Micellar Catalysis In Non-polar Solvents.

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MICELLAR CATALYSIS IN NON-POLAR SOLVENTS

by
David Z. Becher

A Dissertation
Presented to the Graduate Committee
of Lehigh University
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1976

CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 8, 1976
Date

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DEDICATION

To my Father and Mother, Paul and Jane Becher, and my grandfather, Charles Bogin, who introduced me to chemistry.

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ABSTRACT

While the literature on catalysis by micelles in aqueous solution is quite extensive, the number of papers on non-aqueous micellar catalysis is small.[1] The decomposition of benzyl chloroformate and the Diels-Alder reaction between benzoquinone and cyclopentadiene were chosen as model reactions to study micellar catalysis in non-polar solvents. The surfactants chosen as catalysts were the sodium, zinc, chromium, aluminum, and cerium(III) salts of bis(2-ethylhexyl) succinate sulfonic acid. The Hammett acidities of the catalysts were measured in order to determine the effect of a catalyst's acidity on its activity.

The decomposition of benzyl chloroformate in decane was strongly catalyzed (in one case more than 3000 times) by the micelles. The catalytic effectiveness of the different salts was not directly related to their acidity. The zinc salt which was the third most acidic salt was by far the most powerful catalyst and the cerium salt although considerably more acidic than the sodium salt was a weaker catalyst. The activation energies for several of the catalysts were unusually large (Zn^{+2}, $\Delta E = 267 \pm 4$ kjoules/mole; Al^{+3}, $\Delta E = 148 \pm 7$ kjoules/mole). These values which are much larger than the values reported for chloroformate decompositions in solution ($\Delta E \sim 80$ kjoules/mole)[40,42], appear to indicate a change to a more ionic reaction mechanism when the reaction takes place inside the micelles.

The Diels-Alder reaction was moderately catalyzed by these

catalysts. The results were found to depend on certain properties of the catalyst which varied from sample to sample. For this reaction, the catalyst's effectiveness appeared to depend on its acidity. It was observed that drying the aluminum salt under vacuum increased its acidity and made it into a stronger catalyst for this reaction. Unfortunately, it catalyzed an interfering side reaction even more strongly. The activation energy of the catalysis by the aluminum salt was found to be indistinguishable from zero. This is not unreasonable since a similar result has been reported in the literature for the catalysis of this reaction by trichloroacetic acid.[39]

Both reactions show the characteristics typical of micellar catalysis. The dependences of the reaction rates on catalyst concentration are non-linear and extrapolate to a critical concentration below which the catalyst is not effective. The extrapolated critical concentrations are consistent with the literature values of the critical micelle concentration. These results show that micellar catalysis in non-aqueous solvents is a field worthy of further study.

INTRODUCTION

When the aggregates, called micelles, which many amphiphilic molecules form in solution catalyze chemical reactions, the result is called micellar catalysis. This effect has been studied in both aqueous and, for a few cases, non-aqueous solvents.[1] The purpose of this work was to investigate micellar catalysis in non-aqueous solvents more completely.

The word micelle (originally micella) was coined by C. Nägeli in 1877 from the Latin root "mica" which means a crumb and a diminutive ending.[2] He used the new word to describe the tiny crystalline particles which he suggested formed the rigid structures of plants. Later this word was applied to the aggregates of amphiphilic molecules employed by McBain[3] to explain the unusual physical properties of solutions of colloidal electrolytes.

In contrast to the properties of aqueous micellar systems, which have been extensively studied and are now quite well understood, non-aqueous systems have only received a relatively small amount of attention. In recent years, however, there has been an increase in the amount of work done on them. Kertes[4] has recently exhaustively reviewed this field. Despite this the available data is fragmentary and sometimes contradictory. This is shown by an examination of the data available on the micellar properties in non-aqueous solvents of the surfactants used in this work, the metal salts of bis(2-ethylhexyl) succinate sulfonic acid.

In 1949 Mattoon and Mathews[5] detected the existence of micelles of the sodium salt (Aerosol OT ®) in n-dodecane by low angle x-ray scattering, but they made no estimate of their size. Since then a number of authors[6-14] have reported micelle sizes for these surfactants in hydrocarbon solvents. Their results are summarized in Table I. Study of the values shows clearly that the data for these surfactants are fragmentary, a situation which is typical of the whole field. Only a few solvents have been studied by more than one author and six different temperatures over a seventeen degree range are represented. In addition, even when more than one value is available for a solvent at a given temperature the reported values may vary widely. For example, compare the values reported by Kitahara et al.[10] and Eicke and Christen[14] for benzene at 25°C. Even though both used vapor pressure osmometry the values differ by 40 percent. Furthermore, the results of Eicke and Christen for the isomers of hexane show that wide variations in aggregation number are possible even for very similar solvents. Thus, it is not safe to assume that the micellar properties of a surfactant will be similar in related solvents. Micelle size is expected to be a function of temperature, but this effect has not been studied for these surfactants or, for that matter, many others. From the available data it is impossible even to say with certainty whether the micelle size increases or decreases with temperature.

