propionic anhydride was allowed to reflux over magnesium turnings for 24 h before distillation. Deuterium oxide (99.8 atom % deuterium; Aldrich) was distilled from barium nitrate to remove basic impurities. Reagent grade acetonitrile was distilled from calcium hydride or phosphorus pentoxide. Deuterium oxide (99.75 atom % deuterium; Bio-Rad) and acetic anhydride-d_6 (99+%-deuterium; Aldrich) were used as received. Succinic anhydride was purified by multiple recrystallizations from ethanol–chloroform followed by vacuum sublimation.

Methods. Kinetic data were obtained by following the rate of propionic anhydride disappearance at 245 nm with a Cary 118C UV–vis spectrophotometer equipped with a thermostated cell holder and compartment. Expanded absorbance ranges were used to monitor the kinetics as the usual initial substrate concentrations (about 10^{-3} M) gave absorbances conveniently displayed on the 0.1–0.2 absorbance range. The runs were followed for at least 3 half-lives (up to 5 or 6 in many cases). Infinity absorbances were determined at 10 half-lives. Reactions were usually initiated by injecting 25 μL of a solution of propionic anhydride in acetonitrile into 3 mL of thermally equilibrated water (protium oxide, deuterium oxide, or a mixture of the two). Some runs were done by injecting propionic anhydride directly in the absence of acetonitrile to check this solvent effect. A nonlinear least-squares computer program was used to determine the rate constants. Plots of log $(A_t - A_\infty)$ vs. time were used in a confirmatory manner. In most cases 25 or more data points were used for each determination. Repetitive scans of the ultraviolet spectra of some of the anhydrides in various solvents were made by using a Cary digital repetitive scan accessory. The hydrolysis of succinic anhydride was followed in a similar fashion at 222.5 nm as was acetic anhydride at 245 nm. The protium oxide and deuterium oxide solutions were prepared by combination of the appropriate volumes of the purified reagents. The deuterium content of the pure deuterium oxide solutions and some of the H_2O–D_2O mixtures was determined by Josef Nemeth.[9] The secondary β-deuterium isotope effect for acetic anhydride hydrolysis was determined by injecting 10 μL of a substrate solution in acetonitrile into water. Alternating runs with the labeled and unlabeled compounds were done. The γ values for the proton inventories were determined by using a computer program, GAMISO, provided by Professor John Albery and modified to run on our computer.

Acknowledgment. We thank Mr. Phil Huskey for performing the polynomial regression analysis.

Registry No. Propionic anhydride, 123-62-6; succinic anhydride, 108-30-5; acetic anhydride, 108-24-7; deuterium, 7782-39-0; water-d_2, 7789-20-0; water, 7732-18-5.

Intramolecular Hydrogen-Bonding Catalysis of Ester Aminolysis in Acetonitrile

Ennio Ciuffarin* and Aldo Loi

Istituto di Chimica Organica, 09100 Cagliari, Italy

Mauro Isola, Augusto Lupetti, Laura Sagramora, and Lucio Senatore

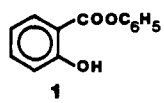
Istituto di Chimica Generale, 56100 Pisa, Italy

Received June 15, 1982

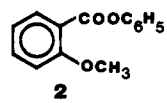
o-Hydroxyphenyl benzoate (**3**) reacts with 1,3-diaminopropane and 1,4-diaminobutane in acetonitrile according to a two-term rate law (eq 1). The first term of this equation becomes constant when the amine concentration is greater than 0.2 M. Addition of hexamethylphosphoric triamide (HMPT) or tetra-*n*-butylammonium chloride inhibits this reaction path completely while leaving almost unaffected the path related to the second term of eq 1. These and other results lead to the conclusion that **3** forms a hydrogen-bonded complex with diamines through its *o*-OH group. HMPT and Bu_4NCl can also form hydrogen-bonded complexes with **3** in competition with diamines, thus inhibiting the reaction path related to the first term of eq 1, whose mechanism is not defined by the present data. On the other hand, the second term of eq 1 relates to a mechanism of intramolecular catalysis by the *o*-OH group of **3** promoted by bases or in general by hydrogen-bond acceptors. These results stress the importance of hydrogen bonding in intramolecular catalysis in aprotic solvents.

