

A KINETIC STUDY OF THE MECHANISM OF
O-ACYLATION IN PYRIDINE

by

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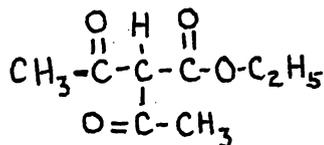
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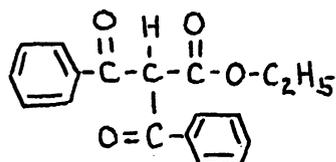
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the isomeric C-acyl derivatives, ethyl diacetylacetate (VII) and ethyl dibenzoylacetate (VIII), respectively, is formed in the reaction. Indeed, there is no known case of the formation of a C-acyl derivative in the reaction of a β -keto ester with an acid chloride in pyridine solution.

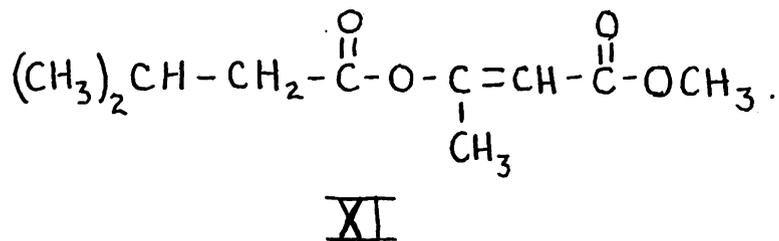
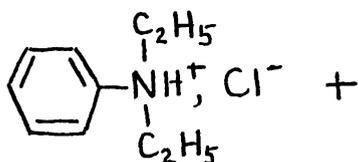
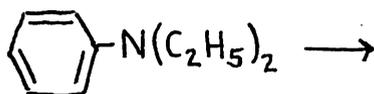
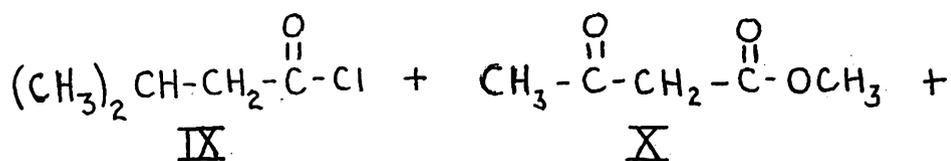


VII

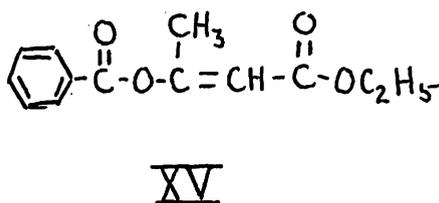
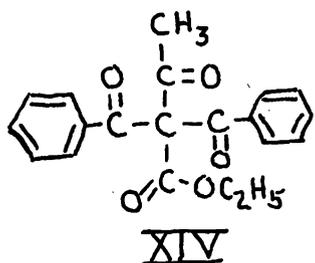
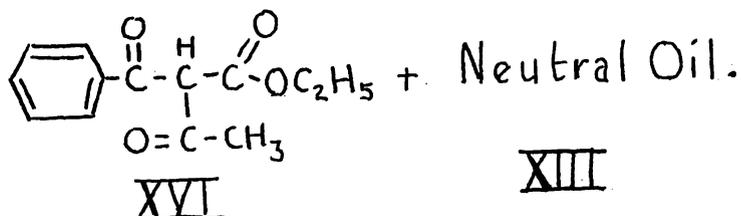
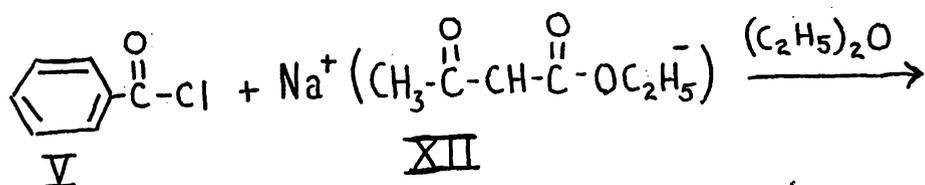


VIII

The situation with respect to the use of other tertiary amines as the solvent is somewhat confused. Claisen and Haase (3) reported that the use of dimethylaniline and antipyrine led to the formation of O-acyl derivatives, but they gave no experimental details. Bouveault and Bongert (4) prepared methyl O-isovalerylacetoacetate (XI) in 55% yield by the reaction of isovaleryl chloride (IX) with methyl acetoacetate (X) in diethylaniline, but they neglected to indicate whether any of the C-acyl derivative was also formed. They did make a qualitative statement, however, to the effect that the conversion to the O-acyl derivative is more complete in pyridine solution than in diethylaniline.

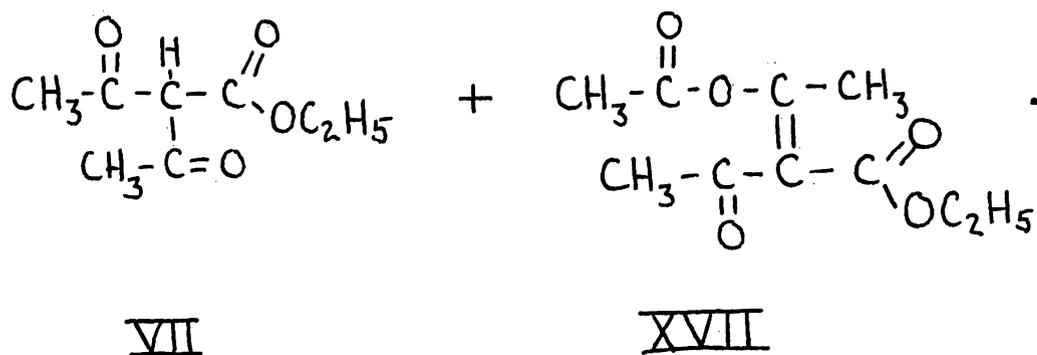
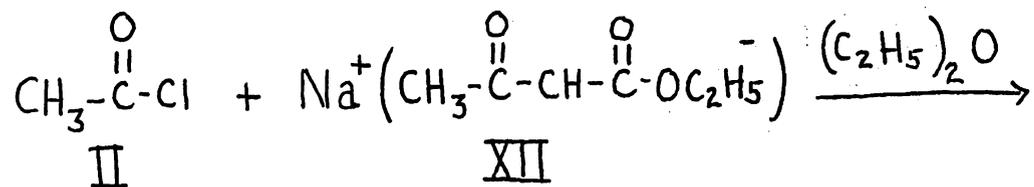


O-acyl derivatives were first discovered as minor products of the action of acid chlorides on the sodium salts of β -keto esters (5, 6, 7). A neutral oil (XIII), obtained as one of the products of the reaction of benzoyl chloride (V) with the sodium salt (XII) of ethyl acetoacetate, was originally thought (5) to be ethyl dibenzoylacetoacetate (XIV). It was later shown (7) that the oil (XIII) had been insufficiently purified before analysis, and that it actually consisted, in part at least, of ethyl O-benzoylacetoacetate (XV).

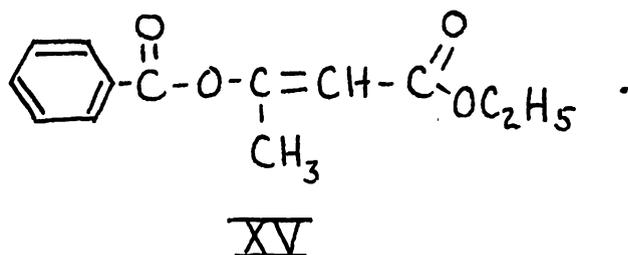
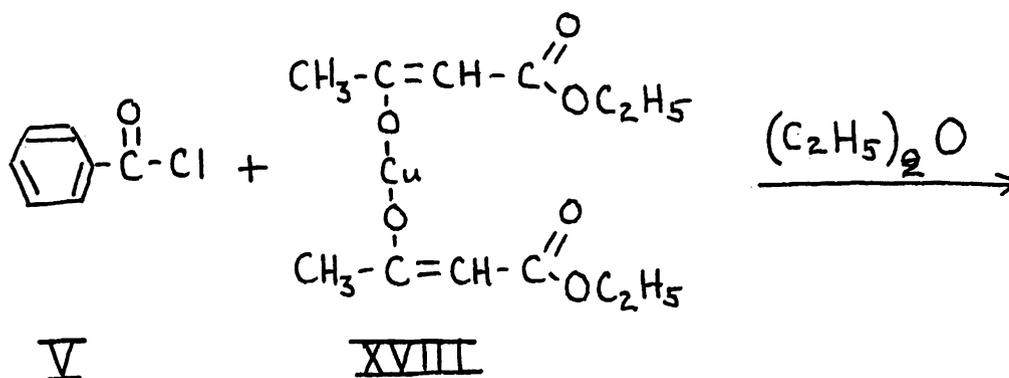


In the process of purification of XIII by fractional distillation (6), only 7 g. of pure XV was isolated from 51 g. of crude neutral product. More recent workers (8) have found that, in the reaction of acetyl chloride (II) with the sodium salt (XII) of ethyl acetoacetate, the O-acyl derivative III was formed only in minute, and in some cases undetectable, quantities. The principal product was the O-acyl derivative, ethyl diacetylacetate (VII). Ethyl O-acetyldiacetylacetate (XVII) was the only O-acylated product to be formed in any quantity. The latter was formed by O-acylation of the diacetyl ester (VII) with acetyl chloride. The reaction of benzoyl chloride (V) with the sodium salt (XII) of ethyl acetoacetate gave a detectable quantity

of ethyl O-benzoylacetoacetate (VI), but it represented only a small fraction of the reaction products.

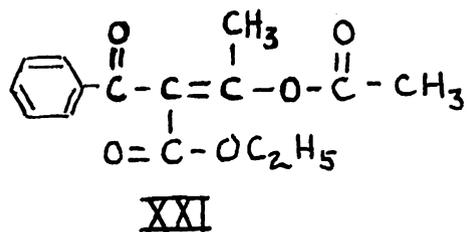
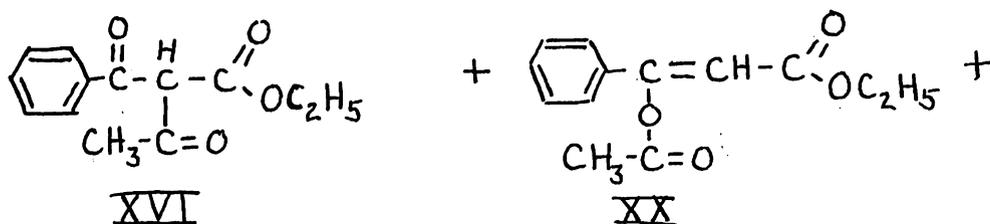
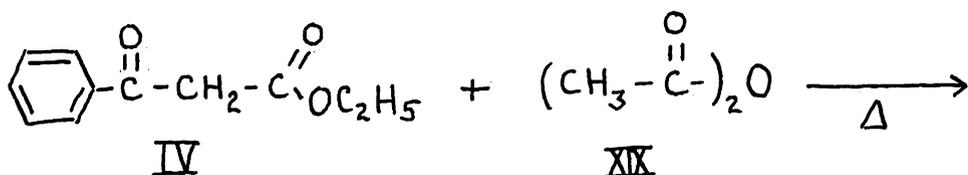


The copper and lead salts of β -keto esters were also found (10) to yield O-acyl derivatives on reaction with acid chlorides. Upon addition of benzoyl chloride (V) to an ethereal suspension of the copper salt (XVIII) of ethyl acetoacetate, there was formed 50% of the theoretical amount of ethyl O-benzoylacetoacetate (XV). This result has been confirmed by Michael and Carlson (9) for benzoyl chloride (V) and a similar result has been observed for acetyl chloride (II).



These authors found the yield of O-acyl derivative to be somewhat greater when benzoyl chloride (V) was used.

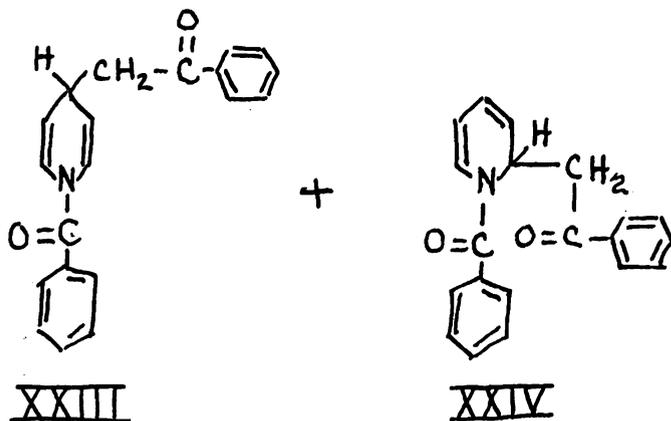
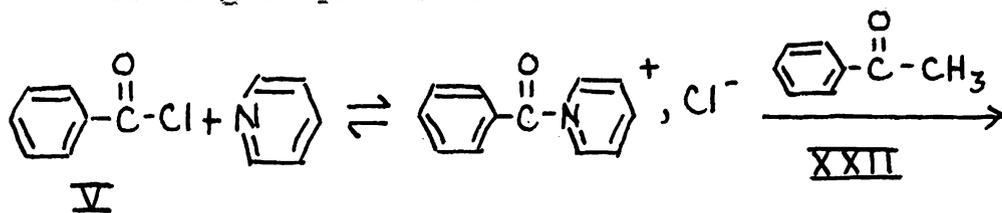
The reaction of ethyl benzoylacetate (IV) with acetic anhydride (XIX) (11) has also been studied. The resulting neutral fraction consisted of ethyl O-acetylbenzoylacetate (XX) and ethyl O-acetylbenzoylacetate (XXI). The major product was the alkali-soluble ethyl benzoylacetate (XVI).



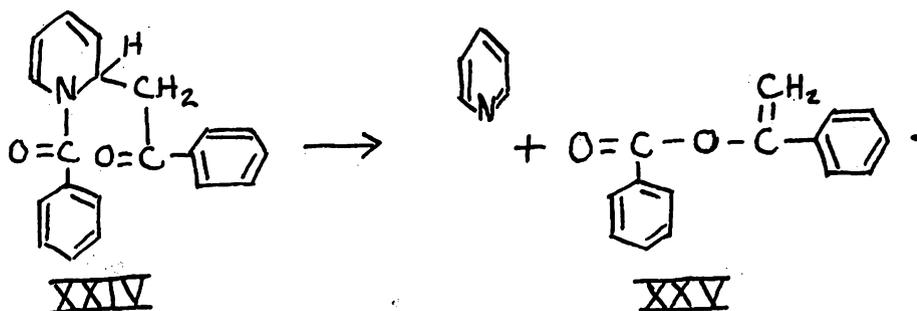
It would be desirable that a mechanism for the reaction in pyridine embody an explanation of the exclusive (within experimental limits) formation of the O-acyl derivative. Quinoline is so similar to pyridine in structure that any mechanism might easily be extended to include it. Dimethylaniline, although a tertiary amine, is quite different structurally from pyridine and quinoline. For the former to be included in a general mechanism for exclusive O-acylation, the mechanism must be free of dependence upon the structure of the base. There is good reason to believe, however, that both dimethylaniline and quinoline do not give the O-acyl product exclusively, but

form the C-acyl derivative as well (14). Therefore, the following discussion will be restricted to reactions carried out in pyridine solution.

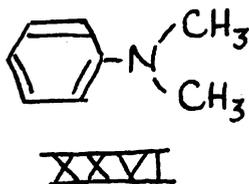
A mechanism which is strongly dependent upon the structure of the tertiary amine used has recently been proposed (12). In an investigation of the reaction of benzoyl chloride (V) and acetophenone (XXII) in pyridine there was obtained, among other products, 1-benzoyl-4-phenacyl-1, 4-dihydropyridine (XXIII) and O-benzoylaceto-phenone (XXVII). Since no 1-benzoyl-2-phenacyl-1, 2-dihydropyridine (XXIV) was isolated, it was postulated that the following steps occurred:



Compound XXIV then rearranges to yield XXV.



XXV was shown not to be an intermediate in the formation of XXIII. The authors suggested that the above mechanism would also be directly applicable to the β -keto ester reaction. Dimethylaniline (XXVI) could not participate in such a mechanism, since the addition product analogous to XXIV could not be formed.



It was felt that an investigation of the kinetics of the reaction of ethyl benzoylacetate with benzoyl chloride in pyridine solution should yield significant, if not conclusive, information concerning the mechanism. If several mechanisms appear possible, the dependence of the rate upon the concentrations of the reactants may be predicted for each.

If the rate of a reaction involving the chemical species A, B, C, ..., is found experimentally to be given by

$$\text{rate} = k (A)^l (B)^m (C)^n \dots$$

then the order of the reaction is defined as the sum of the exponents.

$$\text{Order} = l + m + n + \dots$$

Any of the exponents may be positive, negative, integral or not. Further, two different orders may be defined. In the measurement of the rate of a reaction, the only concentrations known with certainty are those at the beginning of the reaction. The order obtained from a comparison of the initial rates and concentrations has been designated (13) the "true" order of the reaction.

The order determined from the variation of rate with concentrations within one experiment is the order with respect to time. This may or may not be equal to the "true" order. For the comprehensive study of the mechanism of a reaction, both orders should be obtained; the first would reveal the influence of any species whose concentration remains constant within one experiment, the second would reveal any effect of the products on the rate (inhibition or acceleration).

