products. For purposes of following spectrophotometrically the changes in product structure occurring during the course of reaction, 1:6 v/v trifluoroacetic acid–carbon tetrachloride was used as the medium in this phase of the investigation. In solutions in this mixture in which the original concentrations of *o*-nitrobenzhydryl bromide were 2–4 × 10^{-2} *M*, isoxazole (II) and nitroso ketone (I) were observed to form simultaneously, the latter forming rapidly during early phases of reaction and then much more slowly as hydrogen bromide in the medium increased. After at least 10 half-lives elapsed, the yields of isoxazole and nitroso ketone were of the order of 70–80% and 15–20%. In 0.1 *M* concentration in acetic acid the *o*-nitro compound solvolyzed in the initial phases of reaction to produce a small amount of nitroso ketone (6–7%), which decreased in quantity as reaction proceeded due to formation of isoxazole as the exclusive final organic product. The conversion of nitroso ketone to isoxazole by hydrogen bromide, which is very rapid in acetic acid solutions of 0.01–0.1 *M* hydrogen bromide concentration, is apparently somewhat slower in trifluoroacetic acid.

In acetic acid in the presence of sodium acetate, *o*-nitrobenzhydryl bromide solvolyzes to produce exclusively *o*-nitrosobenzophenone. The sodium salt in this case prevents accumulation of hydrogen bromide in the medium. In 1:6 v/v trifluoroacetic acid in the presence of sodium trifluoroacetate the formation of nitroso ketone from the halide is not blocked, and in fact the nitroso ketone and isoxazole are formed in about the same proportions as when salt is omitted from the reaction mixture. It appears that trifluoroacetate ion is a weaker base than bromide ion in trifluoroacetic acid.[17]

In this same context it is interesting to note that nitroso ketone formation in the reaction of the *o*-nitro compound in trifluoroacetic acid–carbon tetrachloride can be eliminated completely by adding *either* hydrogen bromide or lithium bromide. Rate constants, based on the measurement of formation of isoxazole as the reaction product in solutions initially 2–4 × 10^{-4} *M* in *o*-nitrobenzhydryl bromide and 6–10 × 10^{-3} *M* either in hydrogen bromide or lithium bromide, were found to be in good agreement ($k_{25°} \sim 9 \times 10^{-4}$ sec^{-1}). Eaborn, Jackson, and Taylor have observed previously that hydrogen bromide is evolved from a solution of sodium bromide in trifluoroacetic acid.[18]

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Aminolysis Reactions. II. Catalysis of Ester Aminolysis in Chlorobenzene. Correlation with Hydrogen-Bonding Ability of Catalysts

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Abstract: The *n*-butylaminolysis of *p*-nitrophenyl acetate in chlorobenzene at 25° follows the rate equation $k_{1,obsd} = k_3(BA)^2 + k_3'(BA)(cat.)$. Dipolar oxygen bases are very effective catalysts of the reaction; *N*,*N*-dimethylacetamide is more than twice as effective in catalyzing the reaction as *n*-butylamine although it is a 10^{10} times weaker aqueous base. The catalytic abilities of several classes of oxygen and nitrogen compounds correlate with their hydrogen-bonding ability to *p*-fluorophenol in chlorobenzene by the equation $\log k_3' = 1.2 \log K_f - 3.3$. This correlation indicates that there is 10–30% proton transfer to the catalyst in the transition state. The results suggest that amides could serve as general base catalysts in enzymes with hydrophobic active sites.

In 1969 we[1] presented evidence and arguments against the bifunctional or cyclic nonpolar mechanisms for the aminolysis and amidinolysis of *p*-nitrophenyl acetate, *p*-NPA, in chlorobenzene solvent.[2] We proposed that the reactions were general base catalyzed and heterolytic in mechanism and suggested the use of unhindered tertiary amines, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), and intramolecular tertiary amine catalysts as mechanistic probes to differentiate between cyclic and stepwise general base catalysis.[1] Subsequent work by Pietra, *et al.*, has presented additional evidence in favor of the bifunctional catalysis mechanism for benzamidinolysis reactions.[3a] Although additional arguments have also been presented on behalf of the bifunctional catalysis mechanism for ester aminolysis,[3b,c] the most recent work of Menger, *et al.*, provides compelling evidence that the aminolysis of aryl esters in aprotic solvents proceeds by a general base-catalyzed mechanism of the general form given in eq 1.[4] It is surmised that the base catalyst, which may be a second molecule of the nucleophilic amine, func-

