

Kinetics and Mechanisms for the Two-Phase Reaction between Aqueous Aniline and Benzoyl Chloride in Chloroform, with and without Pyridine Catalysis[†]

Carl C. Wamser* and James A. Yates

Department of Chemistry, Portland State University, Portland, Oregon 97207-0751

Received August 3, 1988

This paper reports relative rates and product yields for the reaction of aniline with benzoyl chloride under conditions in which the two reactants begin in separate immiscible phases. Typically the aniline is initially in an aqueous phase over a chloroform phase containing benzoyl chloride, and the lower solution is stirred slowly. Under these conditions, the observed reaction rate, monitored by appearance of chloride into the aqueous phase, is slower than the rate of mass transport of aniline from the aqueous to the chloroform phase. Addition of pyridine as a nucleophilic catalyst significantly increases the reaction rate, in particular when the pyridine is initially in the chloroform phase. The observed rate of chloride ion appearance in the pyridine-catalyzed reaction exceeds the sum of the rates of aniline transport (from water) and benzoylpyridinium chloride transport (into water), indicating that reaction occurs in both phases. In the uncatalyzed reaction, the product is benzanilide, in high yield (80-90%). The benzanilide yields are lower in the pyridine-catalyzed reactions (37-70%), where hydrolysis to benzoic acid competes significantly.

Organic reactions in systems containing two immiscible liquid phases appear in a number of important applications. Phase-transfer catalysis (PTC) is commonly used to enhance reaction rates, making feasible a wide variety of synthetic reactions not possible in a single phase.^{1,2} Such reactions may occur in one or the other bulk phase or at the interface of the two liquids. One notable example of the latter situation is interfacial polymerization, an effective method of casting ultrathin polymer films and membranes at the interface of two immiscible liquids containing mutually reactive monomers.^{3,4} This project was initiated to model the processes that occur in the formation of polyamide interfacial membranes, such as the very successful reverse osmosis membranes made from *m*-phenylenediamine and trimesoyl chloride by interfacial polymerization.^{5,6} The results of this work offer insight into the mechanism of phase-transfer catalysis in general.

The most common arrangement for PTC involves the transport of a water-soluble reactant into an immiscible organic solvent with an appropriate hydrophobic phase-transfer catalyst. The reverse case, transport of a reactant from an organic solvent into an aqueous phase, has been reported in only a few instances^{7,8} and has been called inverse (or counter) phase-transfer catalysis (IPTC).⁸ The typical procedure used to study IPTC has been product analysis after rapid and thorough mixing of the two phases.

We report here a study of IPTC in which the interfacial area and the mixing rate have been intentionally decreased such that we can observe the effects of mass transport limiting the overall reaction. This allows a study of the effects of phase-transfer catalysts on both the kinetics and the products. We have found that the two-phase reaction of benzoyl chloride with aqueous aniline can take place in either phase, depending on the conditions, in particular the presence of pyridine as a phase-transfer catalyst. Specifically, the uncatalyzed reaction occurs in the organic phase to form benzanilide, and the catalyzed reaction occurs in the aqueous phase to give predominantly hydrolysis to benzoic acid.

Experimental Section

Materials. Aniline and benzoyl chloride were purchased from Aldrich and were distilled at reduced pressure. Aniline was

redistilled over zinc at atmospheric pressure. All other materials were reagent grade and used as received, except sodium nitrate, which was oven-dried at 90 °C before use.

Kinetic Reaction Conditions. Conditions were standardized for all runs unless otherwise specified. All reactions were run at room temperature, and no temperature changes during reaction were ever detected, even for reactions expected to be exothermic, such as the direct mixing of benzoyl chloride and pyridine in chloroform. The reaction vessel was clamped about 2 in. above the stirplate to avoid any heat transfer from that source.