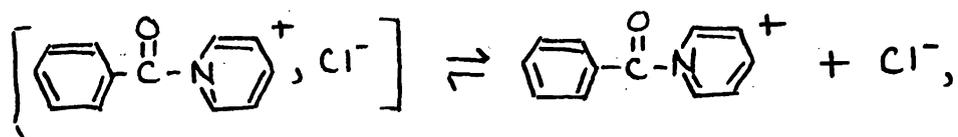
In order to construct a group of tentative mechanisms knowledge concerning the states of the reactants and pro-

ducts in pyridine solution is desirable. Acid chlorides form addition compounds with pyridine and other tertiary amines (14, 15, 16), which are salt-like and powerful acylating agents. Adkins and Thompson (15) have prepared α -furoylpyridinium chloride and propionyltriethylammonium chloride in analytically pure form (i.e., chlorine analyses within $\pm 0.2\%$ of the theoretical value were obtained) whereas they were unable for the sets acetyl chloride-pyridine, acetyl chloride-triethylamine, benzoyl-chloride-pyridine, and propionyl chloride-pyridine, to obtain products giving chloride analyses closer than $\pm 2\%$ to the calculated value. The ortho-, meta- and para-nitrobenzoylpyridinium chlorides have been prepared analytically pure (14). A great deal of trouble is encountered in keeping these salts dry once they are obtained, as they are all very hygroscopic. The benzoylpyridinium chloride prepared by Adkins and Thompson (15) undoubtedly had been contaminated with water. The two react immediately to form benzoic acid, benzoic anhydride and pyridinium chloride.

M. M. Davies (17) studied the conductance of solutions of benzoyl chloride in pyridine. There was an agreement of $\pm 1\%$ in the specific conductivities between two sets of his data. Two other sets were discarded, however, as the specific conductivities were 5-10% higher than the other values. The presence of trace amounts of water in the solvent was given as a possible cause for such erratic behavior. The

pyridine used was carefully purified by distillation first from potassium hydroxide and then from alumina gel. To remove the last trace of moisture, several pyridine samples were electrolyzed by the method of von Hevesy (18) and then distilled. The specific conductivity of the pyridine treated in this manner was lowered from $\kappa = 6 \times 10^{-8}$ to $\kappa = 1.5 \times 10^{-8}$ mhos. The electrolyzed pyridine was not used as solvent in the determination of the specific conductivities of benzoyl chloride in pyridine. Using the sets of data agreeing within $\pm 1\%$, Davies calculated the limiting equivalent conductance of benzoyl chloride in pyridine to be $\Lambda_0 = 32.0 \pm 0.5$ mhos/M/l. at 25°C .

For the process



the dissociation constant was given as $K = (1.30 \pm 0.02) \times 10^{-5}$ at 25°C . The quantity in brackets represents the ion-pair. Pyridine has a relatively low dielectric constant, 12.01 at 25°C . (19), compared with that of water, 78 at the same temperature (20). Salts which are strong electrolytes (completely ionized) in water solution may behave like weak electrolytes when dissolved in solvents of lower dielectric constant (21). In the current explanation of this effect, the notion of complete ionization is retained. The oppositely

charged ions are considered to pair off under the influence of electrostatic forces, no chemical bond being formed. A relatively small number of unpaired ions remain to contribute to the conductivity. The dissociation constant for pyridinium nitrate in pyridine at 25° C. has been determined conductometrically (22) to be $K = 5.1 \times 10^{-5}$. Davies' value would thus seem to be of the right order of magnitude for a strong electrolyte in pyridine.

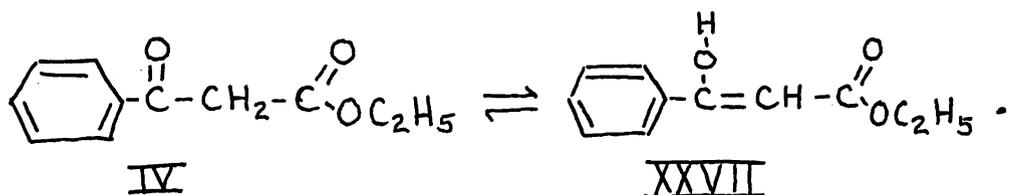
Exposure to light may have contributed to the erratic conductivity of benzoyl chloride in pyridine. Such an effect was first reported by Dehn and Ball (16), who were attempting to prepare benzoylpyridinium chloride in ether. They observed that the crystallization of the salt was accelerated by sunlight. Other evidence has been obtained in this laboratory. Irradiation with ultra-violet light increases the specific conductivity of a pyridine solution of benzoyl chloride, as may be seen in graph V. The solution appeared to be just as strong an acylating agent before as after irradiation, however. There is a need for further investigation of this effect.

The strong acetylating property of acetyl chloride in pyridine has been utilized (23) in a rapid method of analysis of alcohols and phenols. The standard method calls for the use of acetic anhydride in pyridine. The substitution of acetyl chloride shortens the time necessary for the reaction from one hour to 20 minutes. The basis of the

analysis is that, once the acetylation reaction is complete, the addition of water converts all unused acetyl chloride to acetic acid and hydrochloric acid. Since hydrochloric acid is also one of the products of the acetylation reaction, the quantity of alcohol or phenol present is determined from the amount of potential acetic acid used in the acylation. In the analysis of such substances as ethanol, decanol-1, and cresol, the absolute accuracy (95-99% of the theoretical consumption of acetyl chloride) is said to be as good as the anhydride method, but the precision is somewhat less ($\pm 0.5\%$ compared to $\pm 0.2\%$). The interference of aldehydes was also less in this than in the older method.

Contrary to what one would expect, there is very little information in the literature regarding pyridine solutions of hydrochloric acid. Pyridine hydrochloride, of course, is one of the products of the reaction of a β -keto ester and an acid chloride. Hlasko (24) determined the conductance of pyridinium chloride at only one concentration, for the purpose of comparison with other salts at equivalent concentrations. Both the conductance and viscosity at various concentrations were determined recently (25), but in the temperature range $95^{\circ} - 115^{\circ} \text{C}$. In no case were the concentrations low enough (10^{-4} to 10^{-5} M.) to allow an estimate of the dissociation constant.

Ethyl benzoylacetate (IV) may exist in both the keto (IV) and the enol (XXVII) form.



There are no explicit data regarding the extent of enolization in pyridine, but a fair idea may be obtained from the data of K. H. Meyer and P. G. Wilson (26). From the latter, it may be inferred that, other things being equal, the more basic the solvent, the less the enolization. Also the more polar the solvent, the less the enolization. Pyridine is more basic than water ($K_b = 1.6 \times 10^{-9}$ in water at $25^\circ \text{C}.$) (27), but it has a lower dielectric constant than water. As a very crude estimate, one could assume that these two effects would balance one another, so that the ratio, (enol)/(keto), in pyridine would be similar to that in water, in which it is approximately 10^{-2} . β -keto esters also act as weak acids. The extent of ionization of ethyl benzoylacetate (IV) in pyridine is not known. However, according to measurements made in this laboratory the equivalent conductance of a 2.09×10^{-1} M. solution in pyridine at $25^\circ \text{C}.$ was only $2.24 \times 10^{-3} \text{ cm}^2 \text{ mhos/eq./l.}$ The equivalent conductance of a solution of benzoyl chloride in pyridine of the same

molarity was 2.10×10^{-1} cmhos/eq./l. It might be said that a solution of IV in pyridine is essentially un-ionized, and is predominantly in the keto form.

The O-acylated product of the reaction, ethyl β -benzoxycinnamate (VI), does not exhibit keto-enol tautomerism, nor does it have any other remarkable characteristics. It will be considered to exist only in the structure shown.

Several possible mechanisms for the reaction of benzoyl chloride with ethyl benzoylacetate in pyridine solution will now be considered. Provided that enolization of the ester, ionization of the ester and formation of benzoylpyridinium chloride are relatively fast and reversible reactions, the following four reactions might be considered as reasonable possibilities for the slow, or rate determining, step:



$$\text{rate} = k' (\phi\text{COCl}) (\text{enol}) = k (\phi\text{COCl}) (\text{Ester, total}),$$

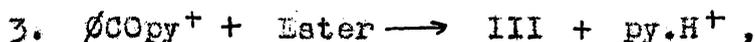
$$\text{since } (\text{enol})/(\text{keto}) = K \approx 10^{-2};$$



$$\text{rate} = k' (\phi\text{COCl}) (\text{ester anion}),$$

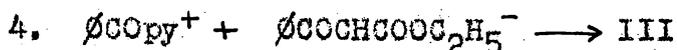
$$\text{but } (\text{ester anion}) (\text{pyH}^{+})/(\text{ester}) = K_3,$$

$$\text{therefore rate} = k (\phi\text{COCl}) (\text{ester})/(\text{pyH}^{+});$$



$$\text{rate} = k' (\phi\text{COpy}^{+}) (\text{Ester}) = k (\phi\text{COpy}^{+}, \text{Cl}^{-}) (\text{ester})/(\text{Cl}^{-}),$$

$$\text{since } K_1 = (\phi\text{COpy}^{+}) (\text{Cl}^{-})/(\phi\text{COpy}^{+}, \text{Cl}^{-});$$



rate = $k'(\phi\text{COPy}^+)$ (ester anion) or, multiplying both numerator and denominator by $(\text{Cl}^-)(\text{pyH}^+)$,

$$\text{rate} = k''(\phi\text{COPy}^+)(\text{Cl}^-)(\text{ester anion})(\text{pyH}^+)/(\text{pyH}^+)(\text{Cl}^-),$$

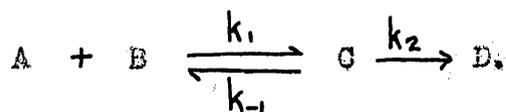
but since $K_1 = (\phi\text{COPy}^+)(\text{Cl}^-)/(\phi\text{COPy}^+, \text{Cl}^-)$,

$$K_3 = (\text{ester anion})(\text{pyH}^+)/(\text{ester}), \text{ and}$$

$$K_2 = (\text{pyH}^+)(\text{Cl}^-)/(\text{pyH}^+, \text{Cl}^-),$$

then $\text{rate} = k(\phi\text{COPy}^+, \text{Cl}^-)(\text{ester})/(\text{pyH}^+, \text{Cl}^-)$.

In none of the above possible mechanisms was the precise nature of the transition state or a possible intermediate mentioned. The implication is that in the above cases, any intermediate is too short-lived to be detected by means presently at hand. It would seem, in this event, that any intermediate compatible with present chemical theory would be acceptable. Under some conditions, however, the nature of an intermediate might affect the order of a reaction. Consider the case of two molecules, A and B, reacting to form D via an intermediate, C.



There are several extreme cases which might occur.

a) $k_1 \gg k_2$, and $k_{-1} \gg k_2$,

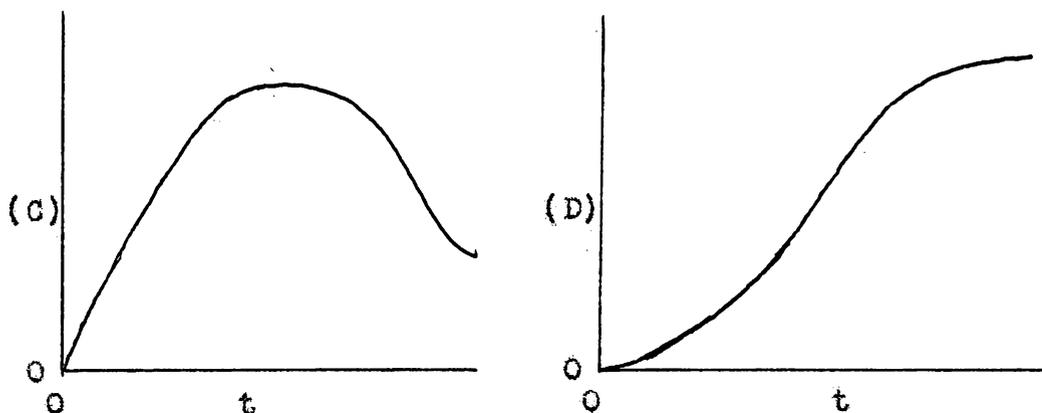
then $(\text{C}) = K(\text{A})(\text{B})$, and no effect of the intermediate will be observed.

b) If $k_1 \gg k_{-1}$, and k_1 is of the same order of magnitude as k_2 ,

then $d(C)/dt = k_1 (A) (B) - k_2(C)$,

while $d(D)/dt = k_2(C)$

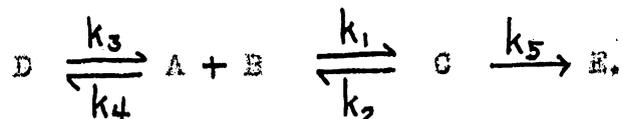
and (C) and (D) would vary with time as indicated in the following graphs:



c) If $k_2 \gg k_1$ and $k_2 \gg k_{-1}$

then $d(D)/dt = k_1 (A) (B)$ and no effect of the intermediate would be observed.

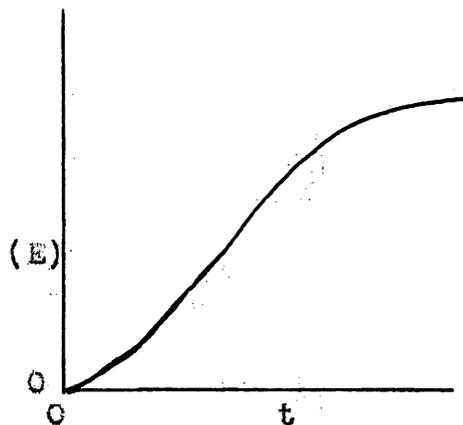
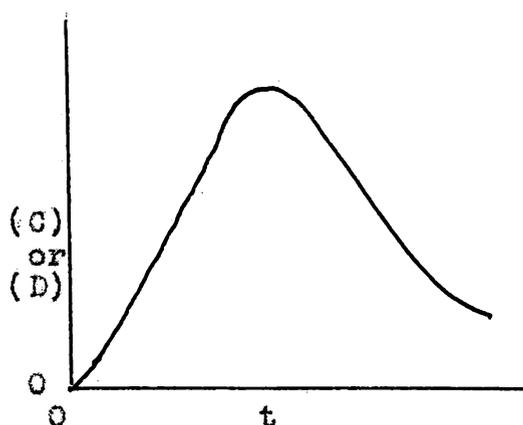
Of special interest with regard to the postulated mechanism (12) described on page , is the system



Let A represent the benzoylpyridinium ion, B the β -keto ester, C the 2-addition intermediate analogous to XXIV, D the 4-addition intermediate analogous to XXIII, and E the products, the O-acyl derivative and pyridinium chloride.

There are two principal cases to be considered. If k_1 , k_4 and k_5 are all of the same order of magnitude, then the concentrations of the species C, D and E will vary as shown in

the following graphs. The solution of the set of differential equations



$$d(D)/dt = k_3 (A)(B) - k_4 (D),$$

$$d(C)/dt = k_1 (A)(B) - (k_2 + k_5) (C),$$

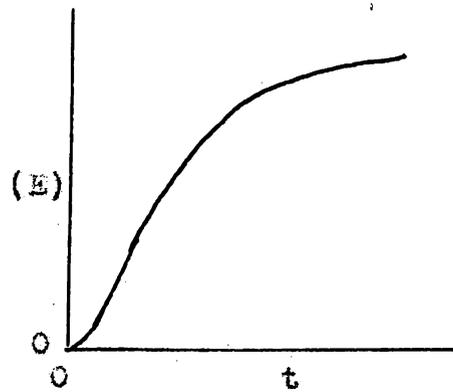
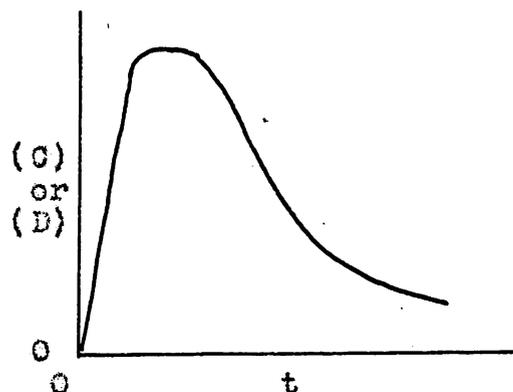
$$d(A)/dt = d(B)/dt = k_2 (C) + k_3 (D) - (k_1 + k_4)(A)(B),$$

and $d(E)/dt = k_5 (C),$

for (E) in terms of time and the initial concentrations of A and B would be exceedingly difficult.

If k_1 and $k_4 \gg k_2, k_3$ and $k_5,$

the concentrations of C, D, and E will vary as shown below.



If the above is the case, then the system, after the first

instant may be considered as



The differential equation for the rate of formation of C is $d(C)/dt = k_3 (D) - k_5 (C)$, while that for D is $d(D)/dt = -k_3 (D)$.

The solution of the above two equations for (C) at time t, is $(C) = (C)_0 \exp(-k_5 t) + K(D)_0 \{ \exp(-k_5 t) - \exp(-k_3 t) \}$, where (C)₀ is the maximum concentration of C near t = 0, (D)₀ is the maximum concentration of D near t = 0, and $K = k_5 / (k_3 - k_5)$. It is now assumed that

$$(D)_0 = K' (C)_0.$$

Then, since

$$(E) = (C)_0 + (D)_0 - \{(C) + (D)\}$$

therefore,

$$(E) = (C)_0 \left\{ (1+K') + (KK'-1)\exp(-k_3 t) - (K' - KK')\exp(-k_5 t) \right\}.$$

There are five parameters to be fixed in this equation. That the experimental results could be fitted to such an expression would not be surprising. Neither would it be proof that the mechanism assumed was operative.