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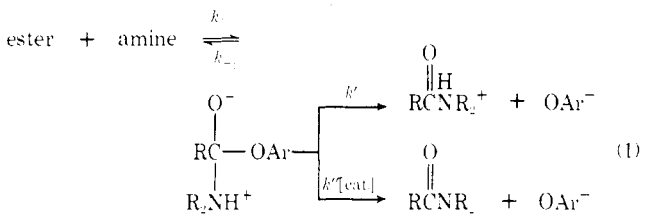
Table I. Rate and Physical Constants of Catalyzed *n*-Butylaminolysis of *p*-NPA in Chlorobenzene at 25°

	Catalyst	[Catalyst]	pK_{BH^+}	H[a]	D[b]	$k_3 \times 10^2$ M^{-2} sec^{-1}	$k_3' \times 10^2$ M^{-2} sec^{-1}	3 + log k_3'
1.	None		10.66[c]	1.76	1.4	6.2[d]		1.79[c]
2.	*N*,*N*-Dimethyl-4-amino-pyridine	0.005–0.01	9.70[e]	2.4	4.31	5.6 ± 0.2	32 ± 2	2.51
3.	DABCO	0.05–0.1	8.6[f]	1.84		6.4[g]	8.4 ± 0.1[g]	1.92
4.	1-Methylimidazole	0.0012–0.061	7.2[e]	2.41	3.6	8.3 ± 1.4	22 ± 2	2.34
5.	2,6-Dimethylpyridine	0.018–0.063	6.60[e]	1.78	1.66	6.3 ± 0.4	0.9 ± 0.7	0.95
6.	4-Methylpyridine	0.01–0.061	6.03[e]	1.69	2.60	5.9 ± 0.2	6 ± 1	1.78
7.	Pyridine	0.06–0.084	5.21[e]	1.55	2.20	7.2 ± 0.4	2.1 ± 0.5	1.3
8.	Triphenylarsine oxide	0.0014–0.0035	0.99[h]	3.17	5.54	6.3 ± 0.4	400 ± 0	3.60
9.	Pyridine *N*-oxide	0.001–0.0054	0.79[i]	2.35	4.20	6.4 ± 0.4	41 ± 8	2.6
10.	2-Pyridone	0.0021–0.14	0.75[j]		2.10	5.7	1000 ± 100	4.0
11.	1-Methyl-2-pyridone	0.005–0.011	0.32[k]	2.00	4.00[l]	5.9 ± 0.5	20 ± 6	2.3
12.	*N*,*N*-Dimethylacetamide	0.01–0.052	−0.39[m]	2.00	3.81	6.6 ± 0.3	15.3 ± 0.2	2.18
13.	Trimethylphosphine oxide	0.0023–0.0079	−2[n]	3.02	4.29[o]	5.5 ± 0.5	190 ± 10	3.25
14.	Tetrahydrofuran	0.051–0.14	−2.08[p]	0.99	1.75	6.3 ± 0.3	0.4 ± 0.3	0.6
15.	Triphenylphosphine oxide	0.0021–0.0061	−2.10[h]	2.72	4.31	6.3 ± 0.3	57 ± 4	2.76
16.	Dimethyl sulfoxide	0.005–0.013	−2.78[n]	2.14	3.9	6.3 ± 0.5	14 ± 3	2.28
17.	Benzonitrile	0.01–0.059	−10.7[q]	0.56	4.05	5.5 ± 0.2	3 ± 2	1.5
18.	Sulfolane	0.0033–0.017	−12.8[r]	1.21	4.69	5.9 ± 0.4	2 ± 1	1.3

[a] H values in chlorobenzene calculated from H values in CCl_4 using constants of Table III, ref 7c. [b] Dipole moments: A. C. McCellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. [c] 3 + log k_3 of *n*-butylamine. [d] Reference 2a. [e] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965. [f] J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Amer. Chem. Soc.*, **87**, 5050 (1965). [g] Reference 1. [h] C. Klofntar, F. Krasonec, and M. Kusar, *Croat. Chem. Acta*, **40**, 23 (1968). [i] H. E. Zaugg, *J. Amer. Chem. Soc.*, **82**, 2903 (1960). [j] S. F. Mason, *J. Chem. Soc.*, 674 (1958). [k] A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956). [l] H. Lumbroso and D. Bertin, *Bull. Soc. Chim. Fr.*, 1728 (1970). [m] P. Haake, R. D. Cook, and G. H. Hurst, *J, Amer. Chem. Soc.*, **89**, 2650 (1967). [n] P. Haake and R. D. Cook, *Tetrahedron Lett.*, 427 (1968). [o] R. S. Armstrong, M. J. Aroney, F. Le, J. W. Raymond, R. K. Pierens, J. D. Jaxby, and C. J. Wilkins, *J. Chem. Soc. A*, 2735 (1969). [p] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 325 (1963). [q] N. C. Deno, R. W. Gaugler, and M. J. Wisotsky, *J. Org. Chem.*, **31**, 1967 (1966). [r] S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).



