3-cyclohexylpropyltrichlorosilane, bp 100° (3.0 mm). About 3.0 g of tarry pot residue remained in the distilling flask.

Hydrosilylation Using Dichlorobis(ethylcyclohexene)-μ,μ'-dichloro-diplatinum(II). 1-Ethylcyclohexene. A mixture of 7.5 g (0.068 mol) of 1-ethylcyclohexene, 9.5 g (0.07 mol) of trichlorosilane, and 10 mg of dichlorobis(ethylcyclohexene)-μ,μ'-dichloro-diplatinum(II) was refluxed for 70 min. After the usual work-up, there was obtained 12.6 g (75%) of 2-cyclohexylethyltrichlorosilane (structure confirmed by comparison of its infrared spectrum and retention time on gas chromatography with an authentic sample).

Allylcyclohexane. A mixture of 8.3 g (0.067 mol) of allylcyclohexane, 19 g (0.134 mol) of trichlorosilane, and 10 mg of the platinum complex was refluxed for about 48 hr. There was obtained 14 g (78%) of 3-cyclohexylpropyltrichlorosilane (structure confirmed by comparison of its infrared spectrum and retention time on gas chromatography with an authentic sample).

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The Effect of Urea and Other Reagents on the Reactivity of Associated *p*-Nitrophenyl Laurate

F. M. Menger and Carolyn E. Portnoy

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322. *Received October 26, 1967*

Abstract: The rate constants for basic hydrolysis of *p*-nitrophenyl laurate decrease with increasing initial concentration of ester in the range 10^{-6}–10^{-5} *M*. The ester molecules must hydrophobically bind to one another, thereby enclosing the ester groups within associated hydrocarbon chains where hydrolysis is retarded. The rate inhibition is appreciable; the second-order rate constant for basic hydrolysis of *p*-nitrophenyl laurate at 1.0×10^{-5} *M* is almost three orders of magnitude smaller than that for *p*-nitrophenyl acetate. The hydrolysis of laurate ester in 0.1 *M* NaOH is accelerated by addition of *n*-butylurea, dioxane, urea, and tetramethylammonium bromide (with a decreasing order of effectiveness). The rate enhancements caused by the additives cannot be ascribed to a medium effect at the chemically reactive site because all four reagents inhibit hydrolysis of a short-chain ester, *p*-nitrophenyl acetate. Thus, while 8.0 *M* urea increases the rate of hydrolysis of *p*-nitrophenyl laurate (1×10^{-5} *M*) by a factor of 33, urea (3.7 *M*) decreases the rate of hydrolysis of *p*-nitrophenyl acetate 2.4-fold. The facilitated hydrolyses are consequently due to exposure of the ester groups to hydroxide attack as a result of perturbation or destruction of the substrate aggregates. The effect is similar to the unmasking of protein groups as a result of denaturation. The mechanism of the additive–aggregate interactions is discussed qualitatively.

The rate constants for basic hydrolysis of *p*-nitrophenyl laurate decrease with increasing initial concentration of ester in the range 10^{-6}–10^{-5} *M* (Figure 1). The simplest explanation for this finding is that the substrate molecules hydrophobically bind to one another, thereby enclosing the ester groups within associated hydrocarbon chains. Ester hydrolysis would be inhibited in such a situation.[1] The rate inhibition is appreciable; the second-order rate constant for basic hydrolysis of *p*-nitrophenyl acetate is 800 times larger than that for *p*-nitrophenyl laurate at 1.0×10^{-5} *M*. We have used this phenomenon as a means of kinetically assaying the ability of reagents to interact with long hydrocarbon chains in water. If a reagent, such as urea, effectively destroys or perturbs the laurate ester aggregates, then a large rate increase could ensue upon addition of urea to the hydrolysis medium. The interaction of urea and related compounds with nonpolar groups in aqueous solutions has already been explored *via* thermodynamic measurements (solubility determinations),[2] but the sensitivity of this approach is poor. For example, urea (8 *M*) increases the solubility of toluene in water only 2.38-fold, whereas the kinetic effect of urea on laurate ester hydrolysis will be shown to be much larger than this. We have studied the effect of four additives (urea, *n*-butylurea, dioxane, and tetramethylammonium bromide) on the hydrolysis rate of associated *p*-nitrophenyl laurate.