In aprotic media hydrogen-bonding interactions of reagents or addenda with the solvent are absent or low so that the catalytic or inhibiting effect of hydrogen-bond donors or acceptors on the rates of reaction can be studied. This is the case of the intramolecular catalysis of ester aminolysis in acetonitrile by the *o*-hydroxyl group, which displays reactivity characteristics that cannot be detected in aqueous solvents.

It has been shown that neighboring hydroxyl groups lead to higher rates of aminolysis of esters. Phenyl salicylate, **1**, reacts 132 times faster than phenyl *o*-methoxybenzoate, **2**, with *n*-butylamine in acetonitrile.[1]

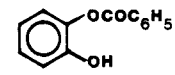


1

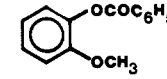


2

o-Hydroxyphenyl benzoate, **3**, reacts at least 850 times faster than *o*-methoxyphenyl benzoate, **4**, with *n*-butylamine in the same solvent.[2]



3



4

However, the mechanisms suggested for catalysis in these reactions of **1** and **3** are different: general acid catalysis was proposed for **1**,[1] and general base catalysis for **3**.[2] The kinetic features displayed by the two substrates are so different that they can hardly be attributed to the same catalytic role of the hydroxyl group. More recently it was suggested that the neighboring OH group of **3** can also react as a general acid.[3] Although we had not ex-

(1) Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 5346.

(2) Senatore, L.; Ciuffarin, E.; Isola, M.; Vichi, M. *J. Am. Chem. Soc.*, **1976**, *98*, 5306.

0022-3263/83/1948-1047$01.50/0

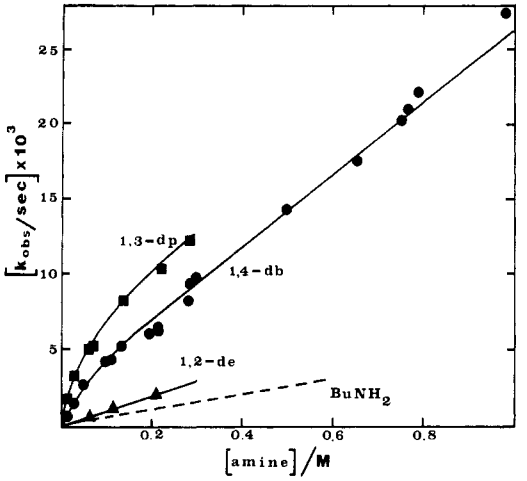


Figure 1. Reaction of *o*-hydroxyphenyl benzoate (3) with 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, and *n*-butylamine[2] at 25 °C in acetonitrile.

cluded this possibility for the undissociated OH group, we suggested that it is completely obscured by the much larger effect due to general base catalysis[2] when the hydroxyl group is ion paired with the nucleophile.[4] Thus, the available data cannot be reconciled under a single type of intramolecular catalysis of the hydroxyl group in aprotic solvents. The mechanism of this catalysis is of interest because of its relevance to the mechanism of enzyme action;[1,5,6] it has been suggested that the active sites of certain enzymes lie in hydrophobic pockets of hydrophobic side-chain groups of amino acids.[7,8] Accordingly, we have extended the study of the reactivity of 3 in acetonitrile.

Results

The rates of reaction of 1,2-diaminoethane (1,2-de), 1,3-diaminopropane (1,3-dp), and 1,4-diaminobutane (1,4-db) with 3 and 4 have been measured in acetonitrile at 25 °C under pseudo-first-order conditions. All reactions are first order in 3 or 4. The order in nucleophile is complex and depends on the nucleophile and on the addend (tetra-*n*-butylammonium salts or hexamethylphosphoric triamide, HMPT).

(1) 1,2-Diaminoethane. The reaction of 3 with 1,2-de is first order in amine. The plot k_{obsd} vs. [1,2-de] is linear and has zero intercept (Figure 1). The rate law is $k_{obsd} = k_1[1,2\text{-de}]$, where $k_1 = 10.5 \times 10^{-3}$ M^{-1} s^{-1}. This amine reacts with 4 much more slowly, and the reaction is second order in amine. A plot (not shown) of $k_{obsd}/[1,2\text{-de}]$ vs. [1,2-de] is linear with zero intercept. The rate law is $k_{obsd} = k_2[1,2\text{-de}]^2$ with $k_2 = 5.8 \times 10^{-5}$ M^{-2} s^{-1}.