Another quantity in addition to the aggregation number which is needed to describe an aqueous micellar system is the critical micelle concentration or cmc. In most non-aqueous surfactant solutions the cmc is not a well defined quantity, since, in comparison with aqueous solutions, the micelle size is smaller and tends to be more concentration dependent. As a result the cmc tends to be very diffuse and not useful as an experimental property.

Bis(2-ethylhexyl) sodium sulfosuccinate, however, has relatively large micelles for a non-aqueous surfactant and the aggregation number does not show much concentration dependence. It is, therefore, possible that a meaningful value can be determined for the cmc. Muto and Meguro[15] have determined its cmc in benzene at 20°C by three methods with the results presented in Table II.

As can be seen, the available information is very incomplete. A further difficulty is the well-known observation[4,16] that the presence of a third component, such as water (or the reactants in a reaction catalyzed by micelles), may change the micellar properties in unpredictable ways. In consequence, it is difficult or impossible with the available data to say what the precise properties of the species catalyzing a reaction really are unless they could be directly measured.

The field of catalysis by micelles has recently been completely reviewed by Fendler and Fendler.[1] The reactions can be divided into three types, those occurring in aqueous, non-aqueous, and mixed solvents. Catalysis by micelles in aqueous solution has been

TABLE I

Solvent	Temp.	$\tilde{n}$	Method	Ref.
n-pentane	25°C	16	vp	14
n-hexane	25°C	15	vp	14
2-methylpentane	25°C	20	vp	14
3-methylpentane	25°C	17	vp	14
2,3-dimethylbutane	25°C	17	vp	14
2,2-dimethylbutane	25°C	34	vp	14
n-heptane	40°C	21	vp	13
2,4-dimethylpentane	25°C	19	vp	14
n-octane	25°C	30	ls	11
iso-octane	25°C	27	uc	7
iso-octane	25°C	23	uc	12
iso-octane	23°C	24	ls	12
iso-octane	40°C	21	vp	13
n-nonane	25°C	27	uc	12
n-nonane	23°C	26	ls	12
n-decane	25°C	37	ls	11
n-dodecane	30°C	32	uc	6
n-dodecane	25°C	44	ls	11
n-dodecane	25°C	28	uc	12
n-hexadecane	25°C	54	ls	11
n-hexadecane	25°C	29	uc	12
cyclohexane	28°C	56±9	ls	8
cyclohexane	37°C	90	ws	9

TABLE I (Continued

Solvent	Temp.	$\tilde{n}$	Method	Ref.
cyclohexane	25°C	39	ls	11
cyclohexane	40°C	18	vp	13
cyclohexane	25°C	17	vp	14
benzene	28°C	23	ls	8
benzene	37°C	18	ws	9
benzene	25°C	22	vp	10
benzene	40°C	14	vp	13
benzene	25°C	13	vp	14
toluene	23°C	21	ls	12
Ca^{+2} salt				
benzene	25°C	20	vp	10
Al^{+3} salt				
benzene	25°C	17	vp	10

$\tilde{n}$ = number of anionic groups per micelle

vp = vapor pressure osmometry

ls = light scattering

uc = sedimentation ultracentrifuge

ws = water solubilization

TABLE II

cmc (mmoles/liter)	cmc (grams/liter)	Method
2.0	0.9	dye adsorption
2.3	1.0	vp depression
2.8	1.2	light scattering
2.4±0.4	1.1±0.2	average

studied extensively since about 1960, when it was proposed as a model for enzymatic catalysis. In general, these systems show no catalysis below the critical micelle concentration. Above the cmc, a region exists where the rate is a linear function of the surfactant concentration, followed by a leveling off of the rate as the surfactant concentration is increased further. This behavior can be explained for unimolecular reactions by the following reaction scheme:[1]

$$\begin{tikzcd} M + R \arrow[r, shift left, "K"] \arrow[d, "k_o"] & MR \arrow[l, shift left] \arrow[r, "k_c"] & P \\ P \end{tikzcd} \qquad (1)$$