Experimental Section

Materials. Reagent grade urea, *n*-butylurea, and tetramethylammonium bromide were recrystallized from 95% ethanol, chloroform–benzene, and methanol, respectively. Each was carefully dried in a vacuum desiccator. Dioxane was distilled twice (once over $LiAlH_4$ and once from a solution of the sodium ketyl of benzophenone) immediately before use. The *p*-nitrophenyl laurate was used as obtained from the Pierce Chemical Co. The white crystals melted at 45–46.5° (lit.[3] mp 46°). The yield of *p*-nitrophenolate upon basic hydrolysis of the *p*-nitrophenyl laurate indicated a satisfactory purity of the ester. *p*-Nitrophenyl acetate had been prepared previously[4] and it melted at 77–78° (lit.[5] mp 77.5–78°).

Kinetics. The rate constants for hydrolysis of *p*-nitrophenyl laurate were obtained in the following manner. A 1.00-cm cuvette was filled with 3.00 ml of 0.1 *N* NaOH and equilibrated in a Cary 14 spectrophotometer set at 400.0 mμ (0.1–0.2 slide wire). After 10 min, 25 μl of an acetonitrile solution of *p*-nitrophenyl laurate was added by means of a small stirring rod flattened at on end. The increase in absorbance was then traced as a function of time. Pseudo-first-order plots are curved since the rate of the reaction accelerates as ester is destroyed (Figure 1). Therefore, absorbance–time data at the initial portion of the reactions had to be used to calculate the rate constants.[6] At the higher concentrations of ester, the k_{obsd} *vs.* concentration curve (Figure 1) is relatively flat and

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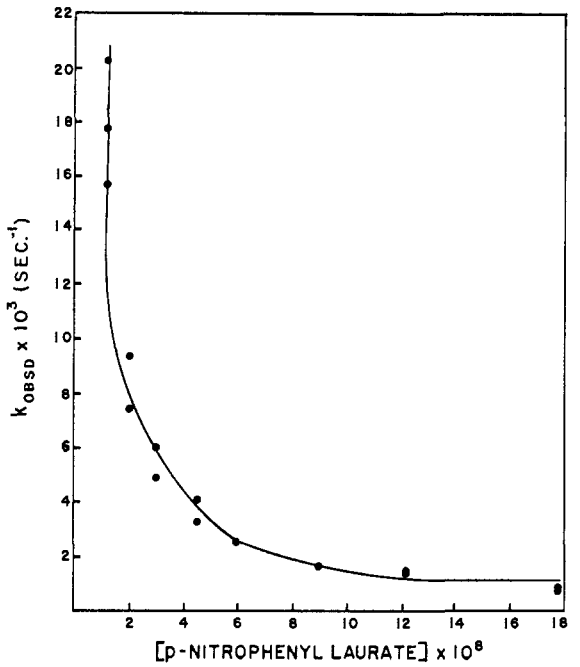

Figure 1. The dependency of observed first-order rate constants for hydrolysis of *p*-nitrophenyl laurate (25.0°, 0.1 *N* NaOH) on the initial ester concentration.

Table I. Second-Order Rate Constants for the Reaction of *p*-Nitrophenyl Laurate with Hydroxide Ion in the Presence of Varying Amounts of Additives[a]

Additive, *M*	$k_2 \times 10^2$, M^{-1} sec^{-1}
None	1.8
Urea	
1.60	3.7
4.00	12
5.60	22
8.00	59
n-Butylurea	
0.210	3.0
0.419	4.6
0.629	8.1
0.838	24
Dioxane	
0.419	2.8
1.05	6.6
1.47	12
2.10	35
$(CH_3)_4N^+Br^-$	
0.200	1.7
0.401	2.1
0.802	2.7
1.00	3.6

[a] 25.0°, initial ester concentration = 1.0×10^{-5} *M*.

the rate constants can be obtained accurately. There is of course considerable error at the lower initial concentrations. All the runs with additives (described below) were performed at a high initial ester concentration of 1.0×10^{-5} *M* where the linearity of the first-order plots is good for about the first half-life.

