the reaction in hexane solution, where they all appear in a much exaggerated degree.

The Reaction in Hexane Solution.—The influence of dilution becomes remarkably great, as may be seen in Figs. 1 and 2 and Table IV. In the table are given average values for four separate series of experiments at each dilution, each series being of the type illustrated in Fig. 1. By working out the " order of reaction " from the dilution effect in the usual way, a value greater than 3 is found. On the other hand, the bimolecular constants, instead of falling during an experiment at a given initial concentration, as they would if the reaction were really termolecular, actually rise considerably at first and then fall again, as shown in Fig. 2. Thus the reaction is autocatalytic, at least in its earlier stages. The autocatalysis is revealed more clearly in experiments with non-equivalent initial concentrations as in Fig. 3. On the upper curve of this figure the shaded circles refer to experiments in which there were 2 equivs. of benzoyl chloride to one of aniline, each being 0·0100*M*, while the open circles refer to initial concentrations of 0·005*M*-benzoyl chloride and 0·0200*M*-aniline. The fact that there are only minor differences, if any, between the two series shows that the concentrations of the two reactants enter in a symmetrical way into the equation for the reaction rate. Thus we cannot conclude from the dilution effect that the reaction is really termolecular, as it might be, *e.g.*, if the interaction of the benzoyl chloride with the aniline only took place in the presence of a

TABLE IV.

Interaction of benzoyl chloride and aniline in hexane solution at 25·1°. *Influence of dilution.*

Initial concns., g.-mol./l.		Time, mins.					
		$t_{\frac{1}{3}}$.	$t_{\frac{1}{2}}$.	$t_{\frac{3}{4}}$.			
$[C_6H_5\cdot COCl]$.	$[C_6H_5\cdot NH_2]$.		(averages.)		" Order " of reaction.		
0·0100	0·0200	15·3	27·8	80·7	3·2	3·2	3·3
0·0050	0·0100	72	125	398	3·1	3·3	3·2
0·0025	0·0050	303	603	1800			

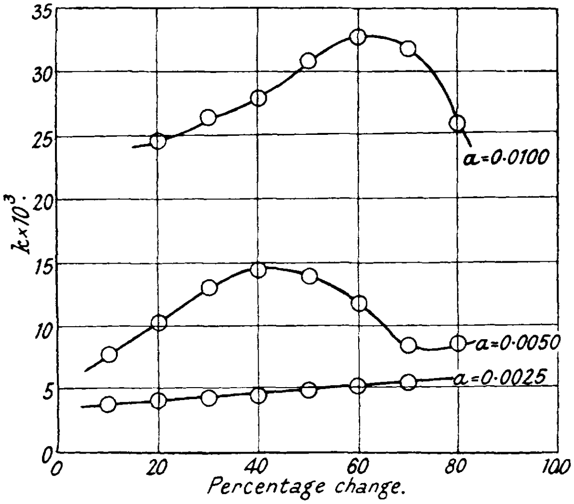
Mean ratio $t_{\frac{1}{2}}/t_{\frac{1}{3}}$ = 1·85 (theoretical for second order, 2·0).
,, ,, $t_{\frac{3}{4}}/t_{\frac{1}{2}}$ = 3·02 (,, ,, ,, 3·0).

second molecule of aniline which could remove as salt the molecule of hydrogen chloride produced, or if an impurity in one of the reactants were a necessary catalyst.

Reactions of this kind are known often to take place much more rapidly in polar than in non-polar solvents; thus the large dilution effect might be interpreted as due to the change in medium caused by the diminished concentration of either reactant, each being assumed to be about equally polar. This would mean that the reaction always required a collision with a third molecule of a polar nature, but that the nature of this third molecule was not all-important. To test this possibility, additions of anisole and of nitrobenzene were made, with the results shown in Fig. 3. The broken curve shows the course of the reaction with 0·005*M*-benzoyl chloride and 0·0100*M*-aniline, and the other two curves show the effect of using as solvent 0·01*M*-solutions of the anisole and nitrobenzene in hexane. The results hardly substantiate the hypothesis of a rather non-specific, but very considerable " medium effect."

FIG. 2.