The initial aqueous solution consisted of 0.10 M NaNO₃ (to provide a constant ionic strength background) and 1.0 × 10⁻⁴ M NaCl (to provide a nonzero initial chloride ion reading); both salts were necessary to stabilize the chloride ion selective electrode. A measured amount of aniline was added to make 50 mL of the aqueous solution, and this solution was placed in a 100-mL beaker with a magnetic stirbar and the chloride ion selective electrode. A solution of 0.093 M benzoyl chloride in chloroform was prepared, and 50 mL of this solution was added by pipet under the aqueous solution; stirring and timing were begun upon completion of the addition, which typically required less than 20 s. In reactions that included pyridine as a catalyst, the pyridine was added to one of the two phases prior to contact between the two phases. A simple diagram of the experimental setup is shown in Figure 1.

The standard reaction vessel was a Kimax 100-mL beaker, with a cross-sectional area of 17.5 cm². This area is a minimum value, since stirring significantly increases the interfacial area. The stir rate was kept constant in all runs, with a stirbar rotation rate of 2.8 per second. This slow rate did not break the interface and created a gentle vortex, about 1 cm deep at the center. The

(1) Weber, W. P.; Gokel, G. W. *Reactivity and Structure Concepts in Organic Chemistry*; Springer-Verlag: New York, 1977; Vol. 4.

(2) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, 1983.

(3) Morgan, P. W. *Condensation Polymers by Interfacial and Solution Methods*; Wiley-Interscience: New York, 1965.

(4) Kesting, R. W. *Synthetic Polymer Membranes*, 2nd ed.; Wiley: New York, 1985.

(5) Cadotte, J. E.; King, R. S.; Majerle, R. J.; Petersen, R. J. *J. Macromol. Sci.-Chem.* 1981, A15, 727-55.

(6) Cadotte, J. E. U.S. Patent No. 4,039,440, August 2, 1977.

(7) (a) Fife, W. K.; Xin, Y. *J. Am. Chem. Soc.* 1987, 109, 1278-9. (b) Smalley, R. K.; Suschitzky, H. *J. Chem. Soc.* 1964, 755. (c) Yamada, M.; Watabe, Y.; Sakakibara, T.; Sudoh, R. *J. Chem. Soc., Chem. Commun.* 1979, 179-80. (d) Trifonov, A.; Nikiforov, T. *J. Mol. Catal.* 1984, 24, 15-8. (e) Ganeshpure, P. A.; Satish, S. *J. Chem. Soc., Chem. Commun.* 1988, 981-2.

(8) (a) Mathias, L. J.; Vaidya, R. A. *J. Am. Chem. Soc.* 1986, 108, 1093-4. (b) Okano, T.; Moriyama, Y.; Konishi, H.; Kiji, J. *Chem. Lett.* 1986, 1463-6.

[†]This paper represents Paper No. 223 from the Environmental Sciences and Resources Program at Portland State University.

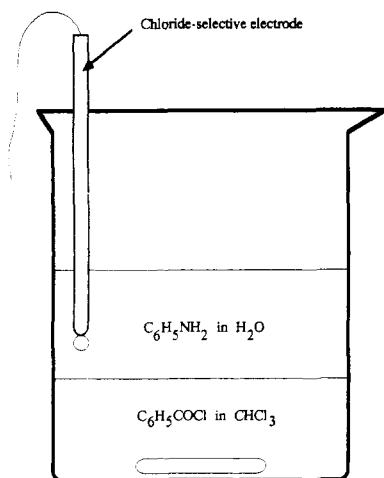


Figure 1. Schematic diagram of the two-phase reaction.

reproducibility of the interfacial area and the stirring rate was verified by the reproducibility of measured transport and reaction rates. The importance of these factors in determining the observed rate was verified by the observation that an intentional decrease in stir rate or increase in interfacial area (a larger beaker) gave corresponding changes in reaction rates (see Table II).

Kinetic Analyses. The reaction was followed by the appearance of chloride ion into the aqueous phase. Chloride ion concentration was measured by an Orion 94-17B chloride ion selective electrode, with an Orion 93-02 reference electrode. Millivolt readings were taken on an Orion 611 pH/mV meter at 30-s intervals after timing was begun. The chloride detection system was calibrated daily with known NaCl standards in an identical aqueous solution. There was no detectable interference in chloride ion detection by the presence of aqueous pyridine or chloroform as a separate underlayer. Aniline had a minor effect on the chloride-selective electrode, but the effect of 0.2 M aniline (our maximal concentration) became insignificant for chloride ion concentrations over 0.001 M (approximately 1% of a typical reaction).