The concentration range used in Figure 1 was limited at the lower end by the resolving power of the spectrophotometer and at the higher end by the solubility of *p*-nitrophenyl laurate in water. There is no doubt that *p*-nitrophenyl laurate is soluble in 0.8% acetonitrile–water to the extent of 10^{-5} *M*. The ultraviolet spectrum of 10^{-5} *M* ester in neutral water does not change with time. The absorbance maximum (276 mμ) has log ε 3.9, which may be compared with λ_{max} 271 mμ (log ε 3.97) for *p*-nitrophenyl acetate. The absorbance–time curve for hydrolysis of 10^{-5} *M p*-nitrophenyl laurate in 0.1 *N* NaOH is smooth; there is no erratic pen behavior often associated with precipitate formation. The laurate molecules are tied up in aggregates whose concentration, of course, must be considerably less than 10^{-5} *M*.

The runs with the additives (urea, *n*-butylurea, dioxane, or tetramethylammonium bromide) were performed as above except that the cuvettes were filled with 3.00 ml of a solution of one of the four compounds in 0.1 *N* NaOH. All solutions were prepared immediately before use. We estimate that the rate constants (Table I) are accurate to within ±12% (which is an insignificant error compared to the large rate enhancements caused by the additives). Observed first-order rate constants were divided by the hydroxide ion concentration (determined titrimetrically for each solution) in order to obtain second-order constants.

Results and Discussion

The decrease in the hydrolysis rate of *p*-nitrophenyl laurate with increasing initial ester concentration in the range of 10^{-6}–10^{-5} *M* (Figure 1) is readily explained by aggregation of the ester as a result of hydrophobic interaction between the long hydrocarbon chains. Some of the ester groups in the aggregates will be surrounded by the hydrocarbon tails of the substrate and therefore be encased in a microscopic region of low dielectric constant. Hydrolysis in such an environment would be inhibited because the rates of ester reactions decrease with decreasing dielectric constant[7] and because accessibility of the nucleophile, hydroxide ion, would be reduced. There is an abundance of data consistent with this interpretation. Menger and Portnoy[1] have shown that the rate constants for hydrolysis of esters adsorbed into the hydrocarbon center of soap micelles are within experimental error of zero. Duynstee and Grunwald[8] and Menger and Bender[9] demonstrated that the reactivity of an ester carbonyl group toward nucleophilic attack is impaired when the substrate is complexed with nonpolar species.

The rate *vs.* concentration profile for *p*-nitrophenyl decanoate (not shown) looks very much like Figure 1 except that it is displaced to higher ester concentrations. This is what would be expected if the hydrocarbon chains of the esters (rather than the aromatic rings) are the principal source of complexation.

The rate data of Figure 1 do not permit determination of the average size of the *p*-nitrophenyl laurate aggregates. It is clear, however, that the equilibrium constants describing association of the ester molecules are enormous. If it is arbitrarily assumed that the aggregates are dimeric, then the association constant would be roughly 10^7 M^{-1}. This is a large value even for an enzyme–substrate system. Chymotrypsin, for example, binds many of its specific substrates with an association constant on the order of 10^4 M^{-1}. The value of 10^7 M^{-1} for association of the laurate ester chains is reasonable with respect to the estimated maximum free energy release of 1.4 kcal/mol per methylene–methylene association as a result of hydrophobic and van der Waals attraction.[10]

The hydrolysis of *p*-nitrophenyl laurate is accelerated by each of the four additives with the following de-

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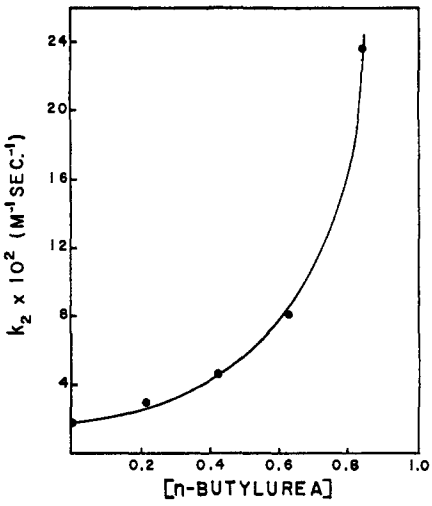

Figure 2. Second-order rate constants for basic hydrolysis of *p*-nitrophenyl laurate (25.0°, initial ester concentration: 1.0×10^{-5} *M*) as a function of the *n*-butylurea concentration.