$$k_\psi = \frac{k_o + k_c \; K[M]}{1 + K[M]} \qquad (2)$$

where R is the reactant; M is the micelle; P is the product; K is the equilibrium constant for solubilization; k_o is the rate constant of the uncatalyzed reaction; k_c is the rate constant of the catalyzed reaction; and k_ψ is the measured pseudo-first order rate constant of the reaction. The same type of kinetics is observed in enzymatic catalysis and was the primary reason for the suggestion that micellar catalysis be used as a model for enzymatic catalysis. As was to be expected, however, micellar catalysis failed to show the other characteristics of enzymatic catalysis, such as extremely large rate enhancements and reactant specificity. These results have led to the partial abandonment of these systems as models of enzymes. They are still worth study for their own sakes and there is still a great deal to be done since much of the work in the literature is scattered and few systems have been intensively studied.

In contrast, only a very small amount of work has been done on micellar catalysis in organic solvents and solvent mixtures. Three different types of catalytic systems can be distinguished: reversed micelles, reversed micelles with a material insoluble in the bulk solvent solubilized in them, and liquid crystalline phases.

It should be noted that catalysis of reactions by amphiphilic molecules does not have to be micellar; it is also possible for the dissolved monomer to act as a catalyst. An example of this has been reported by Takeishi, Kawashima, and Okawara[17] for the catalysis by alkylammonium halides of the reaction of sodium azide and polyvinyl chloride (PVC) in tetrahydrofuran (THF). The authors suggested that the uncatalyzed reaction does not occur because although THF is a good solvent for PVC, it is a poor one for sodium azide. They proposed that the catalysis occurred by means of a metathesis reaction between the sodium azide and the ammonium salt to form a THF soluble ammonium azide which was the reacting species. When they plotted the rate constant as a function of surfactant concentration, it showed the saturation kinetics, which are typical of micellar catalysis, but the authors explained this in terms of saturation of the available reaction sites of the surface of the polymer. When the polymer was replaced by the non-polymeric model compound isopropyl chloride saturation kinetics were not observed. This appears to rule out micellar catalysis for isopropyl chloride. The authors therefore concluded that it is not probable for the case of the polymer. This demonstrates that not all catalysis by surfactants is micellar and that care should be taken to confirm that true micellar catalysis is occurring.

There are a number of papers[18] on catalysis in the liquid crystalline phases formed in solutions which contain a surfactant, an organic solvent with appreciable water solubility and water, but the resulting systems are very complex. In addition, the data are frequently not presented in terms of rate versus surfactant concentration at constant solvent composition, which makes comparison with ordinary micellar catalysis difficult. Ahmad and Friberg,[19] for example, plotted their data for the hydrolysis of p-nitrophenyl laurate in liquid crystalline phases of the hexanol-water-cetyltrimethylammonium bromide system as the rate as a function of the weight percentage of water at a constant hexanol-surfactant ratio. Because of this, only qualitative comparison with the results for reversed micellar systems is possible. It would not be remarkable if these systems showed quite different behavior from micellar ones since their structures are completely different, but there are not enough data available to draw any firm conclusions.

Another variation on simple micellar catalysis is found in systems in which the reacting molecules are so large (e.g. vitamin

B_{12a}) that they cannot possibly be contained in anything resembling a normal surfactant micelle. In these reactions the results may be completely independent of the micellar properties in pure solvent.

The most complicated system yet studied is that discussed by Misiorowski and Wells[20] which consisted of phospholipase A_2, phosphatidylcholine (which is both surfactant and reactant), diethyl ether, methanol, water and various cations. The results they reported are extremely difficult to interpret, since the reaction rates apparently depend on, among other things, the order of the addition of the reactants, which makes any simple comparison with other experiments almost impossible.

Hinze and Fendler[21] showed that in the presence of polyoxyethylene(6) nonylphenol a molecule of hemin dissolved in benzene containing 1 percent by volume of methanol is solubilized by 2100 ± 400 molecules of surfactant. They found that if hemin was reacted with cyanide under these conditions the equilibrium constant was increased by a factor of 960 by comparison with the value in methanol.