The rate data indicate that 3 reacts 360 times faster than 4 at 0.5 M amine concentration.

(2) 1,3-Diaminopropane and 1,4-Diaminobutane. 1,3-dp and 1,4-db react with 3 following a complex rate law. After a steeper increase at low amine concentration (Figure 1) the rates depend linearly on the amine concentration with a term (the intercept) that is not zero and does not depend on the concentration of nucleophile. The rate law at high amine concentration tends to $k_{obsd} = k_0 + k_1$[diamine], where k_0 is the intercept and k_1 is the slope. The overall rate law is satisfied by various mechanisms (described in the Discussion), all of which include an equilibrium of complex formation between 3 and diamines. In each case the rate law is given by eq 1, where K is the

$$k_{obsd} = \frac{k_0K[\text{diamine}]}{1 + K[\text{diamine}]} + \frac{k_1K[\text{diamine}]^2}{1 + K[\text{diamine}]} \quad (1)$$

equilibrium constant of complex formation, k_0 and k_1 the experimental values of the intercept and the slope, respectively.

For the reaction of 3 with 1,3-dp the values of the constants in eq 1 are $k_0 = 7.7 \times 10^{-3}$ s^{-1} ± 16%, $k_1 = 23.1 \times 10^{-3}$ M^{-1} s^{-1} ± 17%, and $K = 21$ M^{-1} ± 22%. Similarly for 1,4-db: $k_0 = 3.6 \times 10^{-3}$ s^{-1} ± 14%, $k_1 = 23.9 \times 10^{-3}$ M^{-1} s^{-1} ± 4%, and $K = 25$ M^{-1} ± 20%. These values have been calculated with the multiparametric curve-fitting CFT3 and VARPAR programs[9] and have been used to draw the solid lines of Figure 1. The rate and equilibrium constants are reliable within the indicated standard errors.

1,4-db reacts with 4 much more slowly, and the reaction is second order in amine. A plot (not shown) of $k_{obsd}/[1,4\text{-db}]$ vs [1,4-db] is linear with zero intercept. The rate law is $k_{obsd} = k_2[1,4\text{-db}]^2$ with $k_2 = 1.6 \times 10^{-4}$ M^{-2} s^{-1}. 3 reacts 360 times faster than 4 at 0.5 M amine concentration.

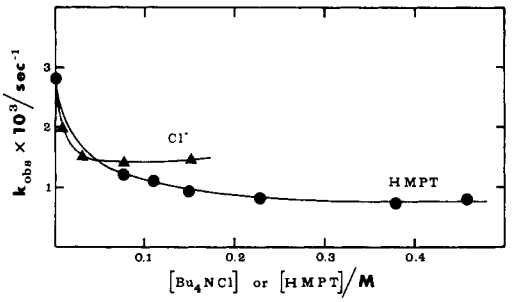


Figure 2. Effect of the addition of tetra-*n*-butylammonium chloride and hexamethylphosphoric triamide on the reaction between *o*-hydroxyphenyl benzoate (3) and 1,4-diaminobutane (*c* 0.049 M) at 25 °C in acetonitrile.

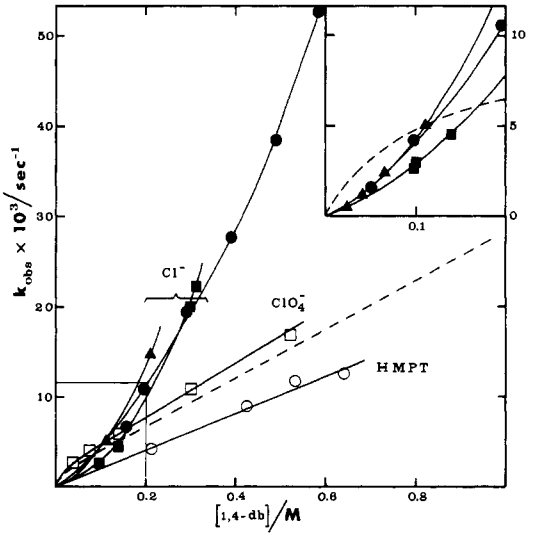


Figure 3. Reaction of *o*-hydroxyphenyl benzoate (3) with 1,4-diaminobutane in the presence of additives at 25 °C in acetonitrile: dashed line, no additive; HMPT, 0.22 M (○); Bu_4NClO_4, 0.074 M (□); Bu_4NCl, 0.071 M (●); 0.1 M (■), 0.154 M (▲).