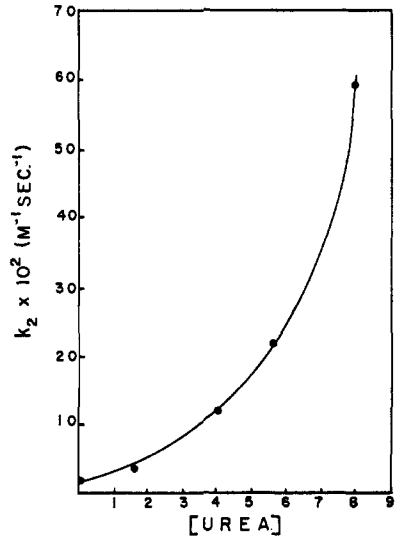

Figure 3. Second-order rate constants for basic hydrolysis of *p*-nitrophenyl laurate (25.0°, initial ester concentration: 1.0×10^{-5} *M*) as a function of the urea concentration.

creasing order of effectiveness: *n*-butylurea, dioxane, urea, and tetramethylammonium bromide (Table I and Figures 2 and 3). For example, the rate enhancement in 0.84 *M* *n*-butylurea corresponds to that in 5.6 *M* urea. The accelerated hydrolyses must be ascribed to a perturbed hydrocarbon–hydrocarbon association (rather than to a medium effect at the reactive ester site) because all four reagents *inhibit* hydrolysis of a short-chain ester, *p*-nitrophenyl acetate (Table II). Thus, while 2.1 *M* dioxane increases the rate of hydrolysis of *p*-nitrophenyl laurate (1.0×10^{-5} *M*) by a factor of 19, it decreases the rate of hydrolysis of *p*-nitrophenyl acetate threefold.

Table II. Second-Order Rate Constants for the Reaction of *p*-Nitrophenyl Acetate with Hydroxide Ion in the Presence of Varying Amounts of Additives[a]

Additive, *M*	k_2, M^{-1} sec^{-1}
None	14.9
Urea	
1.88	7.90
3.75	6.08
n-Butylurea	
0.408	13.2
0.816	11.5
Dioxane	
1.05	8.56
2.10	4.86
$(CH_3)_4N^+Br^-$	
0.501	14.0
1.00	10.8

[a] 25.0°, Borax buffer, $I = 0.1$.

The additives could accelerate hydrolysis in one of two ways. The reagents might *externally* perturb the hydrocarbon association within the aggregates (by either a specific or nonspecific type of interaction) and thereby increase the amount of free laurate ester in equilibrium with aggregated substrate. The liberated ester molecules would no longer have their ester moieties protected from hydroxide ion, and the observed hydrolysis rate would increase. Alternatively, the additives might enter the aggregates and decrease the degree of "masking" of the ester groups by swelling or otherwise perturbing the aggregates. We favor the first rationale, although kinetically the possibilities are indistinguishable since aggregated and nonaggregated ester are related by an equilibrium constant. It has been shown that the distribution of a substance between the bulk aqueous phase and the hydrocarbon interior of molecular aggregates (micelles) is closely related to the solubility of the substance in water relative to that in a hydrocarbon solvent.[11] Now the additives, especially urea and tetramethylammonium bromide, are very water soluble. Except for dioxane, the additives are hydrocarbon insoluble. Therefore, it seems unlikely that the additives would effectively partition into the *p*-nitrophenyl laurate aggregates.

If indeed the additives externally perturb or destroy the *p*-nitrophenyl laurate aggregates, then the question arises as to whether we are observing (a) a specific additive–hydrocarbon interaction or (b) a nonspecific bulk solvent effect. The following evidence, although not conclusive by any means, points to a nonspecific interaction. The rate constant *vs.* concentration curve for urea (Figure 3) is not linear; the log k_2 *vs.* urea concentration plot (not shown) *is* linear, however. Nonspecific solvent effects on thermodynamic (solubility) parameters often follow the Setschenow equation,[12] with a logarithmic increase in solubility with increasing additive concentration. Since the rate enhancements are probably the result of solubilization of the ester from the aggregate "phase" into the aqueous phase (see above), the kinetic parameters should also follow the Setschenow equation if the effects of the additives are nonspecific. The logarithmic increase in the rate constants is therefore consistent with a bulk solvent effect. The solubilizing action of ethanol[13] and

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urea[14] on compounds with hydrocarbon groups is also most easily interpreted as a nonspecific solvent effect.