The transport rates of aniline and pyridine were observed under conditions identical to a normal reaction run. Concentration was determined by removal of 0.10-mL aliquots by pipet from each phase at 1- or 2-min intervals. Each aliquot was diluted to 100-mL, and full ultraviolet spectra were taken. Extinction coefficients were determined from Beer's Law plots at three concentrations. For aniline, the extinction coefficient used was $1600 \text{ M}^{-1} \text{ cm}^{-1}$ in the aqueous solution, measured at the sharp second absorption maximum at 247 nm. For pyridine, the extinction coefficient used was $2900 \text{ M}^{-1} \text{ cm}^{-1}$ in the aqueous solution, at the absorption maximum at 256 nm. Spectra were taken on a Shimadzu 260 spectrophotometer.

Preparative Reaction Conditions. In a typical run, 1.00 mL of aniline (11.0 mmol) was dissolved in 15.0 mL of 0.839 M HCl (12.6 mmol), giving a final solution that was 0.688 M in aniline and 0.787 M in HCl, with a measured pH of 1.8. This solution was placed in a 100-mL beaker over a solution containing 1.28 mL of benzoyl chloride (11.0 mmol) in 20 mL of carbon tetrachloride, a concentration of 0.55 M. A solution of 0.463 M aqueous NaOH was added dropwise while the reaction mixture was stirred slowly and the pH of the aqueous phase was monitored. The pH profile was typical of a strong base titration of a mixture of a strong acid plus a weak acid; there was an early endpoint for neutralization of excess HCl, followed by a gradual rise in pH during the buffer region of anilinium chloride (pH 5–6), and a final rapid rise at the equivalence point (around 50 mL), corresponding to complete neutralization of the original HCl plus 1 equiv of HCl from reaction of aniline with benzoyl chloride. During the addition, benzanilide precipitates. In order to maximize the yield of benzanilide, it is important to carry the titration past the equivalence point to a pH of at least 10. Filtration of the precipitate and washing with CCl_4 gives 1.95 g (90%) of benzanilide, mp 161.0–161.4 °C. An additional small amount (<5%) can be obtained by drying and evaporating the CCl_4 solvent. This procedure has not been optimized for yield.

Table I. Mass Transport Rates between Phases

entry no.	solute	initial phase	partition coefficient ^{a,b}	rate constant, min^{-1}	half-time (calcd, min)
1	PhNH_2^b	H_2O	8.0	0.027	26
2	$\text{C}_5\text{H}_5\text{N}^b$	H_2O	13.2	0.040	17
3	$\text{PhNH}_3^+\text{Cl}^-$	CHCl_3	(v small)	1.1	0.6
4	$\text{PhCOpyr}^+\text{Cl}^-$	CHCl_3	(reacts)	0.040	17

^a Equilibrium concentration ratio in chloroform/water. ^b Determined by UV spectrophotometry. ^c Determined by monitoring Cl^- appearance in the aqueous phase.

Table II. Observed Reaction Rates, Uncatalyzed Reaction^a

entry no.	equiv of aq PhNH_2	half-time (exptl, min)
5	0	(days)
6	2	49
7	2	90 ^b
8	2	42 ^c

^a Based on appearance of Cl^- in the aqueous phase, beginning with 4.6 mmol (0.093 M) of benzoyl chloride in the chloroform phase. ^b Experiments performed at 0.78× the normal stir rate. ^c Experiments performed with 1.27× the normal cross-sectional surface area.