In the third paper, Fendler, Nome, and Van Woert[22] investigated the effect of dodecylammonium propionate and bis(2-ethylhexyl) sodium sulfosuccinate on the rates of formation and decomposition of the glycine, imidazole, and sodium azide adducts of vitamin B_{12a} in benzene in the presence of solubilized water. They found that each molecule of vitamin B_{12a} was solubilized by approximately

300 surfactant molecules and that the forward and reverse reaction rates were dependent on the environment of the vitamin B_{12a} which was affected by the amount of water present. Since, in both of the last two papers cited, the authors reported that the position of the equilibrium was changed, the effect of the surfactant on these reactions is not limited to simple catalysis which would affect only the rates leaving the equilibrium unchanged.

These three reactions are of some biochemical interest, but the great complexity of biochemical systems makes them poor ones to study in an attempt to understand micellar catalysis, a field which is itself not well understood.

In micellar catalysis, when one of the components of the reaction system under investigation is insoluble in the bulk solvent, it must be solubilized in the micelles. Its solubilization in the micellar core forms a pool in which the reaction presumably occurs. This gives a completely different environment for the reaction than the anhydrous core of the micelle. Water is the material which is most commonly found in this situation since it is only slightly soluble in hydrocarbon solvents and it is involved in a great many chemical reactions. Basically, the water can be present for two different reasons. It can be one of the reactants or it can be added to change the properties of the micelle.

An example of the second type is provided by the work of Kon-no, Miyazawa, and Kitahara[23] on the catalysis by alkylammonium propionates of the ketol-enol transformations of acetylacetone and ethyl acetoacetate in cyclohexane. In this work the water was added to the system in order to change the equilibrium keto-enol ratio. The authors found that at a molar ratio of water to surfactant of less than 0.5 the rate of the transformation was independent of the water concentration. At higher values of the ratio the rate fell sharply with increasing water concentration. The rate had a roughly linear dependence on catalyst concentration and appeared to show a critical micelle concentration at about the concentration predicted by measurements in the dry solvent. The rate was also qualitatively proportional to the number of ammonium protons, which indicates acid catalysis by proton donation or hydrogen bonding. The drop in rate at higher water concentrations could be due to interference by hydrogen bonding by the water with the catalytic process.

There are several papers in the literature dealing with the other case, reactions in which water takes part. Five of these papers are concerned with the hydrolysis of esters of nitrophenols, two with hydrolysis or water exchange in inorganic complexes, and one with the formation and decomposition of the Meisenheimer complex of 1-(β-hydroxyethoxy)-2,4,6-trinitrobenzene.

The most important paper is the study by O'Connor, Fendler, and Fendler[24] of the catalysis of the hydrolysis of 2,4-dinitrophenyl sulfate by alkylammonium carboxylates in benzene. Its importance is due to the fact that it is the only paper on micellar catalysis in organic solvents in which activation parameters were calculated. The determination of the extent of micellar catalysis in this system was made more difficult by the fact that the reaction was clearly catalyzed by the surfactant in both the monomeric and micellar forms. The authors divided the effect of the surfactant into two parts by extrapolating the linear dependence of the rate on the surfactant concentration above the apparent critical micelle concentration to infinite dilution, and then ascribed the resulting value to micellar catalysis. The remainder of the catalysis was assigned to the acid-base properties of the monomer. This appears somewhat questionable since it depends on the dubious assumption that the effect of the micelles is independent of their concentration. On this assumption, however, they calculated the enthalpy and entropy of activation for the catalysis by dodecylammonium proprionate from the rate constants at 24.5°C and 39.8°C using the equation:

$$k_r = \frac{kT}{h} \exp\left(\frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT}\right) \qquad (3)$$

where the symbols have their usual meanings. Both the enthalpy and entropy of activation were considerably smaller than the values determined from the rates in bulk water and aqueous micelles. The large decrease they observed in the entropy term was ascribed to the lack of mobility of the reacting molecule in the interior of the micelle, due to the specific orientation between the nitro and sulfate groups and the surfactant. This is interesting, because it implies that it may be possible to obtain information on the nature of the micelle-reactant interactions in this system from the activation parameters.

Kon-no, Matsuyama, Mizuno, and Kitahara[25] have studied the catalytic effect of alkylammonium carboxylates on the hydrolyses of p-nitrophenyl carboxylates in aliphatic and aromatic hydrocarbon solvents. Similarly to O'Connor et al.,[24] they found that the reaction was catalyzed by both the micelle and the monomer and that the catalysis was enhanced by micelle formation. They reported that the catalyses were larger for aliphatic than for aromatic solvents. This is explained by the larger solubilization equilibrium constants in the aliphatic solvents. They also observed that the rate was greater for the acetate than for the hexanoate or the laurate despite the greater solubilization of the larger molecules. It was also reported that the catalytic effect of a surfactant was greater the greater the number of ammonium protons, which indicates acid-base catalysis by the ammonium group.