Limitations on the Concentration Range

The reaction of benzoyl chloride with ethyl benzoyl-acetate in pyridine forms no products other than the O-acetylated compound, ethyl β-benzoxycinnamate, and hydrochloric acid. The reaction is thus free of side reactions. It also goes to completion. In a preliminary experiment,

a pyridine solution, 4.13×10^{-2} M. in benzoyl chloride and 2.78×10^{-2} M. in the ester, was allowed to stand overnight at 25°C . Analysis of this mixture showed that the final concentration of benzoyl chloride was 1.36×10^{-2} M. The latter had thus reacted with all the ester. There are other aspects of the reaction, however, which place limitations on the concentration range within which it can be studied.

The reaction has been found to be so fast that an upper limit on the concentrations of both reactants must be set. The speed of the reaction at concentrations much higher than 5×10^{-2} M. is so great that it is almost 50% complete before the first measurement can be made (see data on page).

The purification procedure employed for the pyridine used in this work (see page 23) does not remove the last traces of moisture. A small amount of water might also be picked up from the atmosphere in the transfer of the solutions. The net result is a concentration of residual water approximately 10^{-2} M. Benzoyl chloride in pyridine immediately reacts with this, forming benzoic acid and hydrochloric acid (for the absence of benzoic anhydride, see page 28). Thus, if the benzoyl chloride concentration is below 10^{-2} M., it is all destroyed before being mixed with the ester solution.

Analytical Methods

There are several possible analytical methods, such as spectrophotometric, polarographic, conductometric, meas-

surement of change of refractive index, dilatometric, and acid-base titrations, which might have been used to follow the reaction. Of these, only the polarographic, conductometric and titration methods were seriously considered. Spectrophotometric methods were rejected because of the similarity of the organic products and reactants. None of the substances in the system is highly colored. Thus it would have been necessary to use the ultra-violet region of the spectrum. Here, the principal absorbing bands would be those due to the benzene and pyridine nuclei, which are common to both the reactants and products and therefore are of no value for analytical purposes.

Analyses of benzoyl chloride in pyridine were attempted polarographically, with lithium chloride as a supporting electrolyte. Maxima were obtained which could not be suppressed by the use of the usual agents. This method was therefore abandoned.

The method of Smith and Bryant (23) was the one finally adapted to the system under study. The sample of reaction mixture removed for analysis was quenched in water, and then titrated with standard sodium hydroxide solution to the phenolphthalein end-point. It was found that a correction was necessary for the amount of base consumed in neutralizing the unreacted β -keto-ester.

II. EXPERIMENTAL

Preparation and Purification of Materials

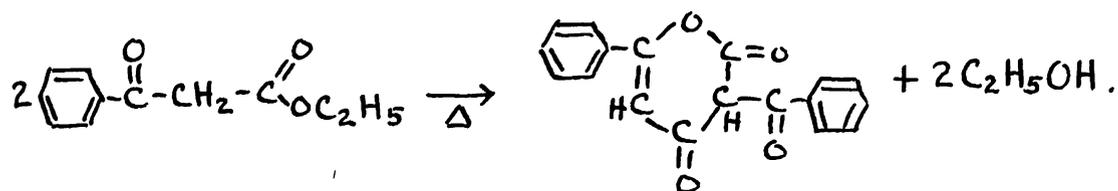
Pyridine. (Baker's C. P. grade) was refluxed over potassium hydroxide pellets for 24 hours and distilled, the first 100 ml. of distillate being rejected. The fraction retained, about 1.5 l., was then placed in a two-liter round-bottomed flask with boiling chips. One-third of a pound of barium oxide (G. Frederick Smith Co.) per liter of pyridine was added. Barium oxide was chosen as the final dehydrating agent since it has been shown (29) to remove traces of moisture more thoroughly than alumina and other common drying agents. The flask containing the pyridine was then placed under a four-foot packed column, and refluxed under an atmosphere of nitrogen for at least 48 hours. When distillation was commenced, the first 100 ml. of distillate was rejected. The pyridine taken off after this had a constant boiling point ($\pm 0.1^{\circ}\text{C}$.). The actual value varied (114-115.5 $^{\circ}\text{C}$.) from day to day with the atmospheric pressure. The latter varied from 730 mm. to 745 mm. The boiling point of pyridine has been determined (30) as 115.5 $^{\circ}\text{C}$. at 760 mm., $\Delta t/\Delta p = 0.43^{\circ}\text{C}$. for 10 mm. changes.

In the kinetic runs the amount of both residual water in the pyridine and that picked up during transfer of solutions was obtained as the difference between the total amount of benzoyl chloride present initially and that which disappeared during the reaction. The concentration of the other

reactant was always made greater than that of benzoyl chloride. The water in the pyridine was in the range $1-3 \times 10^{-2} M.$, representing an impurity of 0.02-0.06% by weight.

Benzoyl chloride (Baker's C. P. grade) was distilled at 6-7 mm. pressure, boiling point $73^{\circ} C.$ Extrapolation of the values given by Timmermans (31) gives the boiling point at this pressure as $72.6^{\circ} C.$ The 40 cm. by 1.5 cm. column was packed with 2 mm. glass beads. The distillate was sealed in a glass-stoppered bottle with sealing wax, and the bottle stored in a desiccator over anhydrous calcium chloride.

Ethyl benzoylacetate (Eastman red label) was distilled at 6 mm. pressure, the fraction boiling in the range $142-143^{\circ} C.$ being taken. The literature value for the boiling point at 6 mm. is $142-148^{\circ} C.$ (32). A self-condensation reaction of the ester occurred in the still-pot during distillation. The following reaction is known to occur upon heating ethyl benzoylacetate (33):



Ethyl alcohol was thus present in the vapor in the still-head. At the low pressure used, very little of the alcohol would have been condensed with the ester. As a

precaution, the distillate was kept at low pressure for two or three hours after heating of the still had been stopped.

Ethyl acetoacetate (Eastman red label) was distilled at 6 mm. pressure, the fraction boiling in the range 60-61°C. being taken. An interpolation between the boiling points at two different pressures was made as a comparison. At 2 mm., the b. p. is 39-40°C. (34). At 20 mm., the boiling point is 80°C. (35). $\Delta t/\Delta \log p$ is thus 40. The interpolated value for 6 mm. is 59°C.

Methyl alcohol (Baker's C. P. grade) was purified by reaction with magnesium (36). The conversion of added magnesium to magnesium methoxide was hastened by refluxing. When all the magnesium had been consumed, the mixture was refluxed for two days, and then distilled at atmospheric pressure. The first 100 ml. of distillate was discarded. That fraction boiling at 64°C. at 740 mm. pressure was collected. The literature b. p. at that pressure is 63.9°C. (37).

Hexanol-1 was purified by distillation. The b. p. was 156-157°C. at 739 mm. The literature value is 156.8°C. at 739 mm. (38).

Pyridinium chloride was prepared by passing anhydrous hydrogen chloride gas through a benzene solution of pyridine. The salt precipitated in the form of white needles. The crude product was recrystallized from absolute ethyl alcohol and dried over phosphorus pentoxide in a vacuum desiccator for three days. The chloride content was determined

gravimetrically as 30.48 and 30.67% compared to 30.67% calculated for pyridinium chloride.

Pyridinium nitrate was prepared by the method of Fincussohn (39). The salt was recrystallized twice from absolute ethyl alcohol and dried under vacuum over phosphorus pentoxide. Titration of weighed portions with standard sodium hydroxide gave equivalent weights of 141.4 and 141.7, compared to 142.1 calculated for pyridinium nitrate.

Lithium chloride (Baker's C. P. grade) was dried over phosphorus pentoxide in a vacuum desiccator for three days. The lithium chloride was then used directly.

Benzoyl Chloride in Pyridine

The transfer of benzoyl chloride, in a weighing buret, to the flask containing pyridine was carried out in a dry-box under an atmosphere of dried nitrogen. The method of analysis adopted for benzoyl chloride in pyridine solution was a variation of that of Smith and Bryant (23). A 5.000 ml. aliquot of the solution was pipetted into 10.0 ml. of water and then titrated to the phenolphthalein end-point with standard sodium hydroxide solution. All titrations were carried out using a five-ml. microburet, graduated in 0.01 ml./division. The reaction upon which the titration is based is:

That the method is suitable may be seen from the results in Table I. The percent average deviation was $\pm 0.5\%$.

Since the buret had to be refilled twice, the final volume reading was based upon six buret readings. This would result in an uncertainty of ± 0.006 ml., or $\pm 0.1\%$. The greatest difficulty came in determining the end-point.

Titration of Ethyl Benzoylacetate-Pyridine Mixtures

In the course of the experiments, it was found that solutions of ethyl benzoylacetate, pyridine and water were acidic enough to require measurable quantities of sodium hydroxide solution to neutralize them to the phenolphthalein end-point. By keeping the pyridine-water ratio approximately constant, the amount of base required could be simply related to the concentration of the ester. In Table II, the results of such experiments are compiled. In the table, b is the molar concentration of the ester in pyridine, and N is the normality of titratable hydrogen ion in the ester solution. In all cases, solutions of the esters were prepared in the dry-box. A 5.000 ml. sample of each solution was added to 10.0 ml. of water, and titrated with standard sodium hydroxide solution to the phenolphthalein end-point. The ml. of base used in each case was not given since the normality of the base varied from experiment to experiment. Each of the values under N is the average of three titrations. The endpoint was faint and difficult to determine. The constancy of the quantity $N/(b-N)$ may be explained by

Table I

Titration of 5.000 ml. of 0.01114 M. COC_2H_5 in Pyridine
with 0.01007 N. base.

Sample	ml. base	N(observed)	N(calculated)	Deviation
1	11.104	2.235×10^{-2}	2.228×10^{-2}	+0.007
2	11.108	2.236	2.228	+0.008
3	11.012	2.215	2.228	-0.013
4*	11.140	2.244	2.228	+0.016

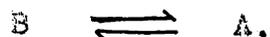
average deviation ± 0.011

* Some of the product, ethyl β -benzoxycinnamate, was added.

Table II

No.	b	N(observed)	N/(b-N)
1	2.02×10^{-1}	1.84×10^{-2}	1.00×10^{-1}
2	1.64	1.30	0.86
3	1.48	1.30	0.96
4	1.33	1.00	0.81
5	0.620	0.583	1.04
6	1.39	1.18	0.93
7	2.82	2.00	0.76
8	1.85	1.51	0.89
9	2.40	1.97	0.89
average			0.905 ± 0.07
average deviation			$\pm 8\%$

assuming an equilibrium to exist between the acidic form (A) of the ester, and some neutral form (B). Thus



where the rates of interconversion are slow compared to the time necessary for titration, and an equilibrium constant K may be defined as

$$K = (A)/(B) = \alpha/(1-\alpha) \quad N/(b-N).$$

α is the fraction of ester in the acidic form A. Taking the average of $N/(b-N)$ in the table as K , then

$$K = 0.905 \times 10^{-1}.$$

Then

$$\alpha = K/(1+K) = 0.083.$$

In the titrations of the system benzoic-acid-hydrochloric acid-pyridine-ethyl benzoylacetate-water, the value of α , determined above, was used to calculate the fraction of the observed normality due to the ethyl benzoylacetate.

Rates of Reaction of Benzoyl Chloride with Ethyl Benzoylacetate in Pyridine at 25°C.

Procedure. All pieces of glassware (used in the following runs) were rinsed with distilled water and dried in a vacuum oven. Solutions (approximately 100 g. and 50 g. respectively) of benzoyl chloride and ethyl benzoylacetate in pyridine were prepared separately in 100 ml. glass-

stoppered volumetric flasks, in the dry-box. Approximately 70 g. of the benzoyl chloride solution was transferred to flask A of the reaction cell (Fig. 1). About 20 g. of the ester solution was placed in the side-arm, B, (Fig. 1). Dow-Corning high-vacuum glass lubricant was used on the standard-taper joints to obtain moisture-proof seals and to lessen the chance of the reaction cell coming apart during a run. Rubber bands provided a mechanical fastening for the various parts. The cell, with the stop-cock C closed, and the stopper D in place, was then removed from the dry-box and placed in a well-stirred water-bath. The relative positions shown in Fig. 1 were maintained throughout this operation. The bath temperature was kept at $25.00 \pm 0.025^{\circ}\text{C}.$, as determined with a Beckmann thermometer which had been checked against an Anschutz thermometer calibrated by the National Bureau of Standards. At least, one hour was allowed for the solution to come to temperature equilibrium.

During this time, the flasks with the remaining benzoyl chloride and ester solutions were weighed to determine the amounts transferred to the cell. The final concentrations of reactants were calculated in the following manner:

$$\text{wt. of } \text{C}_6\text{H}_5\text{COCl in the cell} = \text{wt. of } \text{C}_6\text{H}_5\text{COCl (in flask originally)} \times \frac{\text{wt. of solution added to cell.}}{\text{original wt. of solution}}$$

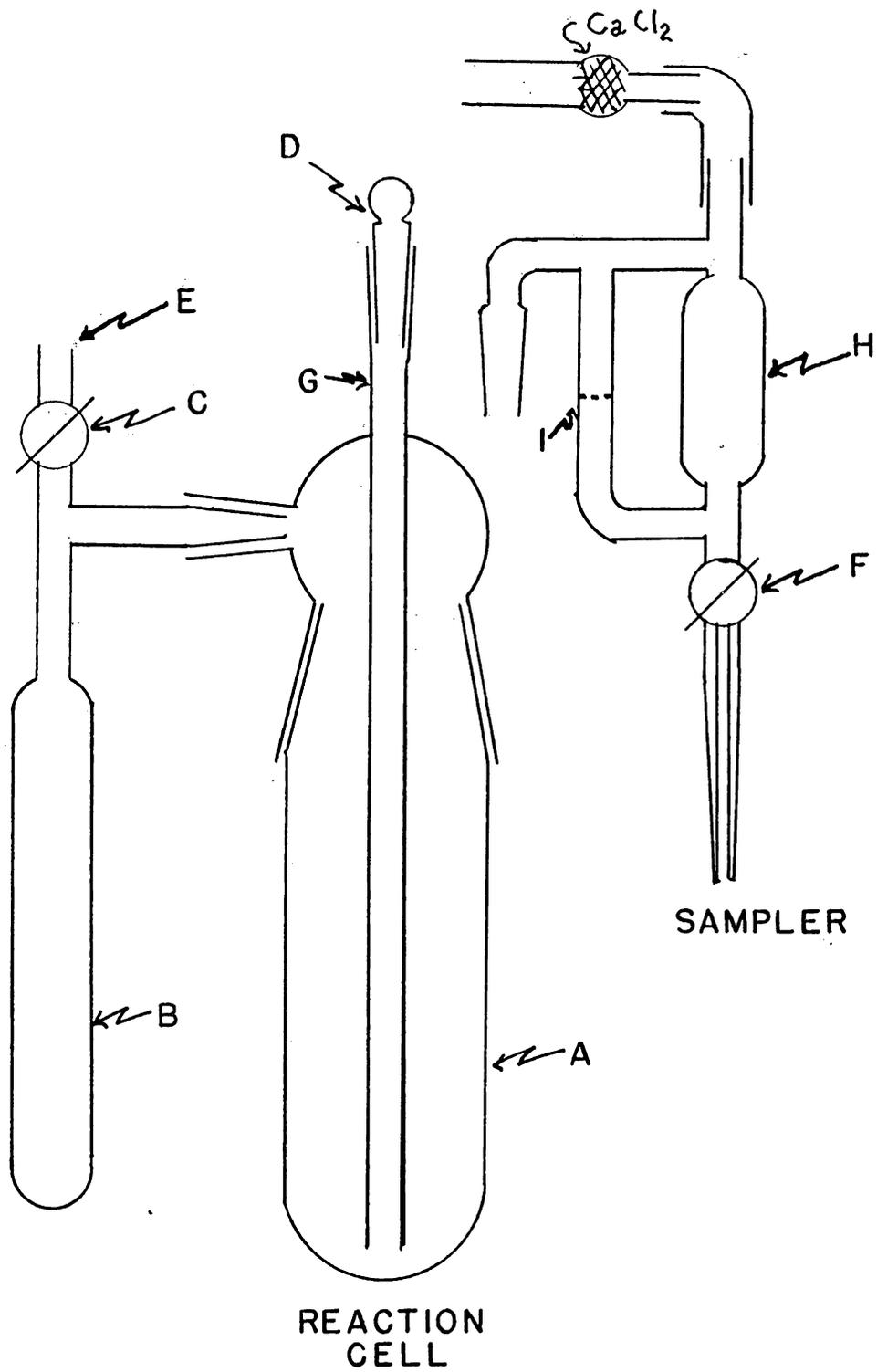


FIGURE 1

wt. pyridine added (as solvent) with $\text{C}_6\text{H}_5\text{COCl}$ =

wt. of $\text{C}_6\text{H}_5\text{COCl}$ solution added - wt. $\text{C}_6\text{H}_5\text{COCl}$ added.