(3) Kirby, A. J.; Lin, K. L. *Tetrahedron Lett.* **1978**, 4079.
(4) Reference 2, footnote 9.
(5) (a) Su, C.-W.; Watson, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 1854. (b) Hajdu, J.; Smith, G. M. *Ibid.* **1981**, *101*, 6192.
(6) Metzer, D. E. "Biochemistry"; Academic Press: New York, 1977; p 376.
(7) Blow, D. M.; Birktoft, J. J.; Hartley, B. S. *Nature (London)* **1969**, *221*, 337.
(8) Verkeij, H. M.; Volwerk, J. J.; Jansen, E. H. J. M.; Puyk, W. C.; Dijkstra, B. S.; Drenth, J.; de Haas, G. *Biochemistry* **1980**, *19*, 743.
(9) Meites, L. "The General Multiparametric Curve-Fitting Program CFT3"; Computing Laboratory, Clarkson College of Technology, Potsdam, NY, 1974.

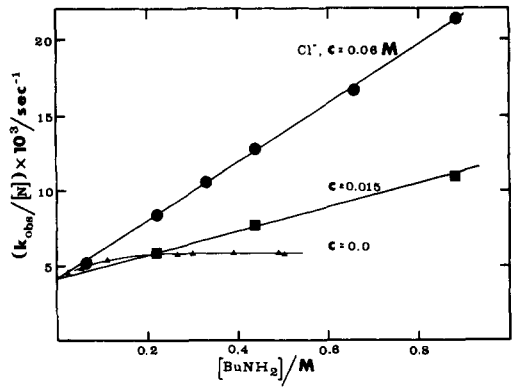


Figure 4. Reaction of *o*-hydroxyphenyl benzoate (**3**) with *n*-butylamine in the presence of Bu_4NCl at 25 °C in acetonitrile. The data in the absence of salt (▲) are taken from previous work.[2]

(3) Hexamethylphosphoric Triamide. Addition of HMPT drastically lowers the rate of reaction of 1,4-db with **3**, and a constant value is reached at HMPT concentration higher than ca. 0.2 M (Figure 2). The first term of eq 1 approaches zero, and a plot of k_{obsd} vs. [1,4-db] of the data obtained in the presence of 0.22 M HMPT shows a linear dependence of the rate vs. the amine concentration (Figure 3). The slope gives $k'_1 = 20.5 \times 10^{-3}$ M^{-1} s^{-1}.

HMPT has a minor retarding effect on the rate of the reaction of **3** with *n*-$BuNH_2$. In the presence of 0.23 M HMPT, $k_1 = 5.3 \times 10^{-3}$ M^{-1} s^{-1}, whereas $k_1 = 5.8 \times 10^{-3}$ M^{-1} s^{-1} was found in the absence of an addend.[2]

(4) Tetra-*n*-butylammonium Salts. (A) Perchlorate. Addition of Bu_4NClO_4 slightly increases the rate of reaction of 1,4-db with **3** but does not change the shape of the plot found in the absence of salt (Figure 3). This is a general salt effect that is not particularly efficient.

(B) Chloride. On the other hand addition of Bu_4NCl produces a quite unusual effect on the same reaction. At low concentration of amine the chloride retards the reaction (Figure 2) while at high amine concentration a large rate increase is observed (Figure 3); the increase is much larger than that seen with perchlorate at the same concentration. The salt effects of the chloride (acceleration or inhibition) must be specific.

The effect of the chloride was also determined on the reaction of **3** with *n*-butylamine. The data are plotted in Figure 4. It is apparent that the salt has a large effect on the slope and a minor effect on the intercept. Thus, addition of salt affects very little the reaction that is first order in amine but influences quite strongly a term second order in amine, which was not detected in the absence of salt.