Menger, Donohue, and Williams[26] determined the rate of the imidazole catalyzed hydrolyses of p-nitrophenyl acetate in water pools solubilized by bis(2-ethylhexyl) sodium sulfosuccinate in octane. They found that the reaction was catalyzed with respect to the bulk solvent, but was slower than in bulk water. This is only marginally a case of micellar catalysis, as the micellar nature of the system does not appear to increase the rate. The reaction proceeds in the water pools as if in bulk water but slower.

Friberg and Ahmad[27] and Friberg, Rydberg, and Lindblom[28] studied the catalysis of the hydrolysis of p-nitrophenyl laurate by cetyltrimethylammonium bromide in the mixed solvents, 1-hexanol-water and 1-butanol-water respectively. These papers differ notably from the others in two respects, i.e., the organic solvents possess considerable water solubility, and the surfactant used is not capable of acting as a simple acid catalyst (as was the case for the other reactions) since it has no ammonium protons. Despite the apparent similarity between the two systems there are significant differences in their phase diagrams. In the hexanol system there exists a phase which the authors suggest contains "reversed micelles" and another phase which contains "normal micelles" with a region containing liquid crystalline phases separating them. The butanol system, in contrast, appears to possess a single continuous phase over the whole composition range from water to butanol. The data in both papers was presented in terms of the rate as a function of the water concentration at a fixed alcohol-surfactant ratio. This makes it impossible to determine the effect of surfactant at a constant solvent composition. In addition, the nature of the catalytic species in the "reversed micelle" region is not well characterized. Small aggregates of some sort are apparently present, but their structure is not necessarily the same as that which would be found for the surfactant in non-polar solvents. At a water content of less than 40 percent the rates of reaction as a function of water content were roughly the same in both systems with maxima whose positions depended on the surfactant concentration. In the hexanol system at high water concentrations a phase change occurs, but in the butanol system there is no phase change and the rate can be followed continuously over the entire range of water concentrations. When the rate is plotted as a function of water concentration for the butanol system, at high water contents the maximum mentioned above is followed by a minimum and then a much larger maximum at about 90 percent water. No rate data were presented for pure water as the solvent since the fixed hexanol-surfactant ratio meant that as the water content approached 100 percent the surfactant concentration became very small. Without knowing the rate in the absence of alcohol and the rate as a function of surfactant concentration it is impossible to draw any valid conclusions about micellar catalysis from the data.

Fendler and Chang[29] studied the reaction of 1-(β-hydroxyethoxy)-2,4,6 trinitrobenzene with hydroxide to give the spiro-Meisenheimer compound, and the decomposition of the resulting compound in benzene containing water solubilized by dodecylammonium propionate. They stated that the catalysis was general basic rather than micellar, but the fact that the rates are comparable to those in water suggests that the reactions may be proceeding in the solubilized water pools exactly as it does in bulk water.

O'Connor, Fendler, and Fendler[30] studied the aquation reactions of some cobalt(III) and chromium(III) complexes in water solubilized by alkylammonium carboxylates dissolved in benzene. They reported that octylammonium tetradecanoate, in the presence of solubilized water at a concentration of 0.110 molar relative to the total volume of the solution, enhanced the rate of the aquation of tris(oxalato)chromate(III) by 5.4×10^6 times the rate in pure water and 100 times the rate in aqueous perchloric acid. Dodecylammonium propionate gave similar results, but hexadecyltrimethylammonium butyrate, which has no ammonium protons did not catalyze the reaction. This, they concluded, indicates acid-base catalysis by the surfactant. The rate of aquation of the cobalt analogue, however, under the same conditions was only catalyzed 1500 times, relative to water and the measured rates were about 4 percent of those for the chromium compound. They also determined the catalytic effect of dodecylammonium propionate on the hydrolysis rates of a number of other cobalt complexes, but they did not observe any other large rate increases, and in one case, azidopentacyano-cobaltate(III), they observed a large rate decrease.

A type of reaction which has some similarities to the reactions involving solubilized water is those in which one of the reactants is insoluble in the bulk solvent and must, therefore, be introduced into the solution by adding it dissolved in a small amount of another solvent, which is soluble in the bulk solvent. This has two effects on the solution. The insoluble reactant is presumably solubilized by the surfactant, and the additional solvent is partitioned between the micelles and the bulk. Both of these effects modify the properties of the micelles. This type of system is the subject of two papers.