Table III. Observed Reaction Rates and Product Yields with Pyridine Catalysis^a

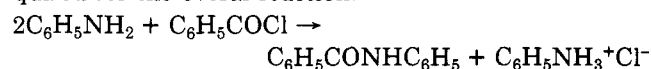
entry no.	equiv of aq PhNH_2	equiv of pyridine ^b	half-time (exptl, min)	benzanilide yield, %	calculated yield, ^c %
6	2	0	49	90	100
4	0	1	20		
9	0	2	13.5		
10	1	1	11.8	52	41
11	1	2	12.8	37	37
12	2	1	9.7	70	58
13	2	2	6.1	54	54
14	2	2 ^b	13.1	89	

^a Based on appearance of Cl^- in the aqueous phase, beginning with 4.6 mmol (0.093 M) of benzoyl chloride in the chloroform phase. ^b Pyridine initially in the chloroform phase except for entry 14, in which pyridine was initially in the aqueous phase. ^c Calculated percentage of benzanilide product, assuming that the transport of aniline gives solely benzanilide and the transport of benzoylpyridinium chloride gives no benzanilide.

Results

Mass Transport Rates. With use of standardized conditions of stir rate, interfacial area, and temperature, rates for mass transport between phases were determined for the various components of the reaction mixture (Table I). In all cases, the observed transport processes were first-order, and the rate constants were determined from the slopes of the appropriate log plots. The reproducibilities of the stir rate and other experimental parameters were verified by repeated runs; for example, the rate constant listed for aniline transport is the average of four runs with a standard deviation of 6%. To facilitate comparison of these transport rates with reaction rates listed in Tables II and III (which are typically not simple first-order processes), half-times are calculated from the rate constants.

Uncatalyzed Reaction Rates. Under conditions identical with those used for the mass transport rates, the rates of reaction of aqueous aniline with benzoyl chloride in chloroform were measured by following the appearance of Cl^- into the aqueous phase. Since no other base or buffer was used in the system, 2 equiv of aniline are required for the overall reaction.



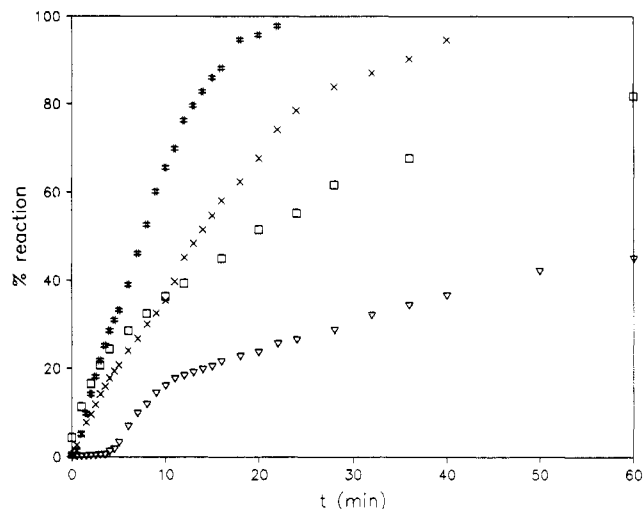


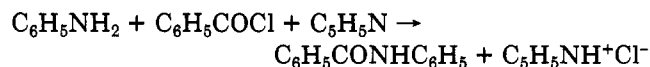
Figure 2. Transport rates and reaction rates for the two-phase reaction between aniline and benzoyl chloride. (□), aniline transport (Table I, entry 1); (×), benzopyridinium chloride transport (Table I, entry 4); (∇), uncatalyzed reaction (Table II, entry 6); (#), catalyzed reaction with 2 equiv of pyridine in CHCl_3 (Table III, entry 13).

The time course of a typical uncatalyzed reaction is illustrated in Figure 2, along with a plot of aniline transport, measured separately, and data for the catalyzed reactions, discussed in the following section. The uncatalyzed reaction shows a distinctive initial lag time, after which the observed reaction rate rises and approximates the rate (slope) of aniline transport. Because of the initial lag time, the rates of the uncatalyzed reactions are not readily described by rate constants. In Table II the reaction rates are summarized as half-times to provide convenient measures of relative rates for comparison with transport rates. In all uncatalyzed reactions, yields of benzanilide were high, typically about 90%.

Table II, entry 5, points out that the inherent reactivity of benzoyl chloride in chloroform with a contacting aqueous phase is very low. There was no significant release of chloride into the aqueous phase during days of stirring. In comparison, with pyridine present, rapid release of chloride results, as expected, from formation of the water-soluble benzopyridinium complex^{7,8} (Table I, entry 4).