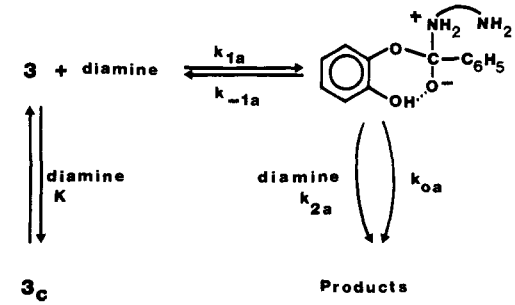
Discussion

The simple addition–elimination mechanism of aminolysis reactions[10] could account for the data of the reaction of **3** with 1,3-dp and 1,4-db, assuming that the addition intermediate is in fast equilibrium with the reagents and that such equilibrium is completely displaced toward the intermediate at high amine concentration. This is contrary to the accepted mechanism of aminolysis of carboxylic esters where only a very small, steady-state concentration of the tetrahedral addition intermediate is assumed.

Thus, in order to explain the observed plots and the two-term rate equation, another fast equilibrium between substrate and amine must be envisaged that is completely displaced to the right at high amine concentration. A hydrogen-bonded adduct between **3** and 1,3-dp or 1,4-db through the OH group of **3** seems a quite likely possibility. The data for 1,3-dp and 1,4-db strengthen the previous suggestion of complexation of **3** with amines.[2]

Our data indicate catalysis of aminolysis by the *o*-OH group, since the *o*-methoxy analogue, **4**, is much less reactive toward all amines studied. However, the rate law does not give any indication whether the catalytic species is the uncomplexed *o*-OH group (acid catalysis)[1] or the complexed *o*-OH group (general base catalysis),[2] because various mechanisms for the two types of catalysis (alone or in combination, eq 2, 5, 6) can be written that have formally the same rate equations. Any mechanism that can be derived from the data for the reaction of **3** with 1,3-dp and 1,4-db in the absence of addends must take into account that **3** forms complexes with these diamines.

Results of experiments in the presence of HMPT exclude an intramolecular general acid catalysis mechanism such as that shown in eq 2, which corresponds to the



(2)

general mechanism of aminolysis reactions[10] with the additional features of intramolecular acid catalysis and formation of an unreactive complex **3c** in fast equilibrium with **3**, the uncomplexed substrate. The rate law for this mechanism is given by eq 3, which is formally similar to eq 1.

$$k_{obsd} = \frac{k_{1a}k_{0a}[\text{diamine}]}{k_{-1a}(1 + K[\text{diamine}])} + \frac{k_{1a}k_{2a}[\text{diamine}]^2}{k_{-1a}(1 + K[\text{diamine}])} \quad (3)$$

Addition of HMPT lowers the rate of reaction (Figure 2). The acid catalysis mechanism (eq 2) does allow for rate depression if **3** and HMPT form an unreactive or much less reactive adduct, **3c**. HMPT, being a nonbasic substance but a strong hydrogen-bond acceptor,[11] can interact with the substrate's hydroxyl group, which cannot therefore act as an acid catalyst. However, in this hypothesis, addition of HMPT should depress both terms of the rate equation to the same degree since both reaction paths (k_{0a} and k_{2a} in eq 2) depend on a common intermediate stabilized by the neighboring hydroxyl group. On the contrary (Figure 3), while the first term of the rate equation (the intercept) is completely suppressed, the second (the slope) is reduced only 14% ($k'_1 = 20.5 \times 10^{-3}$ instead of 23.9×10^{-3} M^{-1} s^{-1}). Accordingly, the acid catalysis mechanism is unable to explain the data in the presence of HMPT and can be ruled out.[12]

Formation of an adduct that is incapable of intramolecular acid and/or base catalysis, upon addition of HMPT, should lower the rate of reaction of **3** with amines

(10) (a) Menger, F. M.; Smith, J. H. *Tetrahedron Lett.* **1970**, 4163. (b) Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 3824. (c) Menger, F. M.; Vitale, A. C. *Ibid.* **1973**, *95*, 4931.