Fendler, Chang, and Fendler[32] reported on the micellar catalysis of the reaction of sodium methoxide, introduced into the solution dissolved in methanol, with 4-nitropyridine-N-oxide in benzene. Neither dodecylammonium propionate nor bis(2-ethylhexyl) sodium sulfosuccinate catalyzed the rection, but polyoxyethylene(6) nonylphenol increased the rate to as much as 1200 times the rate in pure methanol. The rate of the reaction showed a clear maximum when plotted versus surfactant concentration, and increased with increasing sodium methoxide concentration. The effect of varying the methanol concentration was not reported.

The same authors[33] determined the rate of the decomposition of the Meisenheimer complex, sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide, in benzene, chloroform, and carbon tetrachloride, in the presence of various surfactants and small amounts of dimethyl sulfoxide (DMSO) which was used to dissolve the reactant. They observed that in benzene dodecylammonium carboxylates increased the reaction rate by a factor of the order of between 10^4 and 10^5 while cetyltrimethylammonium butyrate (which has no ammonium protons) had no effect. The nonionic surfactant polyoxyethylene(6) nonylphenol was observed to catalyze the reaction by a factor of approximately 10^3. The catalytic effectiveness of two naturally occurring phospholipids, lecithin and phosphatidylethanolamine were also determined. The authors observed that lecithin, which contains a tetraalkyl ammonium group, catalyzed the reaction to about the same extent as the nonionic surfactant, but that the similar phosphatidylethanolamine which contains a protonated ammonium group, was as effective as the dodecylammonium carboxylates. The effectiveness of lecithin as a catalyst was greatly increased by the addition of solubilized water, which presumably acted as a source of protons. Similar behavior was observed for lecithin in the other solvents. The results were complicated by the inhibition of the reaction by the DMSO used to introduce the Meisenheimer complex into the solution, which made it necessary to specify at what DMSO concentration the measurements were made. It is obvious that such a system is not ideal for studying micellar catalysis.

Finally, there are two papers on systems which consist only of solvent, soluble reactants, and surfactant. The first is the catalysis by dodecylammonium carboxylates of the mutarotation of 2,3,4,6-tetramethyl-α-D-glucose in benzene and cyclohexane which was studied by Fendler, Fendler, Medary, and Woods.[34] They found that depending on the carboxylate group and the solvent the reaction was catalyzed between 380 and 860 times in comparison to the rate in pure solvent. The reaction kinetics appear to obey the saturation scheme presented for aqueous systems and generally to resemble them in their behavior.

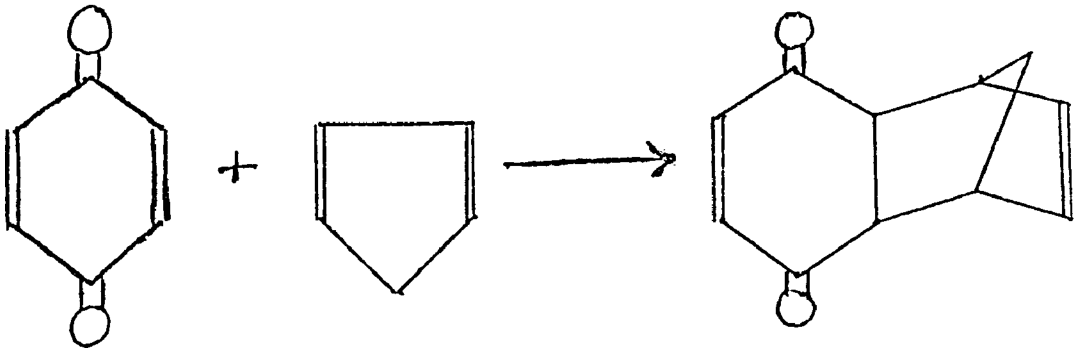
In the second paper, Menger and Vitale[35] reported on the aminolyses reaction of p-nitrophenylacetate with piperidine and imidazole in toluene, catalyzed by tetrahexylammonium benzoate.