Interaction of benzoyl chloride and aniline in hexane at 25·1°. *Variation of bimolecular constants.*



The true explanation of the dilution effect appears to be connected with the autocatalysis. If a reaction follows an equation such as $dx/dt = kx(a - x)^2$, then it is easily seen to be of the third order with respect to dilution, but to give bimolecular constants which, for a given dilution, increase with the amount of substance transformed. The kinetics of the autocatalysis are, however, more complicated than the above equation suggests. The only products are aniline hydrochloride, which is quantitatively precipitated, and benzanilide, which is very sparingly soluble in hexane. Previous saturation of the solvent with benzanilide makes no difference (Fig. 3). Thus the autocatalyst must consist of the minute particles of solid product, probably of the highly polar aniline hydrochloride (the other solid product, however, is not excluded). This hypothesis explains the observations. As soon as the benzoyl chloride and aniline are mixed, a faint opalescence begins to appear uniformly throughout the solution. On the nuclei further reaction presumably takes place much more readily. After a time the fine particles coagulate and much of the solid separates and sinks to the bottom of the tube, though fresh supplies of nuclei are being formed all the time, and the solution remains cloudy. Thus the initial rise and subsequent fall of the bimolecular constants in Fig. 2 can be accounted for.

The extent of the autocatalysis must depend upon the relative rates of formation and growth, coagulation and settling of nuclei, diffusion of reactants, and on the adsorption of the various substances present in the solution, which may poison the nuclei or exert all or any of the influences which foreign substances are known to have on crystallisation phenomena. Thus the effect of adding nitrobenzene and anisole can be understood. The rather erratic results obtained at the intermediate dilution can be explained by some degree of uncertainty in the time of coagulation of the particles, the rate of which process, under the conditions in question, becomes commensurate with the rate of reaction.

If the 80 c.c. reaction tubes were filled with 3-mm. bore glass quill tubing, very little difference occurred in the rate of reaction, as may be seen from Table III.

The influence of temperature is represented in Fig. 4. The initial rate of reaction increases somewhat with temperature, but after about 50% change the curves for all temperatures approach one another closely. No energy of activation can be calculated, since the Arrhenius equation is not followed, but the order of magnitude of *E* would be about 4000—5000 calories for the early stages of the reaction, falling to about 500 only for the later stages. This behaviour is consistent with the assumptions made above, the fall in *E* to nearly zero occurring when the rate becomes mainly dependent on the diffusion of the reactants to the solid particles.

DISCUSSION.

In carbon tetrachloride the reaction is more nearly bimolecular than in hexane. The constants drift less and vary with dilution to a much smaller extent. The temperature influence is more regular and considerably greater. Nevertheless, all the peculiarities of the reaction in hexane appear to some degree in carbon tetrachloride, and there seems to be little doubt that the explanation of the abnormal behaviour is the same.

FIG. 3.

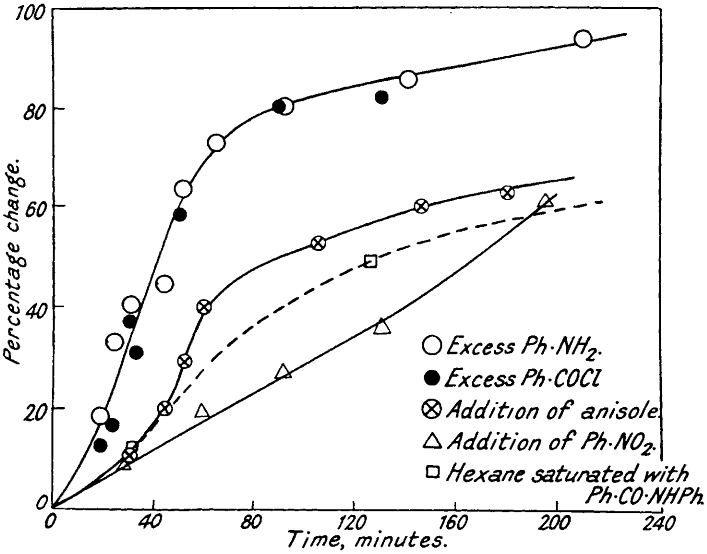
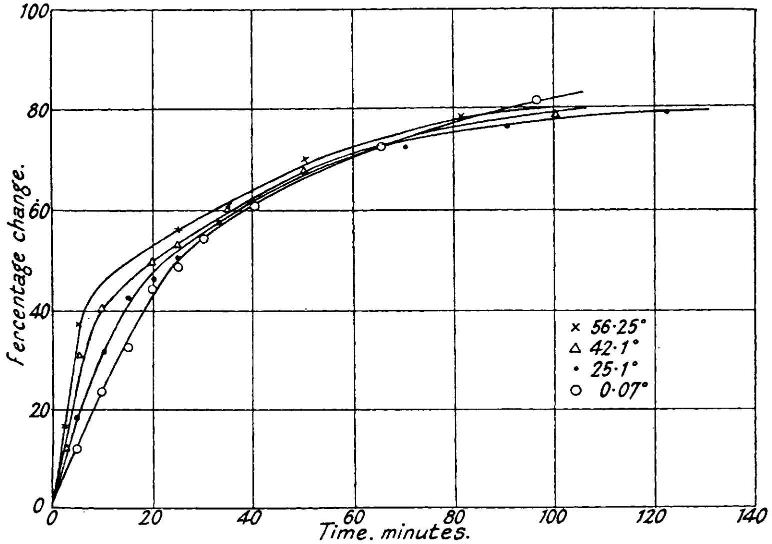