The molar concentration of $\text{C}_6\text{H}_5\text{COCl}$ in cell after mixing =

$$\frac{\text{wt. } \text{C}_6\text{H}_5\text{COCl (in cell)} \times \text{density of pyridine (at } 25^\circ\text{C.)} \times 1000}{\text{Mol. wt. of } \text{C}_6\text{H}_5\text{COCl} \times \text{total wt. pyridine in cell}}$$

The total wt. of pyridine in the cell includes that added with the ester. The concentration of ethyl benzoylacetate was determined similarly. In calculating the molar concentration, it was assumed that the densities of the benzoyl chloride and ester solutions were approximately the same as that of pure pyridine. The density of the latter was taken as 0.978 at 25°C . (30). After the solutions in the cell had reached bath temperature, the cell was removed from the bath. The side-arm, B, was tilted, allowing the ester solution to flow into flask, A, where it was thoroughly mixed with the benzoyl chloride solution. Timing of the reaction (with an electric wall-clock, equipped with a sweep second hand) began at the mid-point of the mixing process. The latter was finished as quickly as possible (10-15 sec.) so that the cell could be replaced in the bath. A one-way syringe was then attached to tube B by a short piece of rubber tubing (10 cm.). The stopper D was removed and the sampler fitted to the cell at the same point.

In taking a sample, stop-cock C was opened, and the solution in A was pushed by means of the syringe up tube

G. Compartment H was filled until the liquid level reached the mark I (placed so that about seven ml. of solution would be delivered). The stop-cock F, otherwise kept closed, was then opened, draining the solution into a dry 25 ml. erlenmeyer flask. A 5.000 ml. sample of this solution was then pipetted into 10.0 ml. of water, shaken thoroughly and allowed to stand for several minutes. The water solution was titrated to the phenolphthalein end-point with sodium hydroxide solution which had been standardized against 5.000 ml. portions of the original benzoyl chloride-pyridine solution in 10.0 ml. of water.

The entire sampling operation took about 20 seconds. The time was noted when half the pyridine solution had drained from the pipet. Temperature changes in the pyridine solution between the time it left compartment A (immersed in the bath) and the half-time of the pipetting were probably not more than $\pm 0.1^{\circ}\text{C}$. The temperature of the surroundings within a run were fairly constant ($\pm 1-2^{\circ}\text{C}$.) and varied over the period within which the runs were made from 18° to 30°C .

After eight or nine samples had been taken, the solution remaining in flask A was transferred to a small glass-stoppered bottle and placed in the dry-box overnight. A sample of this was titrated the next day, when the reaction was assumed complete.

Treatment of Results

The total amount of hydrochloric acid remains constant

within one run, since it is also a product of the reaction being studied. The decrease of benzoylpyridinium chloride with time is evidenced by the decrease of benzoic acid. If

x = concentration of product, or benzoyl chloride reacted,

a = concentration of benzoyl chloride initially,

b = concentration of ester initially,

and N = concentration of titratable H^+ at time t ,

then $[HCl] = a$

$[H^+]$ due to ester = $\alpha(b-x)$

$[O_2COOH] = a-x$

$[H^+]$, total = $N = a + \alpha(b-x) + a-x$

and $x = (2a + \alpha b - N)/(1 + \alpha)$, at time t .

The instantaneous rate of formation of product is dx/dt . The latter was obtained from a plot of x versus time. A smooth curve passing as close to as many of the points as possible was drawn using a flexible rule. A plastic 30° - 60° drafting triangle was placed at a point on the curve, with its plane perpendicular to the plane of the paper. In proper light, the reflected portion of the curve could be lined up with that seen through the plastic triangle. When the two formed an unbroken curve, the length of the triangle was judged to be perpendicular to the curve at that point. The tangent to the curve at that point was readily found by construction.

The slope, S_0 , at time $t = 0$, was difficult to obtain in the above manner. It was found empirically that a plot

of $\log S$, where S is the slope at time t , versus $\log (a-x)$ gave a fairly straight line. The possible significance of this observation will be shown later. This plot was extrapolated to give S_0 .

Calculation of Residual Water

Not all of the water could be removed from the pyridine. Traces of moisture were probably picked up in transferring solutions, in spite of the precautions taken. The initial concentration of benzoyl chloride was adjusted so that it was equal to or less than that of the other reactant. At the end of 24 hours, it was assumed the reaction was complete in each case. The titration of this final reaction mixture showed that in each run some of the benzoyl chloride had apparently not reacted. The quantity of unreacted benzoyl chloride had no relation to the initial concentrations of reactants, but was of the order of magnitude expected for water impurity (1×10^{-2} M.). It was assumed that this quantity represented the amount of water impurity present in the pyridine at the time the reactants were mixed, and that it had immediately reacted with the benzoyl chloride, forming benzoic acid and pyridinium chloride. This last reaction was presumed to be very much faster than the reaction between benzoyl chloride and ethyl benzoylacetate. If benzoic anhydride was produced in the reaction of benzoyl pyridinium chloride with water, then the observed normality in Table I should have been lower than that cal-

culated. In the data to follow, the initial molar concentration of pyridinium chloride due to residual water will be designated as x_0 . The corrected initial molar concentration of benzoyl chloride ($a-x_0$) will be designated as a_0 .

III. EXPERIMENTAL DATA

Experiment # 1

$$a = 1.243 \times 10^{-2}; \quad b = 1.767 \times 10^{-2}; \quad N(\text{NaOH}) = 2.287 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		2.633×10^{-2}	0.000×10^{-2}
187	5.596	2.560	0.067
561	5.410	2.479	0.142
1247	5.240	2.400	0.215
2821	5.101	2.335	0.275
6021	5.091	2.330	0.280
10103	4.970	2.275	0.331
∞	4.863	2.228	0.374

Experiment # 2

$$a = 1.259 \times 10^{-2}; b = 3.378 \times 10^{-2}; N(\text{NaOH}) = 2.261 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		2.798×10^{-2}	0.000×10^{-2}
182	5.740	2.596	0.203
384	5.625	2.544	0.255
691	5.477	2.477	0.322
1152	5.378	2.432	0.367
1633	5.312	2.402	0.397
2371	5.311	2.402	0.398
5549	5.249	2.374	0.425
∞	5.100	2.306	0.493

Experiment # 3

$$a = 1.886 \times 10^{-2}; b = 3.52 \times 10^{-2}; N(\text{NaOH}) = 2.377 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		4.064×10	0.000×10
198	7.600	3.613	0.416
319	7.444	3.539	0.486
483	7.178	3.412	0.602
719	6.926	3.293	0.713
1013	6.772	3.219	0.781
1426	6.551	3.114	0.876
2074	6.457	3.070	0.918
2383	6.259	2.976	1.006
∞	5.964	2.835	1.137

Experiment # 4

38

$$a = 4.484 \times 10^{-2}; b = 4.264 \times 10^{-2}; N(\text{NaOH}) = 4.086 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		9.322×10^{-2}	0.00×10^{-2}
192	10.116	8.267	0.97
320	9.796	8.005	1.22
485	9.358	7.647	1.55
758	9.070	7.412	1.76
1115	8.767	7.164	1.99
1707	8.476	6.926	2.21
2815	8.220	6.717	2.41
5318	7.812	6.384	2.72
∞	7.340	5.998	3.07

Experiment # 5

$$a = 2.516 \times 10^{-2}; b = 5.123 \times 10^{-2}; N(\text{NaOH}) = 4.043 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		5.457×10^{-2}	0.000×10^{-2}
201	5.758	4.656	0.740
342	5.508	4.454	0.927
507	5.410	4.374	1.000
727	5.265	4.257	1.108
1001	5.162	4.174	1.184
1341	4.920	3.978	1.364
1680	4.875	3.942	1.398
3184	4.996	4.040	1.308
∞	4.254	3.433	1.870

Experiment # 6

$$a = 3.415 \times 10^{-2}; b = 2.930 \times 10^{-2}; N(\text{NaOH}) = 4.053 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		7.080×10	0.000×10
193	8.000	6.488	0.546
325	7.717	6.258	0.758
520	7.429	6.025	0.973
740	7.172	5.816	1.166
967	7.054	5.721	1.252
1263	6.920	5.612	1.352
1926	6.661	5.402	1.547
∞	5.694	4.616	2.273

Experiment # 7

$$a = 4.004 \times 10^{-2}; b = 6.587 \times 10^{-2}; N(\text{NaOH}) = 1.172 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		8.569×10^{-2}	0.00×10^{-2}
175	3.131	7.339	1.13
289	2.950	6.915	1.53
500	2.796	6.554	1.86
704	2.730	6.399	2.00
921	2.648	6.207	2.18
1145	2.608	6.113	2.26
1355	2.572	6.029	2.34
1693	2.530	5.930	2.43
∞	2.372	5.560	2.77

Experiment # 8

$$a = 3.483 \times 10^{-2}; \quad b = 4.591 \times 10^{-2}; \quad N(\text{NaOH}) = 1.187 \times 10^{-1}$$

Concentration of added $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} = 5.00 \times 10^{-3} \text{ M}$

t	ml. of NaOH	N(of solution)	x
0		7.841×10^{-2}	0.000×10^{-2}
174	2.932	6.961	0.813
305	2.813	6.678	1.075
448	2.748	6.524	1.217
697	2.594	6.158	1.557
958	2.521	5.985	1.716
1168	2.486	5.902	1.792
1436	2.431	5.771	1.913
1744	2.394	5.683	1.994
∞	2.076	4.928	2.690

Experiment # 9

$$a = 4.357 \times 10^{-2}; b = 5.849 \times 10^{-2}; N(\text{NaOH}) = 1.172 \times 10^{-1}$$

Concentration of added $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} = 3.173 \times 10^{-2} \text{ M.}$

t	ml. of NaOH	N(of solution)	x
0		1.234×10^{-1}	0.00×10^{-2}
186	4.970	1.165	0.72
306	4.838	1.127	1.09
476	4.686	1.098	1.38
721	4.519	1.059	1.77
887	4.489	1.052	1.84
1096	4.410	1.034	2.03
1285	4.355	1.021	2.16
1516	4.310	1.010	2.26
1850	4.241	0.994	2.42
∞	3.952	0.924	3.13

Experiment # 10

$$a = 3.434 \times 10^{-2}; b = 6.558 \times 10^{-2}; N(\text{NaOH}) = 6.848 \times 10^{-2}$$

$$\text{Concentration of added } (\text{CH}_3)_4\text{NBr} = 2.15 \times 10^{-3}$$

t	ml. of NaOH	N(of solution)	x
0		6.868×10^{-2}	0.00×10^{-2}
163	4.738	6.495	0.85
280	4.571	6.266	1.06
488	4.338	5.947	1.35
688	4.134	5.667	1.61
914	4.060	5.566	1.70
1169	3.917	5.369	1.89
1396	3.932	5.390	1.87
1644	3.860	5.291	1.96
∞	3.556	4.865	2.35

Experiment # 11

$$a = 2.941 \times 10^{-2}; \quad b = 4.394 \times 10^{-2}; \quad N(\text{NaOH}) = 6.879 \times 10^{-2}$$

Concentration of added LiCl = 5.636×10^{-2}

t	ml. of NaOH	N(of solution)	x
0		6.246×10^{-2}	0.000×10^{-2}
168	4.487	6.174	0.066
280	4.403	6.058	0.174
424	4.386	6.035	0.195
583	4.347	5.981	0.235
786	4.316	5.939	0.283
982	4.288	5.900	0.329
1296	4.350	5.986	0.240
1560	4.180	5.752	0.456
2111	4.074	5.606	0.591
∞	3.140	4.321	1.777

Experiment # 12

$$a = 3.393 \times 10^{-2}; \quad b = 4.322 \times 10^{-2}; \quad N(\text{NaOH}) = 6.838 \times 10^{-2}$$

$$\text{Concentration of added } \text{C}_5\text{H}_5\text{N} \cdot \text{HNO}_3 = 3.28 \times 10^{-4}$$

t	ml. of NaOH	N(of solution)	x
0		6.786×10^{-2}	0.000×10^{-2}
154	4.849	6.633	0.472
269	4.681	6.404	0.684
437	4.560	6.238	0.837
694	4.361	5.966	1.088
842	4.260	5.828	1.216
1130	4.198	5.743	1.293
1380	4.146	5.672	1.360
1614	4.120	5.636	1.393
∞	3.613	4.941	2.036

Experiment # 13

$$a = 3.187 \times 10^{-2}; b = 5.031 \times 10^{-2}; N(\text{NaOH}) = 1.100 \times 10^{-1}$$

$$\text{Concentration of added } \text{C}_5\text{H}_5\text{N} \cdot \text{HNO}_3 = 3.635 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		10.426×10^{-2}	0.000×10^{-2}
154	4.676	10.287	0.128
276	4.400	9.680	0.689
429	4.280	9.416	0.933
608	4.228	9.302	1.039
835	4.092	9.002	1.314
1090	3.992	8.782	1.520
1340	3.942	8.672	1.620
1637	3.941	8.670	1.622
∞	3.760	8.270	1.990

Instantaneous Rates of the Reaction of Benzoyl Chloride with Ethyl Benzoylacetate in Pyridine at 25.0° C.

The following data were obtained, as outlined previously, from graphs of x , the amount of product formed, versus t , the time. S_0 was obtained from a plot of $\log(S)$ versus $\log(a_0 - x)$.

Experiment # 1

$$a_0 = 3.74 \times 10^{-3}; b = 1.77 \times 10^{-2}; x_0 = 8.69 \times 10^{-3}$$

t	S	$a_0 - x$	$b - x$	$x_0 + x$
250	2.57×10^{-6}	2.91×10^{-3}	1.69×10^{-2}	0.952×10^{-2}
500	1.43	2.37	1.64	1.006
750	1.10	2.05	1.61	1.038
1000	0.821	1.81	1.58	1.062

$$S_0 = 4.61 \times 10^{-6}$$

Experiment # 2

$$a_0 = 4.93 \times 10^{-3}; b = 3.38 \times 10^{-2}; x_0 = 7.66 \times 10^{-3}$$

t	S	$a_0 - x$	$b - x$	$x_0 + x$
100	7.45×10^{-6}	3.60×10^{-3}	3.25×10^{-2}	8.99×10^{-3}
200	4.68	3.02	3.19	9.57
300	3.39	2.61	3.15	9.98
400	2.67	2.31	3.12	10.28

$$S_0 = 1.15 \times 10^{-5}$$

Experiment # 3

$$a_0 = 1.137 \times 10^{-2}; b = 3.52 \times 10^{-2}; x_0 = 7.49 \times 10^{-3}$$

t	S	$a_0 - x$	b-x	$x_0 + x$
100	1.67×10^{-5}	8.92×10^{-3}	3.28×10^{-2}	0.99×10^{-2}
200	1.07	7.55	3.14	1.13
300	0.800	6.58	3.04	1.23
400	0.625	5.85	2.97	1.30

$$S_0 = 2.79 \times 10^{-5}$$

Experiment # 4

$$a_0 = 3.07 \times 10^{-2}; b = 4.26 \times 10^{-2}; x_0 = 1.41 \times 10^{-2}$$

t	S	$a_0 - x$	b-x	$x_0 + x$
125	3.25×10^{-5}	2.32×10^{-2}	3.51×10^{-2}	2.16×10^{-2}
250	1.99	1.98	3.17	2.50
375	1.48	1.65	2.84	2.73
500	1.17	1.58	2.77	2.90

$$S_0 = 6.82 \times 10^{-5}$$

Experiment # 5

$$a_0 = 1.870 \times 10^{-2}; b = 5.12 \times 10^{-2}; x_0 = 6.46 \times 10^{-3}$$

t	S	$a_0 - x$	b-x	$x_0 + x$
100	2.63×10^{-5}	1.343×10^{-2}	4.59×10^{-2}	1.17×10^{-2}
200	1.45	1.137	4.39	1.38
300	0.998	1.010	4.26	1.51
400	0.727	0.925	4.18	1.59

$$S_0 = 8.23 \times 10^{-5}$$

Experiment # 6

48

$$a_0 = 2.27 \times 10^{-2}; b = 2.93 \times 10^{-2}; x_0 = 1.14 \times 10^{-2}$$

t	S	$a_0 - x$	b-x	$x_0 + x$
200	1.83×10^{-5}	1.72×10^{-2}	2.37×10^{-2}	1.70×10^{-2}
300	1.41	1.56	2.21	1.86
400	1.14	1.43	2.08	1.99
500	0.947	1.32	1.98	2.09

$$S_0 = 3.98 \times 10^{-5}$$

Experiment # 7

$$a_0 = 2.77 \times 10^{-2}; b = 6.57 \times 10^{-2}; x_0 = 1.23 \times 10^{-2}$$

t	S	$a_0 - x$	b-x	$x_0 + x$
200	3.38×10^{-5}	1.52×10^{-2}	5.34×10^{-2}	2.48×10^{-2}
300	2.20	1.24	5.06	2.76
400	1.59	1.05	4.87	2.95
500	1.25	0.91	4.73	3.09

$$S_0 = 1.08 \times 10^{-4}$$

Experiment # 8

$$a_0 = 2.69 \times 10^{-2}; b = 4.59 \times 10^{-2}; x_0 = 1.29 \times 10^{-2} \text{ (includes the } C_5H_5N \cdot HCl \text{ added)}$$

t	S	$a_0 - x$	b-x	$x_0 + x$
100	3.66×10^{-5}	2.12×10^{-2}	4.02×10^{-2}	1.86×10^{-2}
200	2.36	1.82	3.72	2.16
300	1.72	1.62	3.52	2.36
400	1.41	1.47	3.37	2.51

$$S_0 = 7.10 \times 10^{-5}$$

$a_0 = 2.89 \times 10^{-2}$; $b = 5.85 \times 10^{-2}$; $x_0 = 4.64 \times 10^{-2}$ (includes
the $C_5H_5N.HCl$ added)

t	S	$a_0 - x$	b-x	$x_0 + x$
100	3.38×10^{-5}	2.49×10^{-2}	5.45×10^{-2}	5.04×10^{-2}
200	2.74	2.17	5.13	5.36
300	2.14	1.92	4.88	5.61
400	1.73	1.73	4.69	5.80

$$S_0 = 4.85 \times 10^{-5}$$

Experiment # 10

With added $(CH_3)_4NBr$

$a_0 = 2.35 \times 10^{-2}$; $b = 6.56 \times 10^{-2}$; $x_0 = 1.08 \times 10^{-2}$

t	S	$a_0 - x$	b-x	$x_0 + x$
100	4.26×10^{-5}	1.66×10^{-2}	5.87×10^{-2}	1.77×10^{-2}
200	2.33	1.43	5.64	2.00
300	1.62	1.23	5.44	2.20
400	1.29	1.08	5.29	2.35

$$S_0 = 1.04 \times 10^{-4}$$

Experiment # 11

With LiCl added.