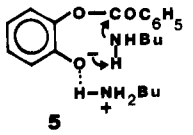
(11) Taft, R. W.; Gurka, D.; Joris, L.; Schleyer, P. v. R.; Rakshys, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 4801.

(12) An interaction of HMPT with diamines as $\overline{NH\text{–}H\text{---}NH_2}$ + HMPT ⇄ $\overline{NH\text{–}H\text{---}HMPT\text{---}H\text{–}NH}$ cannot explain the different effects of HMPT on the two terms of the rate equation.

much more than found experimentally. In fact a complex 3–HMPT should have a reactivity similar to that of 4, which possesses an inert OCH_3 group. In the presence of excess HMPT the rate should be similar to that of 4 reacting with n-$BuNH_2$,[2] 1,2-de, or 1,4-db. Since the rate in the presence of HMPT is, on the contrary, much larger than expected for an inert complex, these experiments indicate that the complex 3–HMPT is quite reactive.

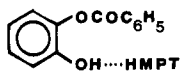
In order to account for this reactivity without resorting to unreasonable mechanisms, we must assume that the o-OH group complexed with HMPT is capable of strong intramolecular catalysis. At the same time, since a hydrogen-bonded OH group cannot act as an acid, its reactivity must be of the general base type.

Intramolecular general base catalysis of the o-OH group has been suggested to explain the much larger reactivity of 3 compared to that of 4 in the n-butylaminolysis reactions.[2] The reactivity of the o-OH group was considered as due to the formation of a hydrogen-bonded ion pair,[4] 5, where the oxygen atom is negatively charged and thus capable of abstracting a proton from the attacking amine.



5

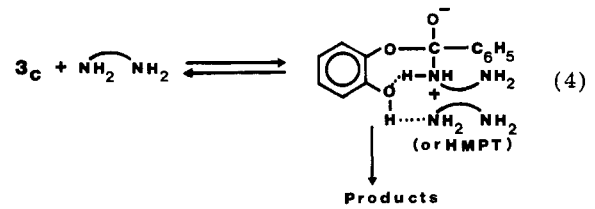
A similar ion-pair interaction of 3 with HMPT is improbable because HMPT is a strong hydrogen-bond acceptor but a very weak base. The hydrogen bond between the OH group and HMPT must form without formal separation of charge as in 6.



6

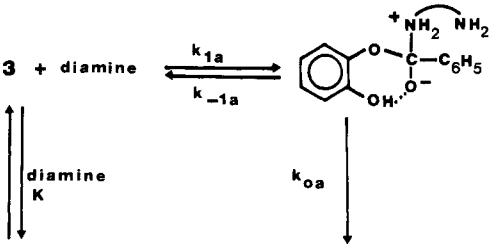
In order to account for the reactivity of 6 as required by the data, we must accept the idea that the OH group can intramolecularly catalyze aminolysis reactions as a hydrogen-bond acceptor and not, or not only, as a general base in the usual meaning, which requires transfer of a proton. In fact, HMPT cannot impart to the hydroxyl group the characteristics of a base.

We have seen that the rate constant in the presence of HMPT is only 14% smaller than in the absence of an addend, so that the adduct with HMPT is only slightly less reactive than the adduct with the amine. The similar reactivity of the two adducts points to a similar type of catalysis, so we suggest that the adduct with the amine is a hydrogen-bonded pair instead of the previously suggested ion pair[4] and that a hydrogen bond is sufficient to activate intramolecular catalysis by the OH group. Thus, the mechanism of the general-base-catalyzed step can be represented as in eq 4. It is not unprecedented that oxygen atoms act as hydrogen-bond acceptors in catalysis mechanisms[13,14] and transition-state stabilization.[15]

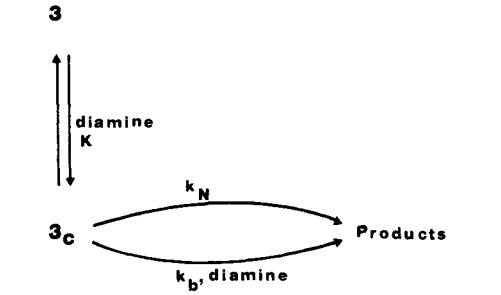


(4)

The rate law of eq 4 (for the complex of 3 with diamines), however, does not account for the term zero order in amine (at high amine concentration) of eq 1. The present data are not sufficient to define the reaction path relative to the first term of the rate equation. This can be related either to an intramolecular acid catalysis mechanism (k_{0a}) of the uncomplexed substrate (eq 5) or to a monomolecular (k_N) decomposition of the complexed substrate (eq 6). We postpone a thorough discussion until more data are available for other systems.