FIG. 4.

Interaction of benzoyl chloride and aniline in hexane at various temperatures.



Several points of theoretical interest now arise. If the unusually large dilution effect in carbon tetrachloride had been slightly smaller, the reaction would have passed for a simple bimolecular change, taking place with measurable speed at ordinary temperatures and possessing a heat of activation of less than 10,000 calories. The rate would thus be several powers of ten less than that calculated from the usual simple exponential formula. We know, however, that when the catalytic influences to which this reaction is subject become more pronounced, as they do in hexane, the apparent energy of activation falls to an extremely small value, and the reaction assumes almost the character of one in which crystal growth is governed by a diffusion process. Thus the question arises whether the low energy of activation in carbon tetrachloride may not be spurious, and indeed, whether other " abnormally slow " reactions may not have hidden diffusion mechanisms even when they appear to be ordinary bimolecular reactions.

This is improbable since not all the reactions of the " slow " type involve the precipitation of a solid product, and, moreover, the Arrhenius equation is sometimes obeyed quite well. Nevertheless, the present results show the need for circumspection. The problem here really is whether the catalytic type of process which predominates in hexane is the only one, or whether it is superposed on an ordinary bimolecular reaction, the latter predominating in carbon tetrachloride. It seems more likely that there are these two processes, and that the varying heat of activation of the reaction in hexane depends upon changes in the relative proportions of the two, while the much more nearly constant value in carbon tetrachloride represents the predominance of the homogeneous process. The assumption that the catalytic reaction plays a much less important part in carbon tetrachloride is consistent with the fact that the total rate is smaller in the latter solvent, except at the greatest dilutions. If this point of view is correct, then the principal reaction in carbon tetrachloride is bimolecular, and takes place at 25° at a speed corresponding to that of a " normal " reaction with an energy of activation of about 20,000 calories. The observed value is under 8000, and even when corrected for any catalytic reaction could scarcely approach 20,000 calories. Thus the reaction definitely belongs to the slow class.

Two final comments on these results may be made. On the one hand, the analogy between the behaviour in hexane and the numerous gas reactions which prefer a heterogeneous to a homogeneous mechanism is worth noting. On the other hand, the action of the solid particles in the present example is possibly to be connected with their polar nature, and if this is so, it is perhaps to be regarded as analogous to the accelerating influence of polar solvents on many reactions.

SUMMARY.

The reaction between benzoyl chloride and aniline in carbon tetrachloride solution is approximately bimolecular, but is anomalous in several respects, especially in showing an unusual fall of the constant with dilution. In hexane the anomalies are accentuated and indicate that the reaction is largely catalysed by the solid particles of the product. The heat of activation is extremely small and variable. Care must be exercised in concluding merely from a small temperature influence that activating collisions are " inefficient," unless complications such as those found in this example are proved to be absent. Although there are similar catalytic effects in carbon tetrachloride solution, which explain the divergences from a simple bimolecular course, yet they are probably subsidiary to the homogeneous reaction, which itself is much slower than the possible rate of activation, in common with a number of other reactions between neutral molecules in solution.

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