The kinetics of the uncatalyzed reaction are complicated, since the rate equation contains terms depending on both the first and second power of the amine concentration. This complicates comparison of the catalyzed and uncatalyzed rates. They observed catalytic rate enhancements of the order of 10^3 times the rate in pure toluene. They also observed, interestingly, that octadecylammonium benzoate only doubled the rate for piperidine, an observation they failed to explain satisfactorily. One possibility is that, since piperidine (pK = 11.1) is more basic than octadecylamine (pK = 10.6),[36] the piperidine equilibrated with the surfactant to form a piperidinium ion and this reduced the rate of the aminolyses. Since the effect of the monoalkyl surfactant on the rate of the aminolysis by the less basic imidazole was not determined, there are insufficient data to draw a definite conclusion. In other respects the results seem to resemble those for typical aqueous systems as was the case in the previous paper.

The review of the literature on micellar catalysis in nonaqueous solvents shows how little work has been done. A number of interesting and possibly useful observations have been made, but a great deal remains to be done before these systems can be said to be understood or before they can be made useful. Most of the papers in the literature are really only initial studies, and any of the reactions could easily be studied in far greater detail. It is clear that this is a field in which the surface has only been scratched.

In order to study micellar catalysis it was necessary to choose some model reactions to be catalyzed. These reactions must meet a number of requirements. The reactions chosen should meet the ordinary requirements for kinetics studies; simple well-known kinetics, no important side reactions and reasonable catalyzed rates at the temperature of interest. In order for a reaction to be catalyzed by micelles certain other characteristics are desirable. The reactants should be soluble in the solvent, but, nevertheless, be more basic or more polar than the solvent, since this will increase their tendency to be solubilized in the micelles. It is also desirable that the products of the reaction have a smaller tendency to be solubilized than the reactants, since otherwise they will tend to reduce the effective catalyst concentration. Reactions in which an acidic reactant takes part are unlikely to be catalyzed as that reactant would not be expected to be solubilized and its concentration in the micelle and consequently the reaction rate would be small. In addition, since the variation of catalytic activity with the acidity of the cationic counterions of the anionic surfactants was to be studied, reactions known to be acid catalyzed were desired. Two reactions were finally chosen, the Diels-Alder reaction between benzoquinone and cyclopentadiene and the thermal decomposition of benzyl chloroformate.

The Diels-Alder reaction chosen was the reaction between cyclopentadiene and benzoquinone to give a one to one adduct.



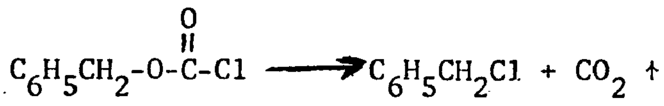
(4)

There are a number of possible side reactions, dimerization or higher polymerization of cyclopentadiene, further combination of the reaction product with cyclopentadiene, and oxidation of cyclopentadiene. In the absence of catalyst, these reactions proceed at rates which are insignificant by comparison with that of the reaction being studied, but one must be sure that this is also true when the catalyst is present. The kinetics of this reaction were first studied by Wassermann;[37] he reported an activation energy of 11.6 ± 0.7 kcal/mole and a log A of 6.5 ± 0.3 for the rate constant with the time in seconds. The same author[38] later reported that this reaction was acid catalyzed; the first example of an acid catalyzed Diels-Alder reaction. Rubin, Steiner, and Wassermann[39] studied the kinetics of the acid catalyzed reaction in more detail. They found that benzene soluble acids such as acetic acid, its chloronated derivatives, and naphthalene-2-sulphonic acid catalyzed the reaction, as did various phenols. The reactions obeyed a two term rate law. The first term was the uncatalyzed rate which was first order in both reactants, and the second term was the catalyzed rate which was first order in both reactants and in the catalyst concentration. For benzene at 25°C some values for the rate constant of the catalyzed reaction were:

CCl_3COOH	$3.17\ \ell^2\text{-mole}^{-2}\text{-sec}^{-1}$
$CH_2ClCOOH$	$0.20\ \ell^2\text{-mole}^{-2}\text{-sec}^{-1}$
C_6H_5OH	$0.13\ \ell^2\text{-mole}^{-2}\text{-sec}^{-1}$

The most interesting results were for trichloroacetic acid, for which the catalyzed reaction had an activation energy of zero within the accuracy of the measurements. This reaction appeared to have all the desired characteristics and was chosen as one of those to be studied.