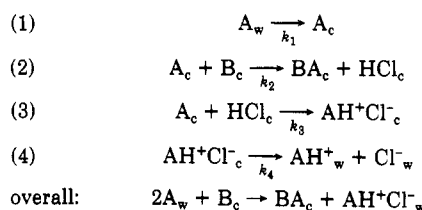
Table II further illustrates the significance of stir rate and interfacial area in controlling the observed reaction rates. An intentional decrease in the stir rate strongly decreased the reaction rate, and an intentional increase in the interfacial area slightly increased the reaction rate. Neither effect is directly proportional to the parameter varied. We did not attempt to quantify these effects; rather we held them as constant as possible for all runs.

Pyridine-Catalyzed Reaction Rates. Comparable reactions were performed that included various amounts of pyridine as phase-transfer catalyst, with all other reaction conditions identical with those of the previous experiments. Reaction rates and isolated product yields are summarized in Table III. With pyridine present, the stoichiometry of the overall reaction is slightly different.



The data of Table III clearly show that all of the reactions with pyridine present are significantly faster than the uncatalyzed reaction (entry 6). Keeping in mind that the reaction rate is monitored by the appearance of chloride ion into the aqueous phase, it is clear that much of

Scheme I. Uncatalyzed Reaction^a (in chloroform solution)



^a Abbreviations: A = aniline; B = benzoyl chloride; BA = benzanilide. Subscripts: c = chloroform phase, w = water phase.

the rate increase is due to transport of benzopyridinium chloride from chloroform into water (entries 4 and 9). Nevertheless, in the presence of aqueous aniline as well, the reaction rates are even faster (entries 10–14). When the pyridine is initially present in the aqueous rather than the chloroform phase, the rate increase is less (entry 14), although still very substantial with respect to the uncatalyzed reaction.

The time course of a typical catalyzed reaction is shown in Figure 2, along with the relevant transport rates and the uncatalyzed reaction. After a few minutes, the rate of chloride appearance in the catalyzed reaction exceeds the rate of transport of either aniline or benzopyridinium ion. However, the catalyzed reaction rate is always less than the sum of the two transport rates.

When pyridine was present, benzanilide yields were significantly reduced compared to the uncatalyzed reactions. In the case of pyridine initially in the aqueous phase, however, the yield remained very high (entry 14).

Discussion

Rates of reactions occurring in two-phase systems depend upon a large number of parameters, including mixing rates, interfacial area, partition coefficients, and mass transport rates, as well as the usual kinetic parameters, such as temperature and reactant concentrations.⁹ We have intentionally controlled the stir rate of our reaction system to very low levels, such that mass transport can be observed to limit the overall rate. All other features of the reaction system are kept as constant as possible.

Uncatalyzed Reaction. In the case of the uncatalyzed reaction, the observed rate of chloride ion appearance into the aqueous phase can be taken as the overall rate of reaction, since it represents the final step in the sequence of steps that are required for the net reaction. An abbreviated mechanistic scheme is presented in Scheme I. The well-known steps by which amines react with acid chlorides¹⁰ are compressed into step 2, since they are not mechanistically distinguishable by our method of monitoring the reaction. The removal of the HCl product from the chloroform phase is expected to be extremely rapid; it may be transported as the aniline salt (step 3) or as HCl. We have demonstrated that the transport of anilinium chloride (step 4) is extremely rapid under our conditions (Table I, entry 3).

The significant lag time of 4–5 min indicates that step 2 is rate-limiting under conditions of very low initial aniline concentration. After the lag time, the rate picks up and roughly follows the rate of aniline transport into chloroform, indicating that aniline transport (step 1) has become rate-limiting.

(9) Bradbury, J. H.; Crawford, P. J. In *Interfacial Synthesis*; Millich, F., Carraher, C. E., Eds.; Dekker: New York, 1977; pp 77–102.

(10) Beckwith, A. L. J. In *The Chemistry of Amides*; Zabicky, J., Ed.; Wiley-Interscience: New York, 1970; pp 73–185.