$a_0 = 1.80 \times 10^{-2}$; $b = 4.39 \times 10^{-2}$; $x_0 = 1.14 \times 10^{-2}$

t	S	$a_0 - x$	b-x	$x_0 + x$
100	6.13×10^{-6}	1.73×10^{-2}	4.32×10^{-2}	1.21×10^{-2}
200	4.99	1.68	4.27	1.26
300	4.39	1.63	4.22	1.31
400	3.82	1.59	4.18	1.35

$$S_0 = 7.30 \times 10^{-6}$$

Experiment # 12

With $C_5H_5N.HNO_3$ added

$$a_0 = 2.04 \times 10^{-2}; \quad b = 4.32 \times 10^{-2}; \quad x_0 = 1.35 \times 10^{-2}$$

t	S	$a_0 - x$	$b - x$	$x_0 + x$
100	2.70×10^{-5}	1.72×10^{-2}	4.00×10^{-2}	1.67×10^{-2}
200	1.92	1.49	3.77	1.90
300	1.45	1.32	3.60	2.07
400	1.13	1.18	3.46	2.21

$$S_0 = 3.99 \times 10^{-5}$$

Experiment # 13

With $C_5H_5N.HNO_3$ added

$$a_0 = 1.99 \times 10^{-2}; \quad b = 5.03 \times 10^{-2}; \quad x_0 = 1.20 \times 10^{-2}$$

t	S	$a_0 - x$	$b - x$	$x_0 + x$
100	2.56×10^{-5}	1.59×10^{-2}	4.63×10^{-2}	1.60×10^{-2}
200	1.80	1.37	4.41	1.82
300	1.40	1.21	4.25	1.98
400	1.17	1.07	4.11	2.12

$$S_0 = 5.72 \times 10^{-5}$$

Rate of Reaction of Ethyl Acetoacetate with Benzoyl Chloride in Pyridine at 25.0° C.

The procedure was the same as that used for the reaction involving ethyl benzoylacetate. The same symbolism is used in the tables to follow, with b being the initial concentration of ethyl acetoacetate. From three titrations, α was determined to be 0.086.

Experiment # 14

$$a = 3.554 \times 10^{-2}; b = 5.171 \times 10^{-2}; N(\text{NaOH}) = 6.869 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		7.555×10^{-2}	0.000×10^{-2}
170	4.976	6.837	0.656
317	4.865	6.684	0.795
566	4.672	6.419	1.038
775	4.503	6.187	1.250
1002	4.430	6.087	1.342
1193	4.318	5.933	1.482
1461	4.230	5.812	1.593
1673	4.191	5.758	1.640
2003	4.047	5.561	1.823
∞	3.176	4.363	2.914

$$a_0 = 2.91 \times 10^{-2}; b = 5.17 \times 10^{-2}; x_0 = 6.40 \times 10^{-3}$$

t	S	$a_0 - x$	$b - x$	$x_0 + x$
100	2.59×10^{-5}	2.51×10^{-2}	4.77×10^{-2}	1.04×10^{-2}
200	1.71	2.30	4.56	1.25
300	1.35	2.14	4.40	1.41
400	1.16	2.02	4.28	1.53

$$S_0 = 5.30 \times 10^{-5}$$

Rate of Reaction of Methyl Alcohol with Benzoyl Chloride
in Pyridine at 25.0° C.

The procedure followed was the same as with ethyl benzoylacetate. In the tables below, b is the initial concentration of methyl alcohol. All other symbols have their former meaning. It was found that a small correction ($\alpha = 0.0022$) for titratable H^+ due to methyl alcohol had to be made.

Experiment # 15

$$a = 1.59 \times 10^{-2}; b = 5.224 \times 10^{-2}; N(\text{NaOH}) = 3.360 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		3.191×10^{-2}	0.000×10^{-2}
200	3.052	2.051	1.14
385	3.015	2.026	1.16
627	2.980	2.003	1.19
969	2.993	2.011	1.18
1262	2.985	2.006	1.19
2460	2.908	1.954	1.24
∞	2.790	1.875	1.32

Rate of Reaction of Hexanol-1 with Benzoyl Chloride in Pyridine at 25.0° C.

The procedure was as before. As with methyl alcohol, it was found that a small correction ($\alpha = 0.0077$) had to be applied to compensate for the base neutralized by the alcohol. All symbols have the same significance as before, with b the initial concentration of hexanol-1.

Experiment # 16

$$a = 2.359 \times 10^{-2}; b = 2.119 \times 10^{-2}; N(\text{NaOH}) = 6.840 \times 10^{-2}$$

t	ml. of NaOH	N(of solution)	x
0		4.700×10^{-2}	0.00×10^{-2}
180	2.420	3.311	1.39
342	2.214	3.029	1.67
531	2.126	2.908	1.79
684	2.082	2.848	1.85
938	2.040	2.791	1.91
1120	2.023	2.767	1.93
1290	2.020	2.763	1.94
1531	2.016	2.758	1.94
∞	1.988	2.720	2.02

Estimates of the Experimental Errors

In preparing the solutions used in the experiments, the weights of all materials used were determined as the difference of two weights as measured on an analytical balance. The latter had a sensitivity of 2.5 divisions per milligram for a load of one milligram. A set of calibrated weights was used. In every case, the quantities of materials were such that the weight was accurate to $\pm 0.2\%$. Since all concentrations were given to three significant figures in the final tabulation of data, only a negligible error in the initial concentrations of all species present might be expected.

The temperature of the bath was maintained, as previously stated, at $25.00 \pm 0.025^{\circ} \text{C}$. Temperature changes in sampling have already been discussed. It is anticipated that no significant errors due to temperature changes occurred.

The time necessary to mix the two reactant solutions and replace the cell in the bath was approximately 10 to 15 seconds. For purposes of timing, the solutions were considered mixed after the first five seconds. This was probably accurate within ± 2 seconds. It is estimated that the error in noting the time for half the solution to drain from the pipet (see procedure) was ± 2 seconds. A total error in the time of ± 4 seconds could thus be expected. The first samples were usually taken at around 200 seconds.

At this point the relative error would be $\pm 2\%$. This would decrease for later times.

The determination of end-points in titrations of reaction samples was probably the greatest source of error. This was undoubtedly due to the presence of the ester. An indication of the uncertainty in these titrations may be obtained from that present in the titrations of solutions of ethyl benzoylacetate in pyridine-water mixtures (Table II). In that case, the average deviation was $\pm 8\%$. The relative error in the titrations of a reaction sample would be much less than this. The titratable hydrogen ion due to the ester is in all cases only about one-tenth of the total. An estimate of $\pm 1\%$ for the relative error in reaction sample titrations should not be too far off.

$$\text{The amount reacted, } X = \frac{2a + \alpha b - N}{1 + \alpha} .$$

The error in the first term is negligible. The error in the second is $\pm 8\%$, and that in the third has been estimated to be $\pm 1\%$. Since the square root of the sum of the squares of the individual errors in a sum or difference gives the error in the final result, the error in x is $\pm 8\%$. For measurements of the instantaneous rate, S , in the initial portion of the reaction, an error as great as $\pm 10\%$ might be expected.

"True" Order of the Reaction of Benzoyl Chloride with Ethyl Benzoylacetate in Pyridine

The rate data for the beginning of the reaction were used in calculating three presumed constants, each corresponding to a particular order for the initial reaction. The results are given in Table III. In the table

$$k_1 = S_0/(a_0 b) ; \quad k_2 = (S_0 x_0)/(a_0 b) ; \quad k_3 = (S_0 x_0^{1/2})/(a_0 b)$$

The second order rate expression corresponding to k_1 may be rejected immediately. It varies, in experiments 1 through 9, from 3×10^{-2} to 8×10^{-2} l./M. sec. The constant k_2 corresponds to the rate expression

$$S_0 = k_2 \frac{(\text{COCOC1})(\text{Ester})}{(\text{py.HCl})} = k' \frac{(\text{COCOC1})(\text{Ester})}{(\text{py.H}^+)(\text{Cl}^-)}$$

$$\text{since } K_2 = \frac{(\text{pyH})(\text{Cl})}{(\text{py.HCl})}$$

Note the increase in k_2 in experiment 9, when excess pyridinium chloride was added. This would indicate that k_2 is not the right expression. The equation used to calculate k_2 could not take into account pyridinium ion available from a salt other than pyridinium chloride. If k_2 were of the correct form, it should decrease markedly when another salt, as pyridinium nitrate, is added. The results for experiment 13 show that it did not decrease.

The rate expression represented by k_3 ,

$$S_0 = k_3 a_0 b / (x_0^{1/2}),$$

Table III

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Experiment	k_1 1/M. sec.	k_2 sec. ⁻¹	k_3 1 /M sec.
1	6.97×10^{-2}	6.05×10^{-4}	6.50×10^{-3}
2	6.90	5.29	6.04
3	6.95	5.20	6.01
4	5.21	7.35	6.19
5	8.59	5.55	6.90
6	5.98	6.82	6.38
7	5.94	7.30	6.59
8	5.75	7.42	6.52
9	2.87	13.3	6.18
10	6.74	7.22	7.00
11	0.923	1.05	0.986
12	4.52	6.11	5.25
13	5.71	6.85	6.25
average (for expts. 1 - 9)			$6.37 \pm 2\%$

Experiment	Added Salt	Concentration (M.)
8	$C_5H_5N.HCl$	0.500×10^{-2}
9	$C_5H_5N.HCl$	3.17
10	$(CH_3)_4NBr$	0.215
11	$LiCl$	5.34
12	$C_5H_5N.HNO_3$	0.033
13	$C_5H_5N.HNO_3$	3.64

fits the initial rate data very well in experiments 1 through 9 as well as in numbers 10, 12 and 13. In numbers 1 through 9, no salt not already present in the system was added. That the concentration of pyridinium chloride appears to the one-half power would lead one to suspect inhibition by either the pyridinium ion or the chloride ion. To determine which of the two was involved, experiments 11 (addition of LiCl), and 12 and 13 (addition of pyridinium nitrate) were performed. The addition of pyridinium nitrate had no effect on the value of k_3 within the experimental error. The addition of lithium chloride in experiment number 11 decreased the calculated rate constant markedly. These two observations would be expected for the rate expression

$$S_0 = k \frac{(\text{PCl}) (\text{Ester})}{(\text{Cl}^-)}$$

Frequently (40, 41), linear combinations of rate expressions for undissociated molecules and free ions are used to represent the experimental data. Davies (41) used one which, extended to the system studied here, would be

$$\text{rate} = k(\text{PCl})(\text{Ester}) + k'(\text{PC}^+)(\text{Ester}) + k''(\text{PCl})(\text{Ester anion}) + k'''(\text{PC}^+) \times (\text{Ester anion}).$$

The rate expression and kinetic order are empirical relationships. It would be desirable, therefore, that the rate expression be as simple as possible. This result is achieved

in this case without the elaborate treatment necessary for a linear combination like the one above. It can be stated that, within the experimental error, and in the concentration range studied, the reaction of the benzoyl pyridinium ion with the ester is the only one contributing to the overall reaction.

The Order of the Reaction with Respect to Time

When the instantaneous rate, S , of formation of product is plotted versus the quantity

$$(a_0 - x)(b - x)/(x_0 + x)^{1/2}$$

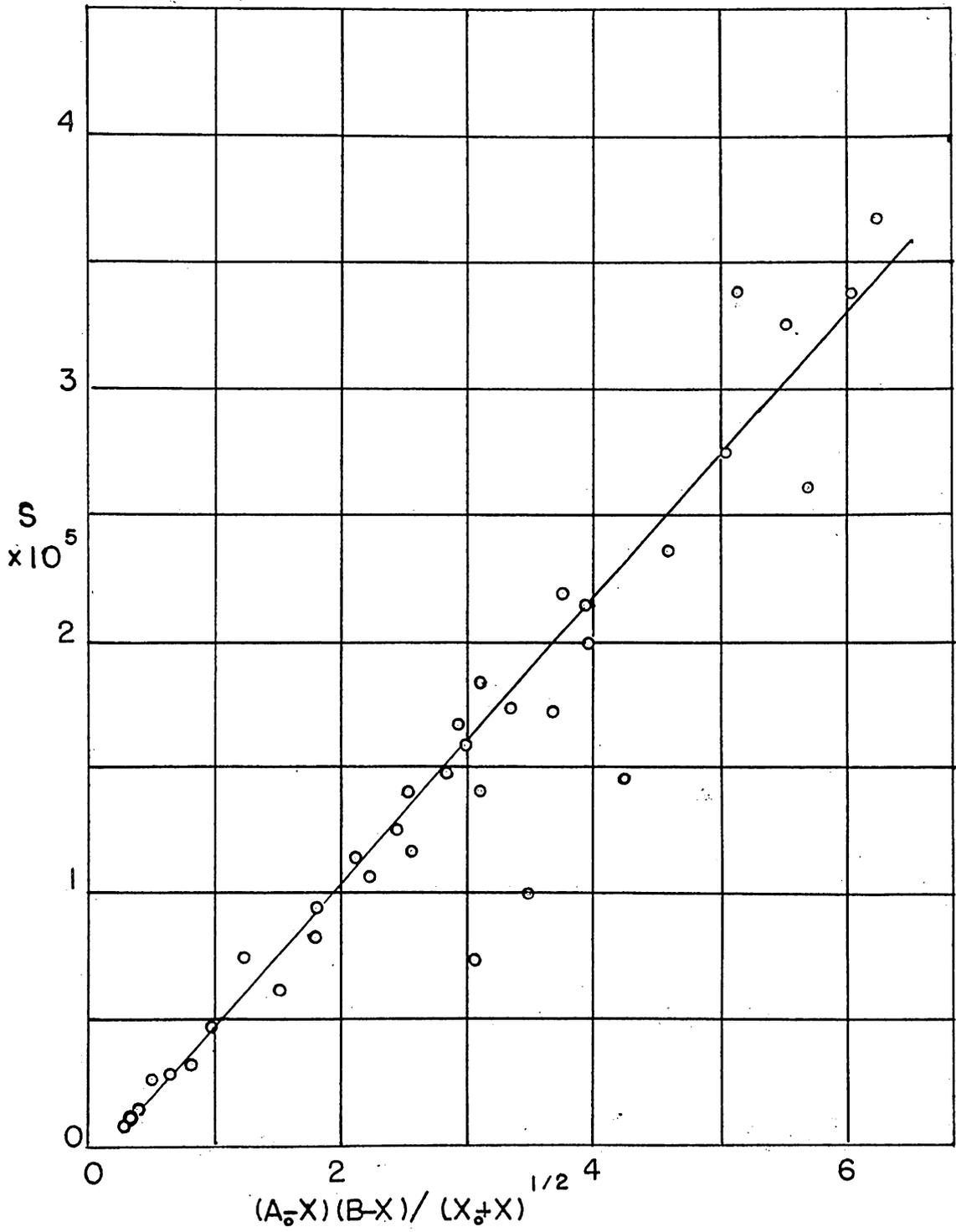
the points are found to be grouped around a straight line, as in Graph I. The data are given in Table IV. The slope of the line, $k_4 = 5.70 \times 10^{-3}$, is somewhat less than that obtained from the initial rate data. The difference, Δ , is defined as

$$\Delta = k_4 (a_0 - x)(b - x)/(x_0 + x)^{1/2} - S \text{ (observed)}.$$

As indicated by Δ , the observed rate, S , decreases faster during the reaction than does that calculated. In the table, the data are given in order of increasing time, corresponding to the data in Table II.