(5)



(6)

The present discussion indicates that the suggested mechanism[2] for the reaction of 3 with n-butylamine, where only one reaction path was detected, was correct in its general outline even though important details had to be modified. The behavior of 1,2-de is similar to that of n-$BuNH_2$ and different from that of higher diamines. The reason for the lack of the first term in the rate equation[16] for 1,2-de will be understood only when the mechanism of the first term of the rate equation for higher diamines is explained.

Since HMPT acts as inhibitor of the process of the first term of eq 1 and leaves the second term almost unaffected, it seemed obvious that other hydrogen-bond acceptors such as Cl^- would be able to compete with the nucleophile in bonding the hydroxyl group. Addition of Bu_4NCl to the reaction of 3 with 1,4-db lowers the rate of reaction as shown in Figure 2. This unusual inhibition by Bu_4NCl is observed only at low amine concentration. As can be seen in Figure 3, where plots of k_{obsd} vs. [1,4-db] at various salt concentrations are shown, at high amine concentrations the salt exerts a large catalytic effect. By comparison (Figure 3) Bu_4NClO_4 exerts only a minor catalytic effect over the whole range of amine concentrations. A reasonable explanation for the inhibiting effect of Cl^- is competition for the hydroxyl group between the Cl^- and 1,4-db. The catalytic effect of Bu_4NCl, on the other hand, may be attributed to catalysis of a bimolecular process (second order in amine), which was not detected in the absence of salt. This is difficult to ascertain in this system where both inhibition and catalysis occur. However, addition of Bu_4NCl to 3 reacting with n-$BuNH_2$, where only the reaction that is first order in amine is observed (except at

(13) Ciuffarin, E.; Isola, M.; Leoni, P. J. Org. Chem. 1981, 46, 3064.
(14) Gandour, R. D.; Walker, D. A.; Nayak, A.; Newkome, G. R. J. Am. Chem. Soc. 1978, 100, 3608.
(15) Singh, T. D.; Taft, R. W. J. Am. Chem. Soc. 1975, 97, 3867.
(16) An intercept cannot be detected within experimental error if $k_0 \leq 4 \times 10^{-4}$ s^{-1}.

very low amine concentration),[4] introduces another path that requires two molecules of amine and about one molecule of salt (Figure 4).

The inhibiting effect of Bu_4NCl on the reaction of **3** with 1,4-db indicates the formation of a complex **3**–Cl (ion paired with Bu_4N^+). The chloride ion is in fact a strong hydrogen-bond acceptor. We may assume that the complex **3**–Cl^- is also the reactive species in the reaction of **3** with *n*-$BuNH_2$ when Bu_4NCl is added. Thus, we can calculate the reactivity of the complex with Cl^- from the intercept of Figure 4. Its value (4.2×10^{-3}), only slightly lower than that in the absence of salt (5.8×10^{-3}),[2] indicates that this adduct has a reactivity similar to that of the complex **3**–NH_2Bu, which is therefore more likely a hydrogen-bonded species than the previously suggested ion pair.

Conclusions

Hydroxyl groups in the appropriate position relative to the reacting center in aminolysis reactions can stabilize the transition state. The free hydroxyl group is capable of acid catalysis as a hydrogen-bond donor as in the case of the aminolysis of phenyl salicylate, **1**.[1] On the other hand, the free hydroxyl group is not capable by itself of providing significant catalysis as a hydrogen-bond acceptor, but it becomes very efficient when hydrogen bonded to bases such as amines or other hydrogen-bond-accepting species such as HMPT or chloride ion as in the aminolysis of *o*-hydroxyphenyl benzoate, **3**. The *o*-hydroxyl group therefore functions as a relay for the action of reagents in solution that do not perform significant intermolecular catalysis but that thus become involved in very efficient intramolecular catalysis.