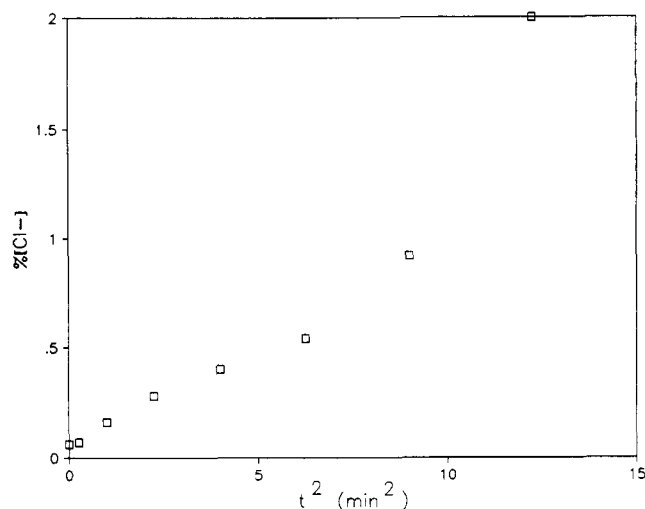


Figure 3. Uncatalyzed reaction rate dependence on t^2 at short times (Table II, entry 6).

The progress of the reaction at short times, before it becomes limited by aniline transport, can be modelled by the kinetic analysis of Scheme I. Assuming that the HCl transport out of chloroform is fast (i.e. steps 3 and 4), then the observed rate will be governed by step 2. At short times, the concentration of benzoyl chloride will not have changed significantly, and the concentration of aniline in chloroform will follow the rate of step 1.

$$+d[\text{Cl}^-]_w/dt = k_2[\text{B}_c]_0[\text{A}_w]_0(1 - e^{-k_1t})$$

Finally, $(1 - e^{-x})$ may be approximated as x for small values of x ($x = k_1t$). For our measured rate constants (0.027 min^{-1} for aniline transport), the approximation is good for about the first 3 min of the reaction. The integrated rate expression is as follows.

$$[\text{Cl}^-]_w = k_1k_2[\text{B}_c]_0[\text{A}_w]_0t^2/2$$

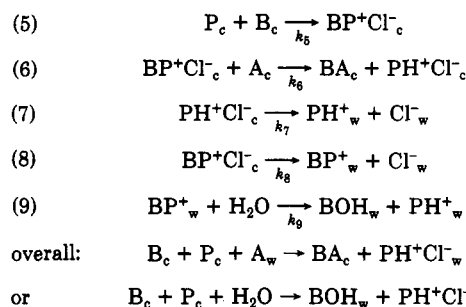
Figure 3 illustrates the plot of measured $[\text{Cl}^-]_w$ vs t^2 . It is reasonably linear through the first few minutes and then diverges upward, eventually assuming the general shape of all of the other rates shown in Figure 2.

Pyridine-Catalyzed Reaction (Pyridine in Chloroform). The appearance of Cl^- is significantly faster in the presence of pyridine initially added to the chloroform phase. Pyridine is known to form a complex with acyl chlorides; in some instances, these are stable enough to be isolated.¹¹ Since the complex is ionic, it is expected to partition preferentially into the aqueous phase.^{7,8} This provides another pathway for release of Cl^- , in addition to the formation of benzanilide from aniline. Additional mechanistic steps are outlined in Scheme II.

In these experiments, both pyridine and benzoyl chloride are added to the chloroform phase prior to the addition of the aqueous phase. The direct reaction between pyridine and benzoyl chloride should be fast;¹¹ thus we expect step 5 to have gone to completion.

Once the benzoyl chloride is converted to benzoylpyridinium ion, the remainder of the mechanism can proceed similarly to Scheme I, i.e. reaction of aniline with benzoylpyridinium ion in the chloroform phase followed by release of Cl^- to the aqueous phase (steps 6 and 7). In competition with these steps, however, the benzoylpyridinium ion could transport to the aqueous phase, where Cl^- will be released immediately as the counterion.