If the order with respect to time is the same as the "true" order, then there are several reasons for the trend in Δ with time. It has been tacitly assumed that the water in the ester solution, when mixed with the benzoylpyridinium chloride solution, reacted instantaneously with the latter. It is more probable that the reaction proceeded at a finite

PLOT OF S VERSUS $(A_0 - X)(B - X)/(X_0 + X)^{1/2}$



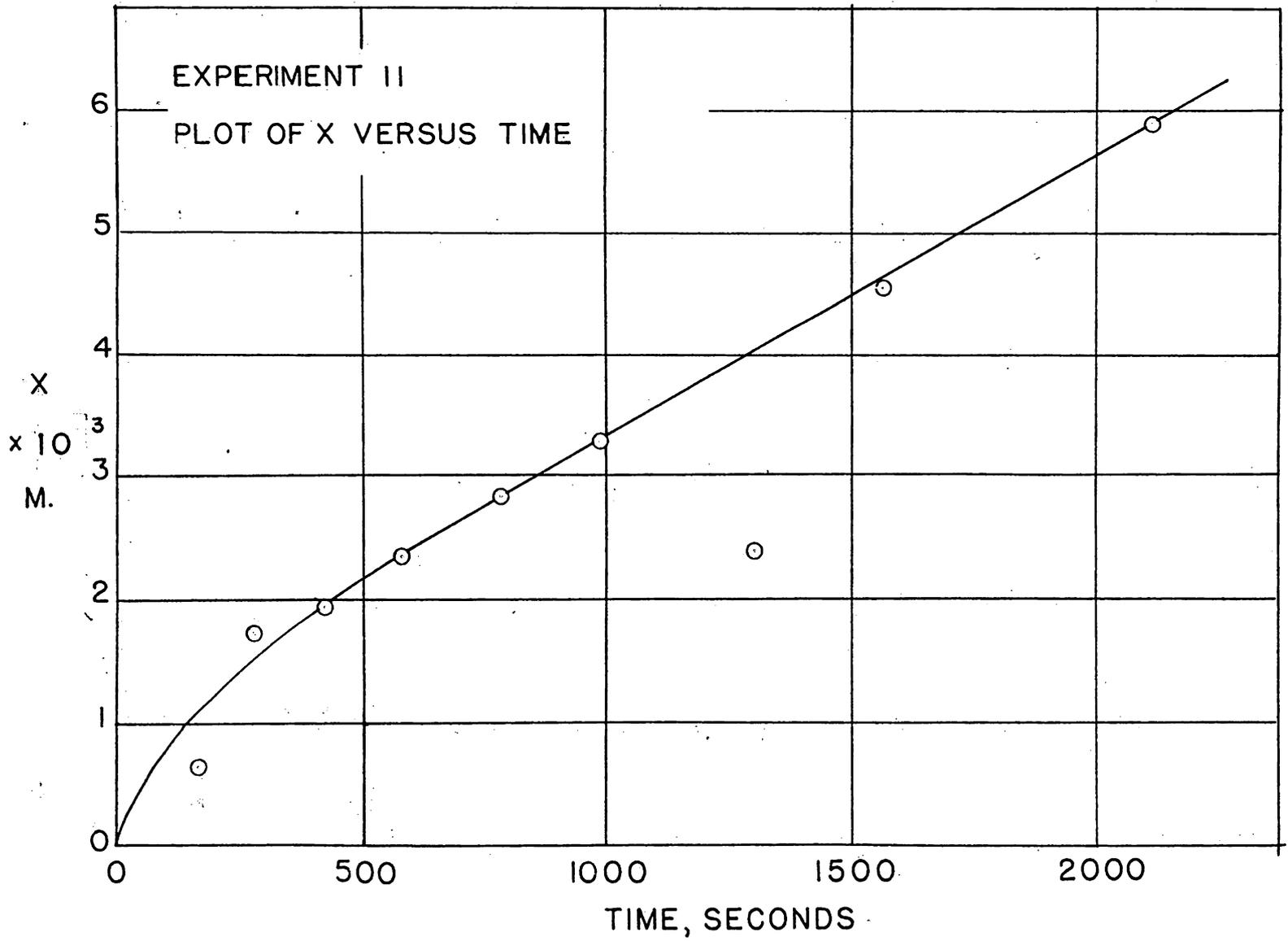
GRAPH I

Table IV

#	S	$\frac{(a_0-x)(b-x)}{(x_0+x)^{1/2}}$	Δ
1	2.57×10^{-6}	5.04×10^{-4}	0.30×10^{-6}
	1.43	3.87	0.77
	1.10	3.23	0.74
	0.82	2.77	0.76
2	7.45×10^{-6}	12.32×10^{-4}	0.44×10^{-6}
	4.68	9.84	1.08
	3.39	8.21	1.28
	2.67	7.11	1.38
3	1.67×10^{-5}	2.94×10^{-3}	0.00×10^{-5}
	1.07	2.23	0.20
	0.800	1.80	0.20
	0.625	1.52	0.24
4	3.25×10^{-5}	5.53×10^{-3}	0.10×10^{-5}
	1.99	3.97	0.27
	1.48	2.84	0.14
	1.17	2.57	0.29
5	2.63×10^{-5}	5.70×10^{-3}	0.61×10^{-5}
	1.45	4.24	0.96
	0.998	3.50	1.00
	0.727	3.06	1.01
6	1.83×10^{-5}	3.12×10^{-3}	0.06×10^{-5}
	1.41	2.53	0.03
	1.14	2.11	0.06
	0.947	1.81	0.08
7	3.38×10^{-5}	5.16×10^{-3}	0.44×10^{-5}
	2.20	3.77	0.06
	1.59	2.98	0.11
	1.25	2.45	0.14
8	3.66×10^{-5}	6.23×10^{-3}	0.11×10^{-5}
	2.36	4.60	0.26
	1.72	3.71	0.39
	1.41	3.12	0.36
9	3.38×10^{-5}	6.03×10^{-3}	0.05×10^{-5}
	2.74	4.81	0.00
	2.14	3.95	0.11
	1.73	3.36	0.18

but fast rate, compared with the reaction with the ester itself. The initial concentration of benzoylpyridinium chloride would be higher than the apparent concentration, a_0 . The latter was calculated from the total amount of benzoyl chloride which reacted with the ester. Since the quantity a_0 appears in the numerator of the calculated rate, the latter would be lower initially than it should be.

Correcting the expression used for the chloride ion concentration, $(x_0 + x)^{1/2}$, to take into account that available from the dissociation of benzoylpyridinium chloride, would not lead to better agreement between calculated and observed rates. Since the total benzoyl chloride concentration decreases during the reaction, the corrected expression would not increase as fast as $(x_0 + x)$. This is opposite to the effect desired. The calculated rates, inversely proportional to the chloride ion concentration, do not decrease fast enough with time. A good test of whether the initial rate expression also holds true within a run should be afforded by the data of experiment 11. In this run, the lithium chloride concentration was $5.34 \times 10^{-2} M$. Note the depression in k_3 in Table V for number 11. In calculating k_3 the concentration of chloride ion due to salts other than pyridinium chloride was not taken into account. It may be noted that in experiment 11, the change in chloride ion concentration during the period in which the instantaneous rates of reaction were measured should be small. If this is granted, then the rate expression $S = k_4 (a_0 - x)(b - x)/$

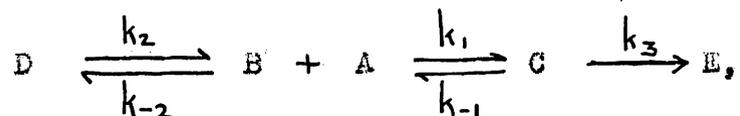


GRAPH II

$(x_0 + x)^{1/2}$ becomes

$$S = k' (a_0 - x)(b - x).$$

The calculated values of k' for experiment 11 are given in Table V. The data for this experiment show that the initial rate expression does not hold true within the run. A glance at Graph II, showing a plot of x versus t for experiment 11, shows that the reaction, after a short time, approaches zero order. That is, the rate of formation of x is constant after about 400 seconds. The order with respect to time is certainly not the same as the "true" order in this case. Indeed, recalling the manner in which Δ (Table IV) varied within the various runs, the two are not the same in any of the runs. This may be explained on the basis of the mechanism proposed by Doering and McEwen discussed on pages 8 and 9. The series of reactions may be written



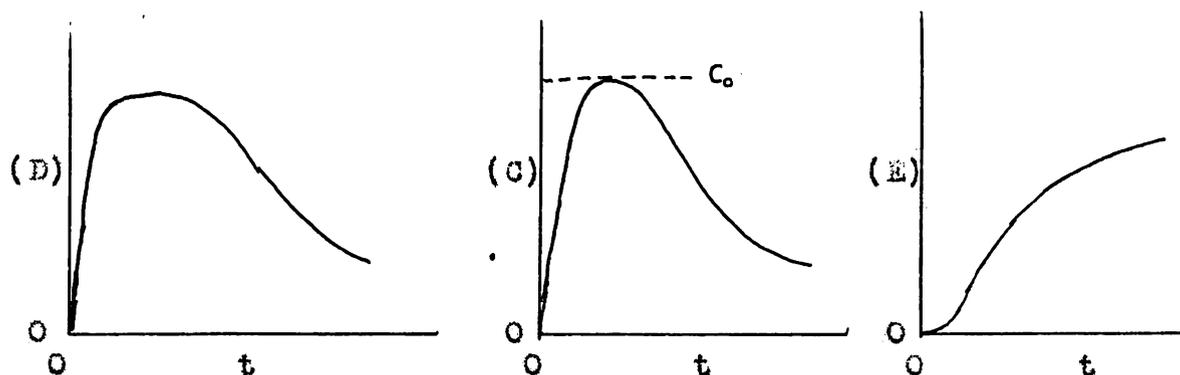
where A is the benzoyl pyridinium ion, B the ester, C the 2-addition intermediate, D the 4-addition intermediate, and E the product. Pyridinium chloride may be either a product of the formation of the addition intermediates or of the formation of E. As in case a on page 19, the following relations between the specific rate constants will be assumed to exist:

$$k_1 \gg k_{-1}, \quad k_2 \gg k_{-2}, \quad k_1 \gg k_3.$$

Table V

t sec.	$k' = S / (a_0 - x)(b - x)$
100	7.92×10^{-2}
200	5.80
300	4.72
400	4.34

In such a case, the variation with time of the concentrations of the three species C, D, and E may be represented as in the three graphs below.



The system could be approximated by



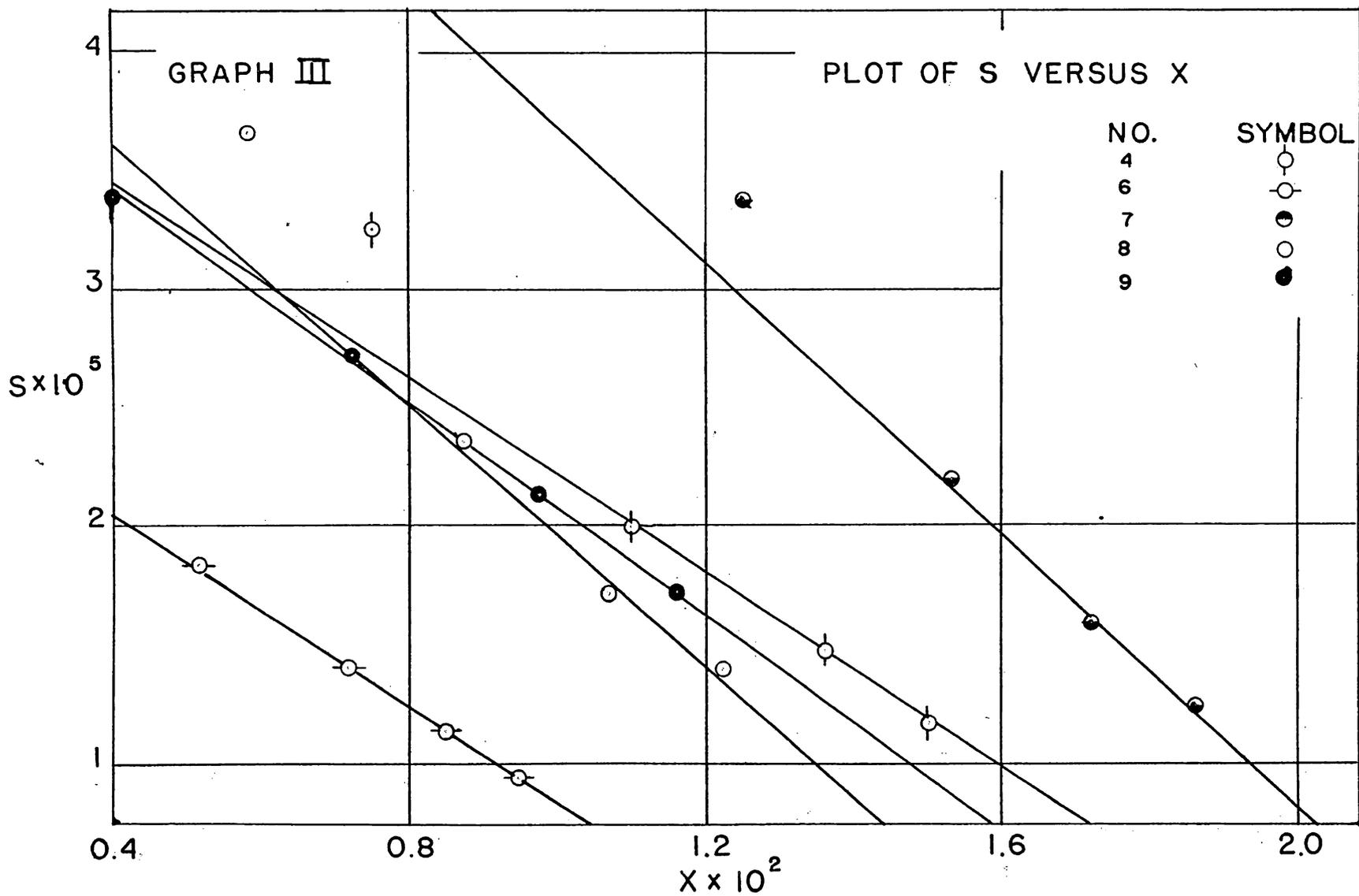
In the early stages of the reaction, after the benzoylpyridinium ion and the ester have formed C and D, it might be expected that the concentration of C may be approximated by $(C_0 - x)$. Thus

$$d(E)/dt = dx/dt = k_3(C_0 - x).$$

If $k_3 \gg k_{-2}$, this approximation becomes much better.

Plots of S versus x have been made (Graphs III and IV) for experiments 1 through 9. The first point in each case has been ignored in drawing a straight line through the points. The slopes, k, and the quantities C_0 are given in Table VI.

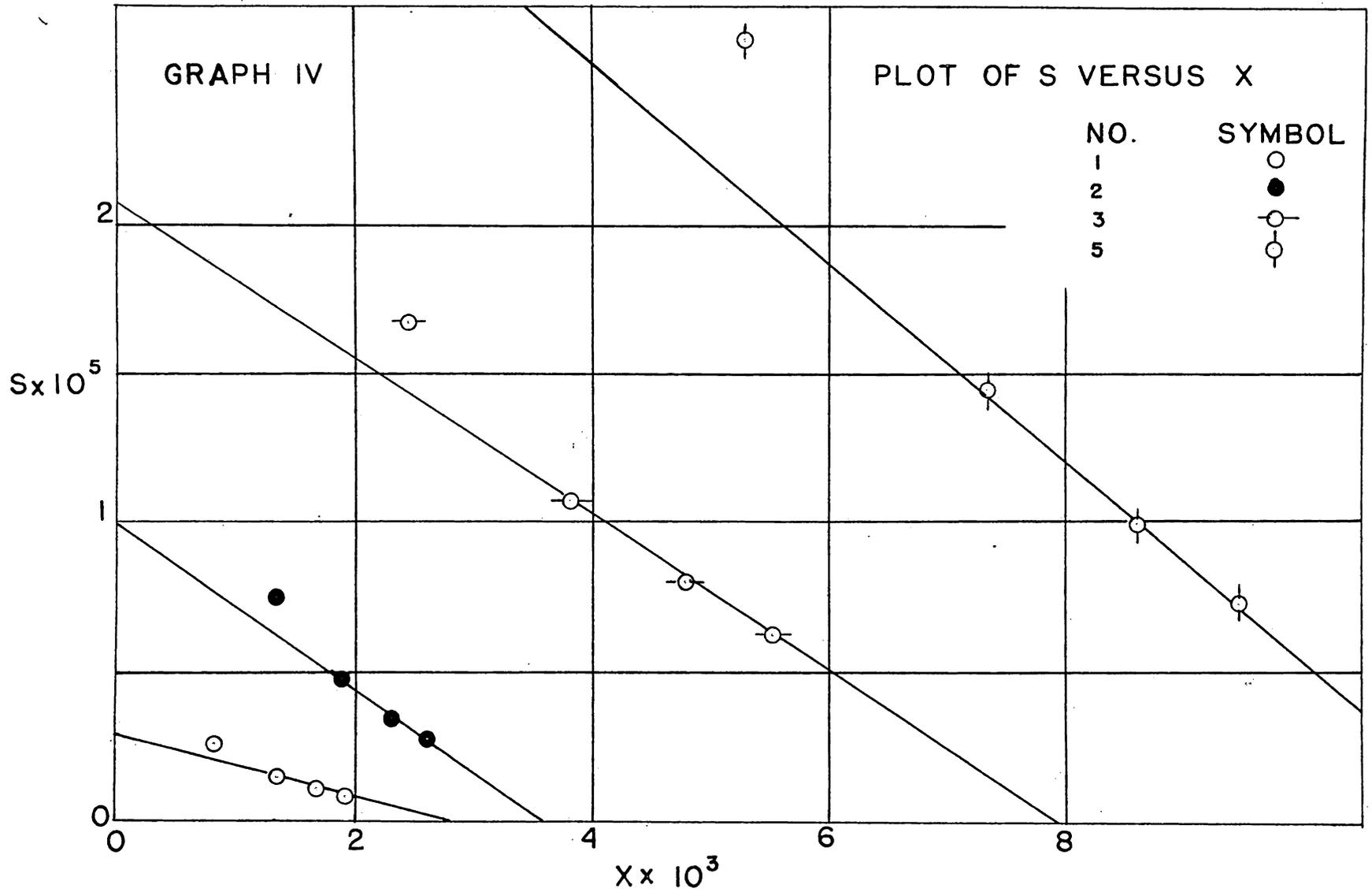
In the early stages of a run it can be shown (see Table VI) that the results empirically fit the equation $S = k(C_0 - x)$, where $k = k'b/x_0^{1/2}$, and $C_0 = ka_0$, as predicted on the basis of



GRAPH IV

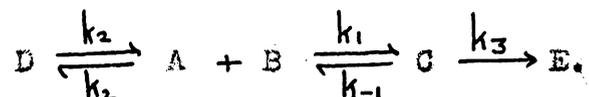
PLOT OF S VERSUS X

NO.	SYMBOL
1	○
2	●
3	○
5	○



the assumed mechanism. If it were not for the behavior found in experiment 11, this might be called a mere happenstance. Over a sufficiently small range, most smooth curves may be approximated by a linear function. Further evidence against a coincidence, however, can be gained by a consideration of the ratio C_0/a_0 . The initial concentration of benzoylpyridinium chloride, always smaller than the ester concentration at the beginning, is the limiting factor in determining how much of the 2- and 4- addition intermediates might be formed. Consider the relative probabilities of formation of these intermediates. Since there are two α -positions and only one γ -position on the pyridine nucleus, the ratio of the 2- to the 4- addition intermediate should be two to one, neglecting all other factors. Of the total formed then, two-thirds should be C and one-third the D isomer. The average value of C_0 is $0.66 a_0$.