(1)

tions to remove the ammonium proton of the tetrahedral intermediate and thereby enables decomposition of the intermediate to the neutral amide rather than to the much more energetic N-protonated amide.[4b]

We report in this paper (1) that a variety of oxygen and nitrogen bases serve to catalyze the *n*-butylaminolysis of *p*-NPA, (2) that the catalytic abilities of the oxygen bases are "exceptionally enhanced" relative to those of the nitrogen bases in this reaction, and (3) that the catalytic abilities of all the bases investigated with the exception of 2-pyridone which functions as a bifunctional catalyst[5] are correlated with their hydrogen-bonding abilities rather than their aqueous basicities. The mechanistic implications of these findings are commented on. Preliminary reports of this work have been published.[6]

Results and Discussion

In the presence of catalysts, the *n*-butylaminolysis of *p*-NPA in chlorobenzene follows the rate expression[1,2]

$$k_{1,obsd} = k_2(\text{amine}) + k_3(\text{amine})^2 + k_3'(\text{amine})(\text{cat.})$$

The k_2 term was not detectable at 25° but is observable at higher temperatures.[6b] With secondary amines k_2 terms are observed at 25°.[4,6b]

The k_3' values listed in Table I represent the average of several kinetic runs covering at least two concentrations of catalysts and at least three concentrations of *n*-butylamine for each catalyst's concentration. A typical data plot is shown in Figure 1 for *N*,*N*-dimethylacetamide. The concentrations of catalysts were kept as low as possible to minimize medium effects. The relative constancy of the k_3 terms around its value in the absence of catalysts of 0.062 M^{-2} sec^{-1} suggests that medium effects due to the presence of the catalysts are small. If the k_3' values were due to medium effects, catalysts with high dipole moments such as sulfolane and benzonitrile would be expected to exhibit large medium effects in the low-polarity, low-dielectric constant solvent chlorobenzene and consequently have large k_3' terms. This is not the case. Sulfolane and benzonitrile have very small k_3' terms suggesting that medium effects are small. Thus, we consider the k_3' terms to represent a specific catalysis effect and not a medium or solvent effect.

In addition to listing the k_3, k_3', dipole moments D, and pK_a for each catalyst, Table I lists the H values for the catalysts. The H values are a measure of the abilities of the catalysts to form hydrogen-bonded complexes with *p*-fluorophenol in chlorobenzene solvent.[7]

$$p\text{-FPhOH} + \text{B} \overset{K_f}{\rightleftharpoons} p\text{-FPhOH}\cdots\text{B}$$

$$\log K_f \equiv H$$

With a single class of catalysts and in the absence of severe steric hindrance, the data of Table I indicate that catalytic ability follows aqueous basicity with a shallow slope; for the pyridines $\Delta \log k_3'/\Delta pK_a \approx 0.3$. How-

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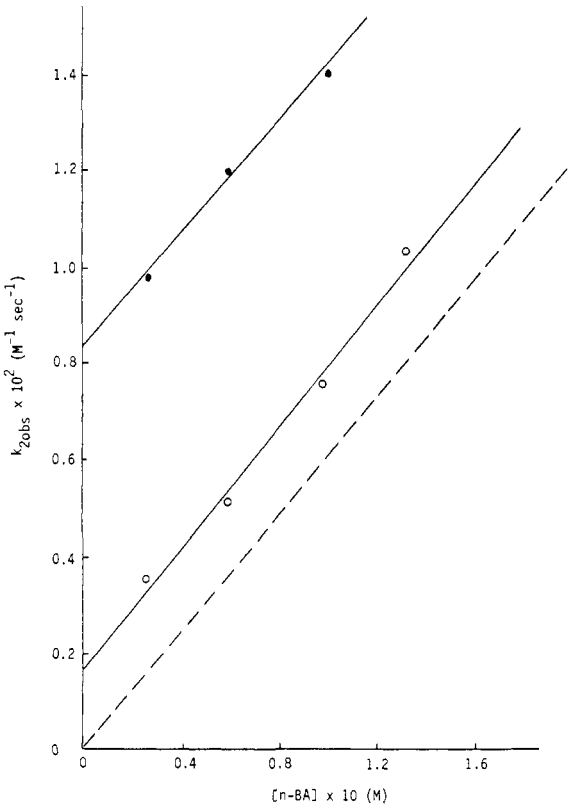