Scheme II. Pyridine-Catalyzed Reaction^a (pyridine in chloroform)



^a Abbreviations: P = pyridine; BP⁺ = benzoylpyridinium; BOH = benzoic acid (other abbreviations are the same as in Scheme I).

The major fate of aqueous benzoylpyridinium ion is expected to be hydrolysis to benzoic acid, since the concentration of other available nucleophiles is very low, e.g. aniline is 0.18 M prior to its transport into chloroform.

Figure 2 provides evidence that both pathways are occurring. The observed rate of appearance of Cl^- is faster than either of the relevant transport rates, yet smaller than the sum of the two. Additional evidence for the competition of the two pathways is obtained from an analysis of the product yield relative to the kinetic data.

When the reaction occurs in the chloroform phase, without pyridine catalysis, an excellent yield of benzanilide is obtained. Pyridine catalysis increases the rate (of chloride evolution) but diminishes the extent of benzanilide formation, leading instead to hydrolysis to benzoic acid. The relative fraction of the benzoyl chloride reaction that proceeds by each of the two pathways can be separated in two distinct ways: based on the relative rates and based on the product yields. The kinetic analysis assumes that the two pathways compete in accord with the rates that would be calculated for the corresponding transport-limited reactions, i.e. the chloroform reaction occurs as fast as aniline transports into chloroform and the aqueous reaction occurs as fast as benzoylpyridinium transports into water. This analysis further assumes that all of the reaction in the chloroform phase gives benzanilide and all of the reaction in water gives benzoic acid.

The comparison of product yields with the calculated yields based on the kinetic analysis are shown in Table III. The agreement indicates that the kinetic catalysis by pyridine results in a comparable decrease in benzanilide product yield. In other words, for these particular reaction conditions (pyridine phase-transfer catalyst initially in the chloroform phase along with the benzoyl chloride), all of the kinetic catalytic effect leads to hydrolysis product rather than benzanilide product. The agreement between the kinetic and product analyses further indicates that the hydrolysis product is primarily the result of transport of benzoylpyridinium ion into the aqueous phase rather than reaction with water in the chloroform phase.

Pyridine-Catalyzed Reaction (Pyridine in Water). The final entry in Table III indicates that the rate of the reaction is substantially increased by aqueous pyridine, although not as much as by pyridine initially in the chloroform phase. Most notably, aqueous pyridine catalysis retains the excellent benzanilide yield while offering substantial rate enhancement.

When the pyridine is initially in the aqueous phase, at least two additional mechanistic steps are required: transport of pyridine into the chloroform phase and re-action of the pyridine with benzoyl chloride. The former reaction is probably the limiting step, since we have shown

(11) Ferscht, A. R.; Jencks, W. P. *J. Am. Chem. Soc.* 1970, 92, 5432 and 5442.

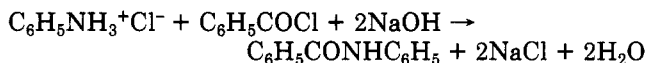
that pyridine transport from water into chloroform is relatively slow, approximately as fast as the transport of aniline from water to chloroform. Given that both aniline and pyridine are transporting into chloroform at comparable rates, it is not surprising that the pyridine is somewhat less effective as a phase-transfer catalyst under these conditions.

The retention of the excellent yield of benzanilide under these conditions indicates that aniline competes very effectively for benzoylpyridinium ion while it is still in the chloroform phase. Benzoylpyridinium ion is formed as pyridine transports into the chloroform phase, at approximately the same rate at which aniline transports into chloroform. The balancing of the rates of generation of the reactive species and the arrival of its coreactant apparently optimizes the kinetic catalysis with a minimum loss of the reactive benzoylpyridinium ion to the aqueous phase, where it would hydrolyze.