The effectiveness of urea derivatives as denaturants is enhanced with increasing substitution of alkyl groups on the nitrogen.[15] Interestingly, the presence of a butyl group on the urea molecule also greatly improves its ability to "denature" the *p*-nitrophenyl laurate aggregates (Table I).

Hydrophobic bonding is of paramount importance in the stabilization of the structure of proteins,[16] enzyme–substrate complexes,[17] biological membranes,[18] and molecular aggregates.[18] A useful feature of this paper is the presentation of a new method for studying the nature of hydrophobic bonding. Clearly, interesting generalizations concerning hydrocarbon–solute interaction could emerge from a thorough structure–activity analysis with a large variety of additives. Our kinetic method is sensitive, fast, and simple to carry out. The solubility method[2] yields data which are somewhat easier to interpret quantitatively, but the method is slow (as much as 7 days may be required to attain equilibrium), and the changes brought about by the additives are generally quite small.[19]

Acknowledgment. We greatly appreciate assistance from the McCandless Fund of Emory University and from the Petroleum Research Foundation (Type G Grant). National Defense Education Act predoctoral support for C. E. Portnoy is also gratefully acknowledged.

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Diethylbis(dipyridyl)iron. A Butadiene Cyclodimerizaton Catalyst

Akio Yamamoto,[1a] Kazuhiko Morifuji,[1a] Sakuji Ikeda,[1a] Taro Saito,[1b] Yasuzo Uchida,[1b] and Akira Misono[1b]

Contribution from the Tokyo Institute of Technology, Research Laboratory of Resources Utilization, Meguro, Tokyo, Japan, and The University of Tokyo, Department of Industrial Chemistry, Faculty of Engineering, Hongo, Tokyo, Japan. *Received August 14, 1967*

Abstract: Diethylbis(dipyridyl)iron (**1**) was isolated from a mixed catalyst system containing iron acetylacetonate, diethylaluminum monoethoxide, and dipyridyl. The structure of the ethyl–iron complex was established from elementary analysis, infrared spectroscopy, and chemical properties of the complex. Zero-valent iron–dipyridyl complexes, bis(dipyridyl)iron (**2**) and tris(dipyridyl)iron (**3**), were prepared by thermal decomposition of **1** at 50° in benzene, both in the absence and presence of excess dipyridyl. The isolated iron–dipyridyl complexes **1**–**3** showed the same catalytic behavior as the mixed catalyst system for butadiene oligomerization. The mechanism of butadiene cyclodimerization to cyclooctadiene and vinylcyclohexene by these iron–dipyridyl complexes was studied by using a deuterated monomer. Diethylbis(dipyridyl)iron was also active as a catalyst of acetylene and acrylonitrile polymerizations.

In mixed catalyst systems composed of transition metal compounds and organoaluminum compounds, the formation of organo–transition metal complexes is often suggested, but in very few cases have these complexes been isolated from the catalyst systems, because of the instability of the transition metal–carbon bond.[2] We found that α,α'-dipyridyl is an excellent stabilizer of the alkyl–transition metal bond and we have isolated from the mixed catalyst systems ethyl–iron,[3a]–cobalt,[3b] and –nickel[3a,4] complexes which catalyze oligomerization of butadiene. In this paper we wish to report the synthesis and properties of the iron complex in detail, and to discuss the mechanism of butadiene oligomerization.

Results and Discussion

The ethyl–iron complex **1** was prepared from iron(III) acetylacetonate, diethylaluminum monoethoxide, and dipyridyl in ether in a yield of 70%. The structure of the complex was established on the basis of elementary analysis, infrared and visible spectra, and chemical properties of the complex.

The infrared spectrum of the complex in benzene shows bands due to ethyl groups and coordinated

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