Figure 1. Plot of the observed second-order rate constants *vs.* concentration of *n*-butylamine for reaction with *p*-NPA in chlorobenzene at 25° in the presence of (1) 0.0 *M* (- - -), (2) 0.0103 *M* (○), and (3) 0.0516 *M* (●) *N*,*N*-dimethylacetamide.

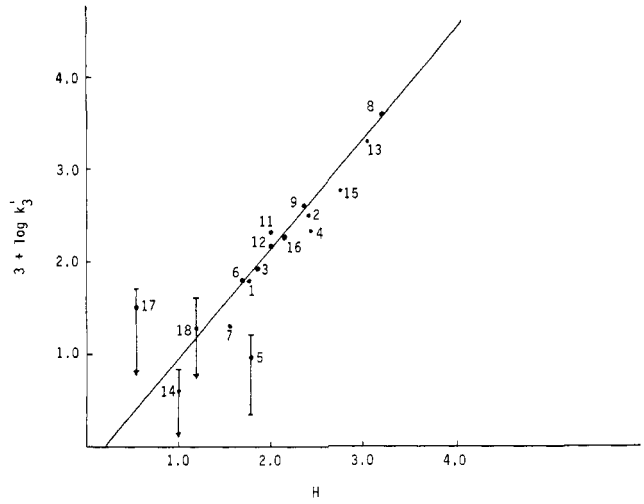

Figure 2. Plot of log k_3' for catalyzed *n*-butylaminolysis of *p*-NPA *vs.* *H* value in chlorobenzene at 25°.

ever, across classes of catalysts there is no correlation of catalytic ability with aqueous basicity. The k_3' values indicate that the dipolar oxygen bases are exceptionally effective catalysts exhibiting catalytic abilities equivalent to those of nitrogen bases which are more than 10^7 times stronger bases in water; *N*,*N*-dimethylacetamide is twice as effective a catalyst for the *n*-butylaminolysis of *p*-NPA as DABCO, although its aqueous pK_a is 9 pK_a units smaller (pK_a −0.39 *vs.* 8.6).

Figure 2 indicates that the catalytic abilities are correlated with the hydrogen-bonding abilities of the catalysts by the equation $\log k_3' = 1.2H - 3.3$. Since $\Delta H/\Delta pK_a$ for several classes of compounds is 0.21[7b] and the slope of Figure 2 is 1.2, $\Delta \log k_3'/\Delta pK_a$ for all classes of catalysts should be approximately 0.25, which is close to the value of 0.3 estimated from the pyridine data of Table I.

The inclusion of the catalytic abilities of *n*-butylamine and DABCO to catalyze the *n*-butylaminolysis of *p*-NPA in the correlation provides strong evidence against proposals that primary and tertiary amines catalyze the reaction by different mechanisms.[3b,c] The possibility that the tertiary amines and oxygen bases catalyze the reaction by nucleophilic catalysis[3c] is made unlikely by the shallow dependence of catalytic ability on basicity, $\Delta \log k_3'/\Delta pK_a \approx 0.3$.

In terms of the mechanism of eq 1, the correlation of $\log k_3'$ with *H* suggests that the catalysts effectively facilitate the expulsion of the phenolate anion from the tetrahedral intermediate by acceptance of the ammonium proton in the transition state to an extent equivalent to that in hydrogen-bonded complex formation with *p*-fluorophenol. It is estimated that in such hydrogen-bonded complexes the extent of proton transfer is 10–30% of full proton transfer.[7a,8]

The effectiveness of this small extent of proton transfer in facilitating the decomposition of the tetrahedral intermediate to products indicates that solvents capable of accepting hydrogen bonds (*e.g.*, ethers or amides) can intervene and catalyze the aminolysis of aryl esters and that nucleophiles with greater internal abilities to stabilize positive charges than primary amines (*e.g.*, secondary and tertiary amines and amidines) may be capable of expelling the phenolate anion from the tetrahedral intermediate without the necessity of proton transfer to a general base.