Experimental Section

Materials. Acetonitrile,[17] *n*-butylamine,[13] 1,2-diaminoethane,[13] 1,3-diaminopropane,[13] 1,4-diaminobutane,[13] hexamethylphosphoric triamide,[13] and tetra-*n*-butylammonium perchlorate[2] were purified according to reported procedures. Tetra-*n*-butylammonium chloride was prepared from the corresponding perchlorate with an ion-exchange resin (Dowex 1, X8 20–50 mesh) in the chloride form because the commercial chloride could not be purified by simple crystallization. After evaporation of the chloride solution in a rotor evaporator, the residual water was eliminated by azeotropic distillation with benzene. After several crystallizations from dry benzene, the solid was desiccated under vacuum.

o-Hydroxyphenyl benzoate and *o*-methoxyphenyl benzoate were those used in previous work.[2]

N-(4-Aminobutyl)benzamide hydrochloride was prepared by mixing benzoyl chloride and 1,4-diaminobutane in diethyl ether in a 1:2 molar ratio. The precipitate was washed with water to separate the hydrochlorides from the disubstituted amine. The hydrochloride of the monosubstitued derivative was separated from the hydrochloride of the unreacted amine by chloroform extraction of the aqueous solution saturated with sodium chloride. After evaporation of chloroform, crystallization from ethanol–ethyl ether yielded white crystals, mp 170 °C (lit.[18] mp 169–170 °C).

Kinetics. All reactions were followed at 25 °C in a thermostated cell compartment of a UV–vis spectrophotometer at 270–280 nm.

Good linear first-order plots were obtained in all cases. All solutions were prepared and kept under a nitrogen atmosphere. The reacting solution was prepared in a cuvette by adding 50 μL of substrate solution to a thermostated cuvette containing 3 mL of a solution containing the nucleophile and if necessary other additives. The final substrate concentration was about 10^{-4} M.

The experimental and mock-infinity values for the reaction of *o*-hydroxyphenyl benzoate with 1,4-diaminobutane agreed within experimental error. The mock-infinity value was prepared with the hydrochloride of the amide because HCl does not absorb in the spectral region used for the experiments.

All kinetics performed with the diamines reacting with **3** gave isosbestic points at 287 and 257 nm, indicating that only a single reaction occurred after a fast preequilibrium.

Acknowledgment. This work was supported by CNR, Rome.

Registry No. **3**, 5876-92-6; **4**, 1523-19-9; 1,2-diaminoethane, 107-15-3; 1,3-diaminopropane, 109-76-2; 1,4-diaminobutane, 110-60-1; hexamethylphosphoric triamide, 680-31-9; tetrabutylammonium perchlorate, 1923-70-2; tetrabutylammonium chloride, 1112-67-0; butylamine, 109-73-9.

(17) Deacon, T.; Steltner, A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1778.

(18) Kanewskaja, S. *J. Russ. Phys. Chem. Ges.* **1927**, *59*, 639.

Selective Formation and Trapping of Dihalocarbonyl Ylides Derived from Dihalocarbenes and Substituted Benzaldehydes

Harpal S. Gill and John A. Landgrebe*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

Received August 10, 1982

The thermal decompositions of several phenyl(trihalomethyl)mercury compounds in the presence of substituted benzaldehydes **1** and dimethyl acetylenedicarboxylate (**7**) in dry benzene at 80 °C resulted in 2-halo-5-arylfuran-3,4-dicarboxylates **9** in isolated yields (not optimized) that ranged from 13% to 64%. These products appear to be the result of selective attack by dihalocarbene on the aldehyde followed by preferential capture of the resulting carbonyl ylide by the acetylenic dipolarophile and loss of hydrogen halide. The substitution of diethyl fumarate (**12**) for acetylene **7** produced a mixture of the *E* and *Z* isomers of dihydrofuran **14** in a ratio of 70:30. Tetrasubstituted dipolarophiles failed to give comparable products. The intermediate dihalocarbonyl ylides were shown to undergo halogen exchange.

Previous experimental work[1] has provided a body of evidence that the thermal decomposition of phenyl(trihalomethyl)mercury in the presence of various aromatic aldehydes **1** involves initial generation of dihalocarbene

0022-3263/83/1948-1051$01.50/0