To return to the curious results of experiment 11, consider the system

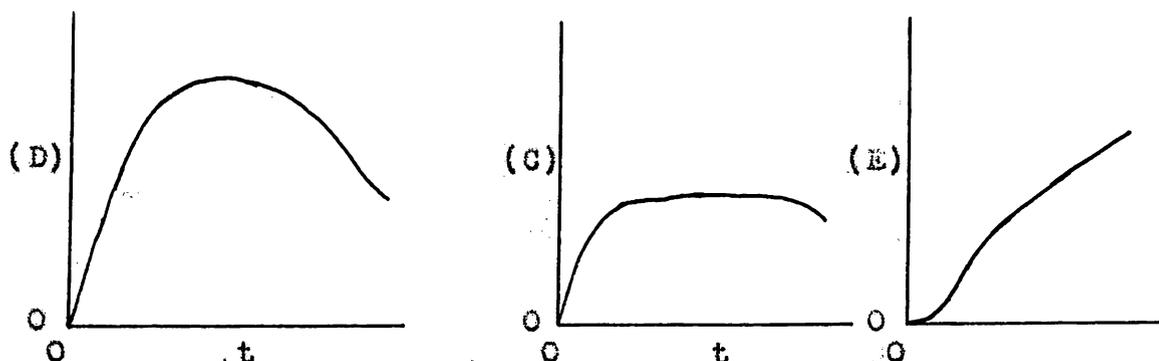


When the chloride ion concentration is high, the same relations hold between the k 's as before. Then, the relative concentration of benzoylpyridinium ion will be comparatively low. In that instance, the rate of formation of C and D will be decreased. The variation in time of the concentrations of C,

Table VI

Expt.	k	C_0	C_0/a_0	$k^2 = kx_0^{1/2}/b$
1	1.33×10^{-3}	0.22×10^{-2}	0.64	7.02×10^{-3}
2	2.91	0.35	0.75	7.52
3	2.65	0.79	0.69	6.52
4	2.19	2.01	0.66	6.09
5	3.43	1.16	0.62	5.38
6	1.92	1.37	0.65	6.99
7	3.19	2.23	0.59	5.38
8	2.32	1.84	0.68	5.73
9	2.07	1.99	0.69	7.60
average			0.66	$6.47 \pm 11\%$

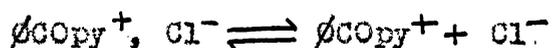
D and E would be represented by the graphs below. This may



be seen from the following consideration:

$$d(C)/dt = k_1 (A)(B) - (k_3 + k_{-1})(C).$$

If the rate of formation of E is constant, then $d(E)/dt = k_3(C)$ constant. This requires that $d(C)/dt = 0$. If (C) is constant, then (A)(B) must also be constant. A is the benzoylpyridinium ion. Assume that the dissociation and recombination processes



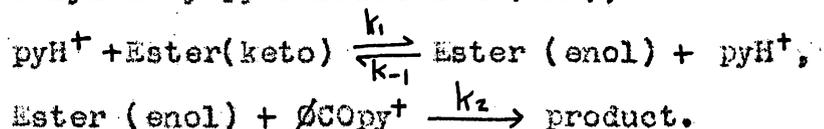
are equilibrium ones, i. e., much faster than any of the other reactions. Then, if the chloride ion concentration, including that due to other electrolytes like lithium chloride is high, the concentration of A will be small. If the concentration of A is sufficiently small, it will be replaced from the ion-pairs as fast as it disappears in reaction with B. Since

$$d(a)(B)/dt = (A) d(B)/dt + (B) d(A)/dt,$$

then if (A) is small and $d(A)/dt = 0$, $d(A)(B)/dt = 0$.

The linear portion of the (E) versus t curve corresponds to the relatively flat section of the (O) versus t curve. This is just the behavior found in experiment 11.

The foregoing phenomena cannot be explained in any of the more usual ways. If the slow step within the reaction were the formation of the enol form of the ester which subsequently reacted with the benzoylpyridinium ion, then the following equations could be written. Since the enolization is catalyzed by pyridinium ion (42),



If the concentration of the enol form reaches a steady state, then

$$d(\text{ester, enol})/dt = k_1 (\text{Ester, keto})(\text{pyH}^+) -$$

$$k_{-1} (\text{Ester, enol})(\text{pyH}^+) - k_2 (\text{Ester, enol})(\text{O}^+\text{COPy}^+) = 0,$$

$$dx/dt = k_2 (\text{Ester, enol})(\text{O}^+\text{COPy}^+).$$

Solving for (Ester, enol) and substituting this into dx/dt ,

$$dx/dt = \frac{k_1 k_2 (\text{Ester, keto})(\text{O}^+\text{COPy}^+)(\text{pyH}^+)}{k_{-1} (\text{pyH}^+) + k_2 (\text{O}^+\text{COPy}^+)}$$

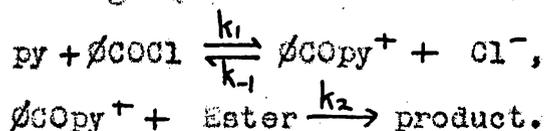
$$\text{Then } S = dx/dt = k \frac{(\text{Ester, keto})(\text{O}^+\text{COPy}^+)(\text{pyH}^+)}{K(\text{O}^+\text{COPy}^+) + (\text{py.HCl})},$$

$$\text{and } k = \frac{S [K(\text{O}^+\text{COPy}^+) + (\text{py.HCl})]}{(\text{Ester, keto})(\text{O}^+\text{COPy}^+)(\text{py.H}^+)}$$

There are two reasons why this equation doesn't fit the experimental data. Ignoring the pyridinium ion concentration factor, the term, $K(\text{O}^+\text{COPy}^+)$, in brackets would result in the

factor in brackets increasing more slowly within a run than is found. The factor (pyHCl) by itself doesn't prevent k from decreasing within a run. The (py.H^+) factor in the numerator would require that the rate increase with increasing pyridinium ion concentration. This latter effect is not observed, (experiments 12 and 13).

From the dependence of the rate within a run upon a first-order function of the benzoyl chloride concentration, it might be argued that the slow step was the ionization of benzoylpyridinium chloride, or the formation of the latter from benzoyl chloride. If this were the case, then the following equations should hold.



Assuming the benzoyl pyridinium ion concentration reaches a steady state, then

$$d(\text{BCOpy}^+)/dt = k_1(\text{BCOCl}) - k_1(\text{BCOpy}^+)(\text{Cl}^-) - k_2(\text{BCOpy}^+)(\text{Ester}) = 0$$

$$\text{and } dx/dt = S = k_2(\text{BCOpy}^+)(\text{Ester}).$$

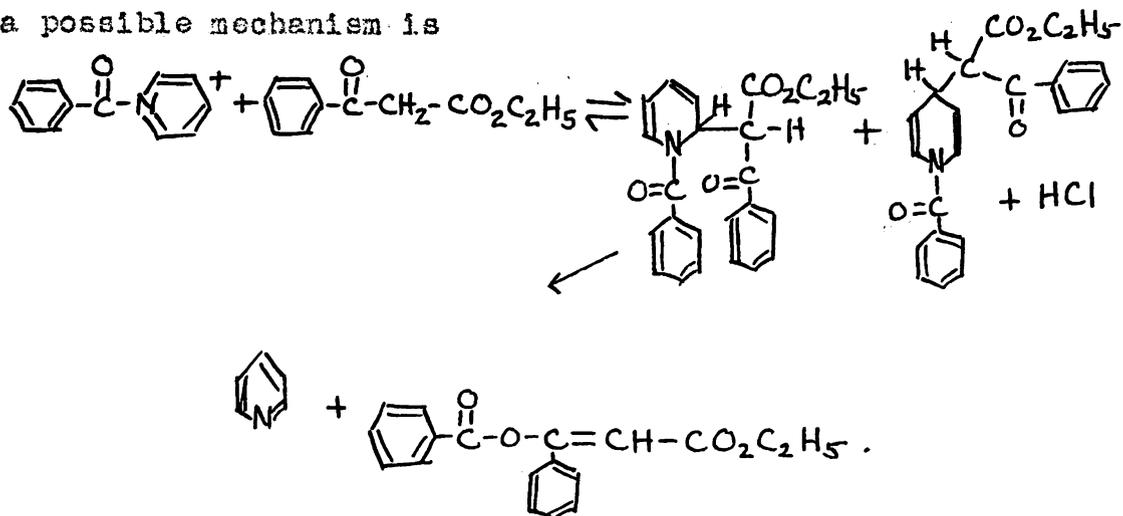
Solving for (BCOpy^+) and substituting in S , it is found that

$$k = \frac{S [K(\text{Ester}) + (\text{Cl}^-)]}{(\text{BCOCl})(\text{Ester})}$$

Again, the quantity within brackets, due to the decreasing concentration of ester, would not increase fast enough with time to match the data.

It is concluded that, within the experimental limits,

a possible mechanism is



The fast, initial step, the formation of the 2- and 4-addition intermediates, results in the initial rate, S_0 , having the dependence

$$S_0 = k a_0 b / x_0^{1/2} = k \frac{(\text{OOCCl})(\text{Ester})}{(\text{Cl}^-)}$$

In the early stages of a run, the relatively slow rearrangement of the 2-addition isomer to yield the product results in the rate following the equation

$$S = \frac{kb}{x_0^{1/2}} (Ka_0 - x)$$

The Reaction of Ethyl Acetoacetate with Benzoyl Chloride in Pyridine at 25.0°C.

If the foregoing treatment is applied to the data of experiment 14, in which ethyl acetoacetate was substituted for ethylbenzoylacetate, the results in Table VII are obtained.

Table VII

t, sec.	$\frac{S}{(Ka_0 - x)}$	$\frac{kx_0^{1/2}}{b}$
100	2.40 x 10 ⁻³	
200	1.97	
300	1.91	
400	1.97	
500	2.01	

$k' = 2.98 \times 10^{-3}$ and $K = 0.51$, from the graph.

From the initial rate, S_0 , obtained as before,

$$k_3 = \frac{S_0 X_0^{1/2}}{a_0 b} = 2.82 \times 10^{-3}.$$

Again, the agreement between k_3 and k' is very good. Tentatively, the rate of this reaction follows the same pattern as that observed for ethyl benzoylacetate. The same mechanism may be used to account for the observations with this system.

The Reaction of Benzoyl Chloride with Two Alcohols

Methanol. This reaction, experiment # 15, took place at too great a rate for any reliable measurements to be made. The reaction was 80% complete at the time the first sample was taken.

Hexanol-1. Simple alcohols cannot form an addition intermediate with benzoylpyridinium ion such as that postulated for β -keto-esters. The reaction should be relatively uncomplicated. The rate might be

$$dx/dt = k (\text{O}^+\text{COPy})(\text{ROH}) = k' (\text{O}^+\text{COPyCl})(\text{ROH})/(\text{Cl}^-),$$

where (ROH) is the concentration of alcohol. Since no intermediate of the type encountered before is present, then the above equation might be applicable within the run. Using the same notation as before, then

$$S = dx/dt = k'(a_0 - x)(b - x)/(x_0 + x)^{1/2}$$

The values of S , x , and k' calculated from the data for this reaction are given in Table VIII. Contrary to the experience with the esters, the value of k' increased with time. This

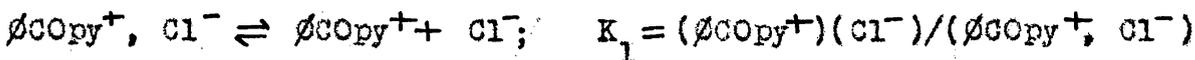
Table VIII

$a_0 = 1.94 \times 10^{-2} \text{ M.}; b = 2.12 \times 10^{-2} \text{ M.}; x_0 = 0.42 \times 10^{-2} \text{ M.}$

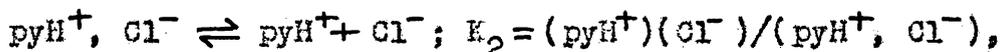
t	S	$a_0 - x$	$b - x$	$x_0 + x$	k'
200	2.04×10^{-5}	0.50×10^{-2}	0.68×10^{-2}	1.86×10^{-2}	8.18×10^{-2}
300	1.21	0.33	0.51	2.03	10.3
400	0.810	0.23	0.41	2.13	12.5
500	0.536	0.16	0.34	2.20	14.6

$$S_0 \approx 1.85 \times 10^{-4},$$

would be expected if $(x_0 + x)^{1/2}$ were not a good approximation to the chloride ion concentration. The corrections discussed on page 49 will now be made. Utilizing the equations corresponding to the equilibria



and



and defining α_1 = the fraction of total benzoylpyridinium chloride dissociated

α_2 = the total pyridinium chloride dissociated,

one obtains $K_1 / K_2 = \alpha_1 (1 - \alpha_2) / \alpha_2 (1 - \alpha_1)$.

If now, α_1 and α_2 are small compared to unity,

$$K_1 / K_2 = \alpha_1 / \alpha_2$$

The total $(\text{Cl}^-) = \alpha_1 (a_0 - x) + \alpha_2 (x_0 + x)$,

$$\text{or } (\text{Cl}^-) = \alpha_2 \left\{ x_0 + x + K_1 (a_0 - x) / K_2 \right\}.$$

Substituting this value in K_2 , it is found that

$$K_2 = \alpha_2^2 \left\{ x_0 + x + K_1 (a_0 - x) / K_2 \right\}.$$

This may be solved for α_2 . The latter is now substituted in the equation for the (Cl^-) .

$$(\text{Cl}^-) = K_2^{1/2} \left\{ x_0 + x + K_1 (a_0 - x) / K_2 \right\}^{1/2} = K_2^{1/2} \left\{ x_0 + K_1 a_0 / K_2 + (K_1 / K_2 - 1) x \right\}^{1/2}$$

$$\text{Then } S = k(a_0 - x)(b - x) / \left\{ x_0 + K_1 a_0 / K_2 + (K_1 / K_2 - 1) x \right\}^{1/2}$$

Squaring both sides, and rearranging,

$$\left(\frac{x_0 + a_0 K_1 / K_2}{K_1 / K_2 - 1} \right) + x = \frac{k^2 (a_0 - x)^2 (b - x)^2}{(K_1 / K_2 - 1) S^2}$$

$$\text{or } C + x = k' (a_0 - x)^2 (b - x)^2 / S^2.$$

In Table A, x and $(a_0 - x)^2 (b - x)^2 / S^2$ are tabulated. These

were fitted to the equation above, and the slope, k' , as well as the values of C calculated for each point, are given.

Table A

t(sec.)	x	$(a_0 - x)^2(b - x)^2/s^2$	C
200	1.44×10^{-2}	2.78	-1.98×10^{-2}
300	1.61	1.93	-1.98
400	1.71	1.34	-1.97
500	1.78	1.02	-1.98

$$k' = -1.93 \times 10^{-3}$$

Both C and k' are negative. From these two values, and the relations derived before, K_1/K_2 and k may be calculated.

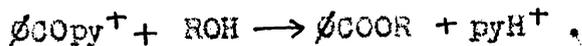
$$C = (x_0 + a_0 K_1/K_2)/(K_1/K_2 - 1).$$

$$\text{Rearranging, } K_1/K_2 = (x_0 + C)/(C - a_0) = 0.40.$$

This is the ratio of the dissociation constant of benzoylpyridinium chloride to that of pyridinium chloride.

$$k = [k'(K_1/K_2 - 1)]^{1/2} = 3.4 \times 10^{-2}.$$

There are not enough data on this reaction to be sure, but there is good indication that the rate-determining step in the over-all reaction is



Note On the Temperature Effect

The apparent energy of activation, E_a , for a chemical reaction, is usually obtained from the temperature coefficient of the specific rate constant, k , and the Arrhenius equation

$$k = A \exp(-E_a/RT),$$

where A is a constant, and R is the gas constant. It is not possible, without extra-kinetic information, to determine the energy of activation, E_A , for the reaction between benzoylpyridinium ion and ethyl benzoylacetate. The specific rate constant measured, k_3 , is not the specific rate constant for the above reaction, but is related to it. The relation may be derived as follows:

$$k = \frac{S}{(\phi\text{COpy}^+) (\text{Ester})} = \frac{S_0 (\text{Cl}^-)}{K_1 (\phi\text{COCl})_0 (\text{ester})}$$

as previously. Also $(\text{Cl}^-) \approx K_2^{1/2} (\text{HCl})^{1/2}$.

$$\text{Then } k = \frac{K_2^{1/2}}{K_1} \frac{S_0 x_0^{1/2}}{a_0 b} = \frac{K_2^{1/2}}{K_1} k_3.$$

The variation of K_1 and K_2 with temperature would have to be known before that of k could be calculated from the temperature coefficient of k_3 . Such information is not available in the literature. Indeed, it is doubtful that a good value for K_1 will ever be determined, unless some new and highly effective process is developed for removing water from pyridine.