There has been interest in the possible mechanisms of action of enzymes with hydrophobic active sites.[2,4b,9] Our results indicate that with such enzymes attention should be given to the possibility that dipolar groups generally not considered to be general bases may function as general base catalysts, especially amides and other dipolar oxygen compounds. For example, in this study the amide *N*,*N*-dimethylacetamide is essentially as effective a catalyst of the ester aminolysis as the imidazole *N*-methylimidazole and more effective a catalyst than the primary amine *n*-butylamine, although it is respectively a 10^7 to 10^{10} times weaker aqueous base. Thus, we have the intriguing prospect that an amide group of an enzyme with a hydrophobic active site may function as a general base catalyst.

A subsequent paper will present data which suggest that the relative kinetic "basicities" of different classes of bases vary with the extent of proton transfer in the reaction.[10]

Experimental Section

All distillations and preparations of *n*-butylamine, DABCO, and chlorobenzene were conducted as previously described.[1] Reagent grade pyridines were twice distilled from either KOH–zinc dust or calcium hydride under nitrogen. Gas chromatography on 5 ft Carbowax or XF-1150 fluorosilicone columns showed only single peaks.

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N,N-**Dimethylacetamide** was vacuum distilled twice, bp 52° (9 mm). The 2,4-dinitrofluorobenzene test showed less than 5×10^{-6} g/ml of dimethylamine in the amide.[11]

1-Methyl-2-pyridone was vacuum distilled twice, bp 107–8° (2.8 mm) (lit.[12] bp 121° (10 mm)).

2-Pyridone was recrystallized twice from benzene and then sublimed, mp 105–107°.

Dimethyl sulfoxide was vacuum distilled twice from CaH_2, bp 68–69° (4.5 mm).

Benzonitrile was dried over P_2O_5 for 2 days then distilled through a 3 ft long column filled with raschig rings, bp 188°.

Sulfolane was twice vacuum distilled, bp 116° (1.6 mm).

Tetrahydrofuran was refluxed with CaH_2 overnight and then twice distilled under dry nitrogen, bp 65.5°.

Pyridine *N*-**oxide** was recrystallized from ligroin containing a little benzene and then sublimed. The very deliquescent crystals were vacuum dried with P_2O_5, mp 62–63° (lit.[13] mp 65–66°).

Triphenylarsine Oxide. The hydrate was recrystallized twice from chloroform–hexane and then sublimed twice at 170° (0.2 mm), mp 195–197° (lit.[14] mp 197°).

Anal. Calcd for $C_{18}H_{15}AsO$: C, 67.09; H, 4.69; As, 23.25. Found: C, 66.63; H, 4.74; As, 23.07.

Triphenylphosphine oxide was recrystallized twice from benzene–hexane and then sublimed, mp 154–156°.

Trimethylphosphine oxide was prepared as previously described,[15] mp 139–141° (lit.[15] mp 137.5–138.5°).

N,N-**Dimethyl-4-aminopyridine.** To a solution of 6.5 g of dimethylamine hydrochloride and 3.2 g of sodium hydroxide in 30 ml of water, 4 g of 4-chloropyridine hydrochloride was added. The mixture was heated in a sealed tube at 135° for 7 hr and then at 160° overnight. The solution was made basic and extracted with benzene. Evaporation of the benzene extract gave a yellowish solid, crude yield 83%. With decolorization and recrystallization from toluene–benzene white crystals were obtained, mp 110–111° (lit.[16] mp 108–109°).

Kinetics. All reactions were carried out in 3-ml Teflon stoppered, 10-mm fused silica cells, contained in the thermostated cell holder of a Cary 15 spectrophotometer equipped with a Cary automatic sample changer. The reactions were initiated by placing the appropriate volume of *p*-nitrophenylacetate in chlorobenzene solution on the rim of a flattened end of a stirring rod and then vigorously and quickly stirring the thermostated *n*-butylamine and catalysts in chlorobenzene solution with the rod. If the automatic sample changer was used in the rate determination, a reference cell was employed to correct for instrument drift and the interval between readings was measured accurately with a stopwatch. Kinetics were conducted under the pseudo-first-order conditions of excess *n*-butylamine.[1,2] Pseudo-first-order plots of log (Abs_∞ − Abs_t) *vs.* time were linear in all cases, with the slope taken as equal to $k_{1,obsd}$. The observed second-order rate constant, $k_{2,obsd}$, was obtained by dividing $k_{1,obsd}$ by the amine concentration. At constant catalysts, concentration plots of $k_{2,obsd}$ *vs.* *n*-butylamine concentration were linear with slope k_3 and intercept $k_2 + k_3'$·[catalyst]. The k_2 term was taken as less than 2×10^{-4} M^{-1} sec^{-1}.[2]