The above analysis also speaks to the point of whether or not pyridine may truly act catalytically, that is, in less than stoichiometric ratios. To do so, pyridine used to activate one benzoylpyridinium chloride would have to be released after reaction in order to activate another benzoyl chloride. For reactions that would recycle entirely within one phase, as the aqueous pyridine-catalyzed reaction appears to do, this would be a straightforward process. For true phase-transfer catalysis, pyridine would have to transport between phases for each cycle of catalysis. Since aqueous pyridine does show significant rate enhancement with respect to the uncatalyzed reaction, it seems quite feasible that it could function as a recycling (substoichiometric) catalyst, even under our relatively unusual conditions of mass-transport limited reaction. Under the more normal conditions of vigorous mixing, true catalytic activity is much more feasible and is observed.^{7,8}

Improved Method for Two-Phase Amide Synthesis.

A slight modification of our approach allows for a very convenient synthetic method for amide preparation. The aniline is dissolved in aqueous acid and placed over a benzoyl chloride solution in CCl₄. No reaction takes place until the aniline is liberated by titration with aqueous base. Aniline thus can be released in a controlled fashion, subsequently entering the organic phase where it reacts with benzoyl chloride to form benzanilide, which precipitates. The HCl released in the amide-forming reaction requires that 2 equiv of base be titrated for each amide formed.



This method compares very favorably with the traditional method of amide synthesis from aryl acid chlorides, the Schotten-Baumann method.¹² Unlike the Schotten-Baumann method, there is never an excess of base, which could compete with the amine. Furthermore, the product precipitates nicely from CCl₄ solution. If the base titration is continued to a relatively high pH, any benzoic acid side product will be extracted into the aqueous solution, making isolation of the final product simpler.

A similar two-phase method of amide synthesis from amine hydrochlorides has been reported.¹³ In that case, a toluene solution of acid chloride is heated with an aqueous amine hydrochloride solution. Presumably HCl is gradually driven off to initiate the phase transfer of the amine. The current base titration method is essentially based on the same premise but employs much milder conditions and offers a much higher yield in the case of benzanilide.

Summary

These results indicate that the two-phase reaction of benzoyl chloride with aniline ordinarily occurs in the organic phase, and the reaction can be limited by aniline transport under conditions of very slow mixing. Pyridine acts as an inverse phase transfer catalyst for the transport of benzoyl chloride (as benzoylpyridinium chloride) into the aqueous phase, where it hydrolyzes to benzoic acid. Under appropriate conditions, both processes can be observed; both the product yields and the reaction rates can be analyzed in terms of the competition of the two pathways. Optimum yields of benzanilide product are obtained by utilizing aqueous pyridine catalysis or by slow neutralization of aqueous anilinium hydrochloride by base titration.

Acknowledgment. This work comprised the undergraduate honors thesis project of J.A.Y. and was presented by J.A.Y. at the 42nd Northwest Regional Meeting of the American Chemical Society, Bellingham, Washington, June 18, 1987. Partial financial support was provided by the U.S. Department of Energy, Advanced Energy Projects Division of the Office of Basic Energy Sciences, Grant DE-FG06-85ER-13389.

Registry No. Aniline, 62-53-3; benzoyl chloride, 98-88-4; pyridine, 110-86-1.

(12) Vogel, A. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman: Essex, England, 1978; p 682.

(13) Shama, S. A.; Tran, T. L. *J. Chem. Ed.* 1978, 55, 816.

Correlation of the Rates of Solvolysis of 2-Adamantyl 2,2,2-Trifluoroethanesulfonate: A Y_{OTf} Scale¹

Dennis N. Kevill* and David C. Hawkinson

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received July 28, 1988

Specific rates of solvolysis of 2-adamantyl 2,2,2-trifluoroethanesulfonate (tresylate), determined in a variety of organic and aqueous organic solvents at 25 and/or 50 °C, have been used for the determination of a scale of solvent ionizing power (Y_{OTf}). The Y_{OTf} values give an excellent linear correlation with Y_{OTs} values, with a very small intercept and a slope of essentially unity. Additional Y_{OTs} values (for 2,2,2-trifluoroethanol-ethanol mixtures) have been determined from the specific rates of solvolysis of 2-adamantyl *p*-toluenesulfonate.

Several months ago, we presented² a scale of solvent ionizing power for a 2,2,2-trifluoroethanesulfonate (tresy-

late) leaving group (Y_{OTf}) based upon the rates of solvolysis of 2-adamantyl tresylate. The recent publication³ of a