It was felt that under such circumstances, the temperature coefficient of k_3 would be of little value. Consequently, it was not determined.

V. SUMMARY

The initial rate of the reaction of benzoyl chloride with ethyl benzoylacetate in pyridine solution at 25 C. has been found to obey the rate law

$$\left(\frac{dx}{dt}\right)_{t=0} = k_3 \frac{(\text{COCOCl})(\text{ester})}{(\text{HCl})^{1/2}}$$

where $k_3 = 6.37 \times 10^{-3}$. The rate during the initial portion of the reaction has been found to fit the equation

$$\frac{dx}{dt} = \frac{K(\text{Ester})_0 \{k(\text{COCOCl})_0 - x\}^{1/2}}{(\text{pyHCl})_0^{1/2}}$$

where $k = 6.5 \times 10^{-3}$ and $K = 0.66$

A mechanism proposed previously (12) has been found to be consistent with these observations. One experiment indicates that such a mechanism may explain the analogous reaction with ethyl acetoacetate. In the latter case,

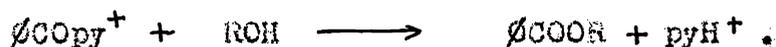
$$k_3 = 2.82 \times 10^{-3}, \quad k = 2.98 \times 10^{-3}, \quad \text{and} \quad K = 0.51$$

The reaction of benzoyl chloride with hexanol-1 in pyridine has been investigated in a limited way. Tentatively, the results indicate that the rate law

$$\frac{dx}{dt} = k_4(\text{COCOCl})(\text{ROH}) / \left\{ (\text{pyHCl}) + (\text{COCOCl})K_1/K_2 \right\}^{1/2}$$

is obeyed during the reaction. $k_4 = 3.4 \times 10^{-2}$, and $K_1/K_2 = 0.40$.

This result is compatible with the uncomplicated rate determining step



VI. APPENDIX

1. The Dissociation Constant and Limiting Equivalent Conductance of Pyridinium Chloride in Pyridine at 25.0°C.

Measurements of the conductance of dilute solutions of an electrolyte in a solvent of low dielectric constant may be used to calculate both the dissociation constant, K , for the ion-pairs, and the limiting equivalent conductance of the electrolyte. There are two methods currently in use for treating the conductance data, those of Fuoss and Kraus (43), and of Shedlovsky (44). The latter method was used in the present work. For salts with a dissociation constant less than 10^{-3} , both methods give the same results (45).

The equivalent conductance, in ohms⁻¹ cm.²,

$$\Lambda = 1000 \kappa / c ,$$

where κ = specific conductance = f/R , in ohms⁻¹ cm.⁻¹,

f = cell constant, in cm.⁻¹,

R = resistance, in ohms, of the cell containing a solution of concentration c , in equivalents per liter of solution. A rough estimate of the limiting equivalent conductance, Λ_0 , is first made. A good guess, based upon knowledge of the Λ_0 's for other salts in the same system, may suffice. A closer approximation may be obtained from a Kraus and Bray (46) plot of

$$\frac{1}{\Lambda} \approx \frac{1}{\Lambda_0} + \frac{1}{K\Lambda_0^2} c \Lambda .$$

The Λ_0 so determined is then used to calculate other terms of the equation

$$S = 1 + Z + \frac{Z^2}{2} + \frac{Z^3}{8} - \dots$$

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_0} - \frac{1}{k\Lambda_0^2} \Lambda c S y_{\pm}^2.$$

$Z = \frac{(B\Lambda_0 + C)}{\Lambda_0^{3/2}} (\alpha c)^{1/2}$, where B and C are the constants of Onsager's conductance equation (47). The quantity y_{\pm} is the mean ionic activity coefficient, calculated from the Debye-Huckel limiting law (48)

$$\log y_{\pm} = -A(\alpha c)^{1/2},$$

in which A is a constant, dependent only on the solvent and the temperature, and α is the fraction of the electrolyte which is dissociated:

$$\alpha = \frac{\Lambda}{\Lambda_0} S.$$

From a plot of $1/(\Lambda S)$ versus $(\Lambda c S y_{\pm}^2)$, a new estimate of Λ_0 is obtained. This is then used to calculate anew all of the quantities mentioned previously. This process is continued until the value of Λ_0 obtained from the plot agrees with that used in the calculations.

2. Experimental Procedure

The pyridine and pyridinium chloride were the same as used in the kinetic measurements. The conductance cell used was patterned after the cell of Jones (49), designed for solutions of high resistance. The electrodes were bright platinum. The cell was first cleaned with chromic acid solution, steamed for several hours, rinsed with distilled water, and

then dried in a vacuum oven for 24 hours at 50°C. The cell constant, f , was then determined as will be described shortly. Afterwards, the cell was again rinsed several times with distilled water, and dried in the vacuum oven for 24 hours at 30°C. It was then rinsed with successive portions of solvent until the measured resistance no longer increased. This latter value was used to calculate the specific conductivity of the solvent. The resistance of the most dilute solution was measured first, the cell was then rinsed several times with the next most dilute solution, its resistance was measured and the process repeated for all of the solutions analyzed.

The bridge used was a Leeds and Northrup model No. 1854-A-2.

The measurement of a resistance in the 10,000 ohm range could be reproduced within ± 1 ohm. The circuit was such that the resistance, R , of the cell was given by

$$R = \frac{R_0 R_s}{R_0 - R_s},$$

where

R_0 = setting of the decade box with the cell disconnected ($R_0 = 10,000$ ohms for all measurements recorded), and

R_s = setting of the decade box with the cell connected.

All measurements were made with an alternating current of 2000 c.p.s. frequency.

The thermostat was the bath previously described, with the water replaced by mineral oil (U. S. F.). The cell con-

stant, f , was determined by use of an indirect method, since the resistance of the cell containing solution had to be of the order of magnitude of 10,000 ohms in order to minimize polarization at the bright platinum electrodes. A 0.01 decimol (1 decimol = 1 g. mole of solute in 1 cubic decimeter of solution at 0°C.) solution of potassium chloride (Baker's Analyzed) was prepared. The potassium chloride (0.7453 g.) was weighed into a one-liter volumetric flask, and diluted to the mark with conductivity water. The error caused by using the volume of the solution rather than the weight, as Jones (50) specifies, is estimated to be not greater than $\pm 0.3\%$. This solution was used to determine the cell constant of a Henry type of platinized cell of intermediate constant ($f = 0.6445$). Jones' value for the specific conductance ($\kappa = 0.0014088$) at 25°C. of the 0.01 D solution was used. The value of R_s (437.4 ohms) was the average of four determinations. A very dilute solution of potassium chloride in conductivity water was then prepared. The specific conductance ($\kappa = 4.671$ ohms cm.) of the dilute solution was calculated from its resistance in the Henry cell ($R_s = 5798$ ohms). The cell constant for the Jones type of cell was determined from its resistance ($R_s = 2034$ ohms) when filled with the dilute potassium chloride solution. The cell constant was found to be $f = 0.1193$ at $25.00 \pm 0.025^\circ\text{C}$.

The lowest value of R_s obtained with pure solvent was 9988.7 ohms, the average of three values. The specific conductance of the solvent is therefore $\kappa = 1.35 \times 10^{-8}$ ohms

cm. The results of the measurements of the conductivity of pyridinium chloride in pyridine are recorded in Table IX.

The Kraus and Bray plot yielded an approximate value for Λ_0 of 31. This was then used to calculate the quantities for the Shedlovsky plot. The values of the various constants used in the calculation were as follows:

$$T = 298.1^\circ\text{A}$$

$$D \text{ (dielectric constant of solvent)} = 12.01 \text{ (19),}$$

$$\eta = \text{(coefficient of viscosity)} \text{ (22)}$$

$$B = \frac{1.970 \times 10^6 \times 0.2929 \times (2)^{1/2}}{(DT)^{3/2}} = 3.807 \quad (51)$$

$$C = \frac{28.98 \times 2 (2)^{1/2}}{\eta (DT)^{1/2}} = 155.1 \quad (51)$$

$$A = \frac{1.823 \times 10^6}{(DT)^{3/2}} \quad (52)$$

The values of $1/(\Lambda S)$ and $(\Lambda cSy \pm^2)$ for an approximate Λ_0 of 31 are tabulated in Table X.

The calculated value of $\Lambda_0 = 33 \pm 3$ is sufficiently close to that assumed (at least it is within the average deviation indicated) that no further calculations were deemed justified. The calculated value of $K = 1.4 \times 10^{-5}$ is not an unreasonable one. The dissociation constant of pyridinium nitrate in pyridine at 25°C . has been found (22) to be $K = 5.1 \times 10^{-5}$.

It is believed that the greatest source of error in the above experiments was in the preparation of the solutions. Pyridinium chloride is very hygroscopic. Even though all transfers were carried out in an atmosphere of nitrogen,

Table IX

 $R_0 = 10,000$ ohms.

No.	c	R_s	$\kappa - \kappa_0$	Λ
1	14.58×10^{-4}	7181	4.674×10^{-6}	3.21
2	6.113	7827	3.313	5.41
3	4.710	8180	2.639	5.60
4	1.856	8811	1.599	8.63
5	0.4142	9510	0.6010	14.5
6	0.2488	9661	0.4068	16.4
7	0.0680	9855	0.1621	23.8

The quantity, $\kappa - \kappa_0$, is the specific conductance of the solution corrected for the conductance due to the solvent.

Table X

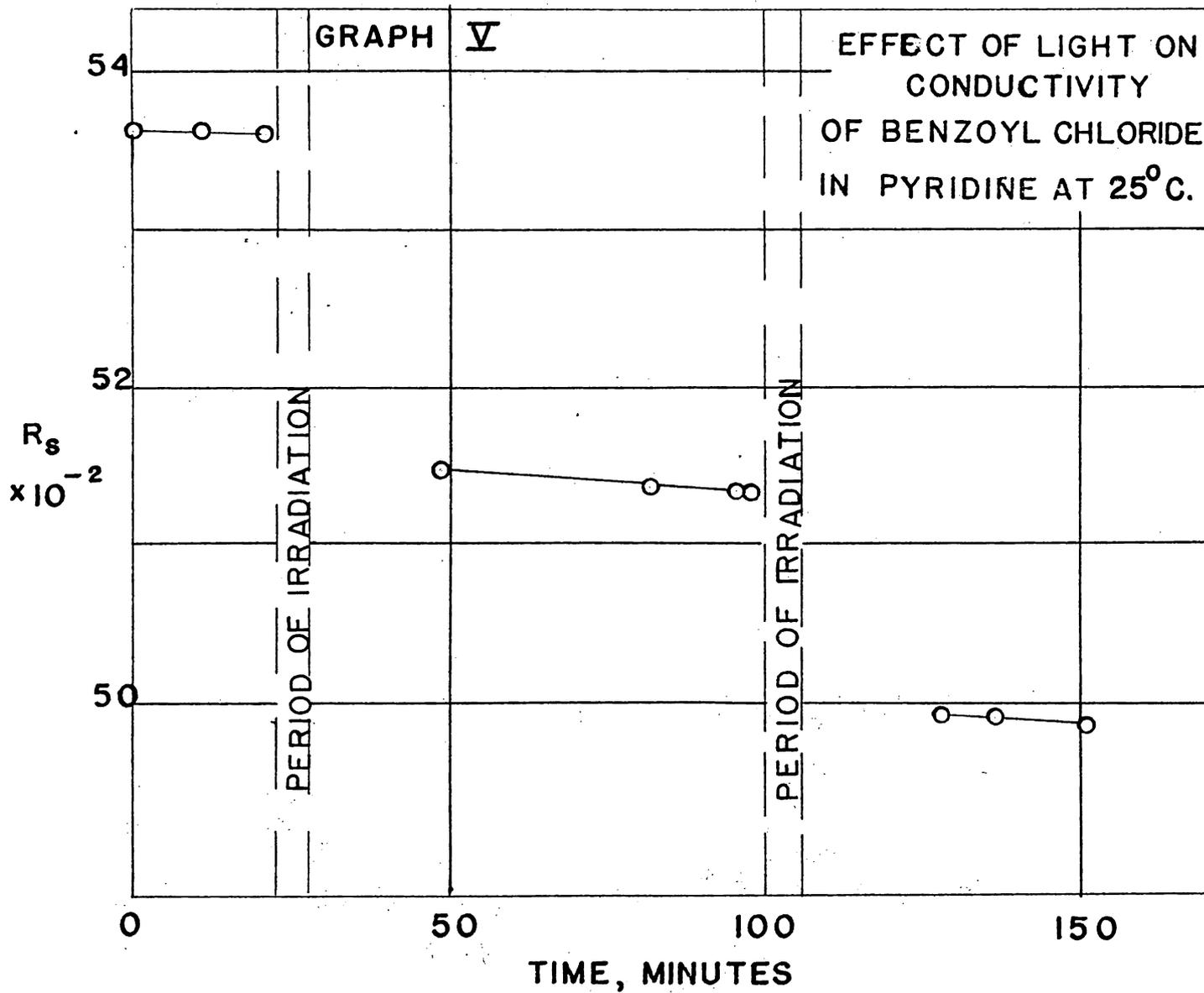
No.	$1/(\Lambda S)$	(ΛcSy_{\pm}^2)	$1/\Lambda_0$
1	27.9×10^{-2}	31.4×10^{-4}	6.5×10^{-2}
2	16.9	23.7	0.71
3	16.5	19.6	3.07
4	10.9	12.8	2.18
5	6.63	5.24	3.06
6	5.93	3.63	3.45
7	4.11	1.51	3.08

Slope of plot of $1/(\Lambda S)$ versus (ΛcSy_{\pm}^2)
 is $1/(K\Lambda_0^2) = 68.2$.

both the salt and the solvent could have picked up moisture. The solutions were prepared by adding pyridinium chloride to a weighed 25 ml. volumetric flask. The weight of salt added was determined as the difference between the weight of the flask before and after addition of the salt. Pyridine was then added, and its weight was found in the same manner. If the salt in the flask had picked up moisture, then the true concentration would be lower than that calculated from the weighings. The calculated values of Λ , being inversely proportional to the concentration of electrolyte, would be lower than the actual values. That they are of the right order of magnitude may be seen from a comparison with Davies' values for benzoyl chloride in pyridine, $k = 1.30 \times 10^{-5}$ and 32.0 ± 0.5 at 25°C .(17). These were determined in a manner similar to that employed in this work. Since the concentration of water ($M \approx 10^{-2}$) in his pyridine was probably greater than the concentration of benzoyl chloride, as has been intimated earlier, Davies was probably measuring the conductivity of a mixture of benzoic acid and pyridinium chloride. Since his solutions also contained benzoic acid, his value for Λ_0 might have been expected to be larger than the value of Λ_0 determined in this study. It is not clear why this did not turn out to be the case.

3. Irradiation of Benzoyl Chloride - Pyridine Solutions

Irradiation with ultra-violet light of a solution of benzoyl chloride in pyridine was found to increase the conductance



of the solution by as much as ten percent. In the experiment, the benzoyl chloride solution ($3.28 \times 10^{-2} M.$) was placed in a Henry type of conductance cell, with bright platinum electrodes. The cell constant f was 0.144. The cell was allowed to reach thermal equilibrium in the oil bath at $25^{\circ}C.$ The resistance of the cell was determined with the bridge previously described, and the time noted. The cell was then removed from the bath. A General Electric Co. Sunlamp was used to irradiate the cell. No effort was made to cool the cell during this period. The exposure time was noted, and the cell returned to the thermostat. A period of twenty minutes was allowed for the cell to come to temperature equilibrium. The resistance was again measured, and the time noted. This process was repeated several times. The resistance R_s was plotted versus time in graph V. From the relation

$$R = \frac{R_0 R_s}{(R_0 - R_s)} ,$$

R increases as R_s increases. Since the conductance is inversely proportional to the resistance R , then the conductance will increase or decrease as R_s increases or decreases. Note the slow decrease in resistance even while the cell was not exposed to the sunlamp. This effect was probably due to the overhead fluorescent lamps.

The titratable benzoylpyridinium chloride was not affected by irradiation. Samples of a solution of benzoyl chloride in pyridine were first titrated without exposure to

the sunlamp. The solution was then irradiated for one hour. Several samples were taken, and titration showed neither a substantial increase nor decrease in the volume of base required for neutralization. A 5.000 ml. sample of the benzoyl chloride-pyridine solution was pipetted into 25 ml. of water and titrated to the phenolphthalein end-point with standard sodium hydroxide solution. The results are recorded in Table XI.

Table XI

Sample	Ml. of NaOH
1	2.323
2	2.328
3	2.320

Solution irradiated for one hour, cooled to 25°C in bath.

4	2.340
5	2.327
6	2.328

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