Determination of 2-Pyridone Rate and Dimer Constants

The 2-pyridone was assumed to dimerize predominantly to the noncatalytic cyclic dimer[5] and the rate and dimerization constants were calculated as follows. Taking M as the concentration of 2-pyridone monomer and T as the stoichiometric concentration of 2-pyridone, the equilibrium and dimerization constants are

$$K = (T - M)/2M^2$$

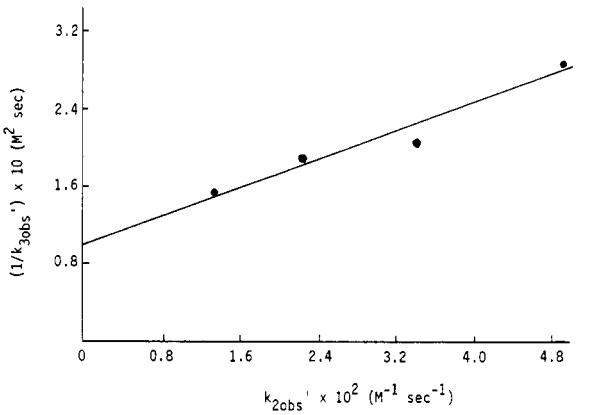

Figure 3. Plot of $1/k_{3,obsd}'$ *vs.* $k_{2,obsd}'$ for 2-pyridone catalyzed 0.1445 *M* *n*-butylaminolysis of *p*-NPA in chlorobenzene at 25°.

$$k_{2,obsd} = \frac{\text{rate}}{[p\text{-NPA}][\text{amine}]} = k_3[\text{amine}] + k_3'M$$

then by rearrangement and definition

$$M = \frac{k_{2,obsd} - k_3[\text{amine}]}{k_3'} = \frac{k_{2,obsd}'}{k_3'}$$

At constant amine concentration, a term $k_{3,obsd}'$ may also be defined as

$$k_{3,obsd}' = k_{2,obsd}'/T$$

$$k_{3,obsd}' = k_{2,obsd}'/M(1 + 2KM)$$

$$k_{3,obsd}' = k_{2,obsd}'/(k_{2,obsd}'/k_3')[1 + 2K(k_{2,obsd}'/k_3')]$$

$$k_{3,obsd}' = (k_3')^2/(k_3' + 2Kk_{2,obsd}')$$

then

$$\frac{1}{k_{3,obsd}'} = \frac{1}{k_3'} + \frac{2K}{(k_3')^2} k_{2,obsd}'$$

A plot of $1/k_{3,obsd}'$ *vs.* $k_{2,obsd}'$ should be linear with an intercept equal to $1/k_3'$ and a slope equal to $2K/(k_3')^2$. From the data of Table II and Figure 2, a k_3' of 10 ± 1

Table II. The Rate Constants for 2-Pyridone Catalyzed 0.1445 *M* *n*-Butylaminolysis of *p*-NPA in Chlorobenzene at 25°

[2-Pyridone]	$k_{2,obsd}$, M^{-1} sec^{-1}	$k_{2,obsd}' = k_{2,obsd} - k_{2,obsd}^0$ M^{-1} sec^{-1}	$1/k_{3,obsd}' =$ [2-pyridone]$/k_{2,obsd}'$, M^2 sec
0.0	0.00823		
0.0021	0.02171	0.01348	0.1558
0.0042	0.03040	0.02217	0.1895
0.0070	0.04250	0.03427	0.2042
0.014	0.05742	0.04919	0.2846

M^{-2} sec^{-1} and a dimerization constant, K, of 200 M^{-1} in 0.145 *M* *n*-butylamine–chlorobenzene are calculated. These values are comparable to those reported for the same reaction in 0.10 *M* *n*-butylamine–benzene: k_3' = 17 M^{-2} sec^{-1} and K = 1400 M^{-1}.[5]

Acknowledgment. We are grateful to the National Institutes of Health (Grant AM-11987) for support of this research.

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