The other reaction chosen was the thermal decomposition of benzyl chloroformate to benzyl chloride and carbon dioxide.



$$C_6H_5CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl \longrightarrow C_6H_5CH_2Cl + CO_2 \uparrow \qquad (5)$$

The literature on the decomposition of chloroformates in solution is not very extensive, but it is known that the rates are dependent on solvent properties. Wiberg and Shryne[40] determined the rates of decomposition of substituted 1-phenylethyl chloroformates in dioxane and toluene. They found that the rates in dioxane were approximately three to six times larger. They also determined one value for benzyl chloroformate in dioxane at 90°C. While there is no value which is directly comparable, its decomposition is at least two orders of magnitude slower than that of 1-phenylethyl chloroformate under the same conditions. Olivier and Young[41] studied the thermal decomposition of α-methylallyl and crotyl chloroformate. These materials give mixtures of products owing to the possibility of rearrangements. They found that the rate of the decomposition of α-methylallyl chloroformate was strongly solvent dependent and appeared generally to increase with increasing solvent dielectric constant and polarity over a range of 10^4, on going from decane to nitrobenzene. Kevill and Weitl[42] studied the decomposition of 1-adamantyl chloroformate in decane, benzene, nitrobenzene, and benzene-nitrobenzene solvent mixtures. They found the rate depended on solvent in the expected manner. Addition of tetrabutylammonium chloride in nitrobenzene caused a slight catalysis, but this material would not be expected to be micellar under the conditions of the reaction and the authors attributed the increase to a positive salt effect. They concluded that the mechanism of the decomposition was intermediate between a cyclic covalent and an ionic mechanism, the exact characteristics depending on the solvent and the ester group. Benzyl chloroformate was chosen for the micellar catalysis studies because it is readily available and gives only one decomposition product, benzyl chloride. Silebi[43] in this laboratory began by studying the effect of solvent on the reaction rate. His value for the rate constant for the reaction in dioxane at 90°C agreed within a factor of two with that of Wiberg and Shryne.[40] He found that while there was some correlation of reaction rate with solvent dielectric constant, in strongly acidic or basic solvents (such as trichloroacetic acid and tri-n-butylamine), rates far greater than those in nitrobenzene were observed despite the solvents' low dielectric constants ($\epsilon<5$). This indicates that the reaction is both acid and base catalyzed. Marmo[44] did some initial measurements to determine if the salts of bis(2-ethylhexyl) succinate sulfonic acid would catalyze the reaction. He found that in decane at about 95°C, under which conditions the uncatalyzed reaction rate was negligible, the salts catalyzed the reaction in the order $Cr^{+3} > Al^{+3} > Ca^{+2} > Na^{+}$, which is the order of their acidities. These preliminary results indicated that this would also be a suitable reaction to study.

It was my intention to study the micellar catalysis of these reactions in non-polar solvents by using the metal salts of bis(2-ethylhexyl) succinate sulfonic acid in an attempt to begin to achieve a more complete understanding of the nature of micellar catalysis.

EXPERIMENTAL

MATERIALS

Solvents. The decane and ethylbenzene were purchased from Eastman Kodak Company (Rochester, N.Y.). The methanol and benzene were obtained from either the J. T. Baker Chemical Company (Phillipsburg, N. J.) or Lehigh Valley Chemical Company (Easton, Pa.). The benzene used in the kinetics studies was dried with Davison Type 4A molecular sieve obtained from the Fisher Scientific Company (Fair Lawn, N.J.). The molecular sieve was dried by heating under vacuum. Distilled water was obtained from the department still.

Reactants. Benzyl chloroformate was obtained from RSA Corporation (Ardsley, N.Y.). A sample was analyzed by the method of Michels[45] and was found to consist of approximately 70 percent benzyl chloroformate and 30 percent benzyl chloride. Cyclopentadiene was prepared fresh daily by the fractional distillation of dicyclopentadiene obtained from Matheson, Coleman, and Bell (East Rutherford, N.J.) through a 450 millimeter Vigreaux column into a flask immersed in an ice bath. Benzoquinone from the Aldrich Chemical Company (Milwaukee, Wis.) was purified by sublimation at atmospheric pressure.

Catalysts: Bis(2-ethylhexyl) sodium sulfosuccinate was obtained from the Aldrich Chemical Company. Aluminum chloride, aluminum nitrate, cerous nitrate, zinc nitrate, and chromium nitrate were obtained from the Fisher Scientific Company.

The sodium salt was used without further purification. The other salts were prepared by a modification of the method of Kitahara _et al._[10] About 30 grams of the sodium salt were dissolved in approximately 300 milliliters of methanol. A small fraction of the sodium salt would not dissolve in the methanol, but since removing it did not measurably change the catalytic activity of the product its presence was usually ignored. A somewhat greater than stoichiometric amount of the appropriate metal salt was dissolved in about 150 milliliters of distilled water and the two solutions were mixed. Additional distilled water was then added, until at a solvent composition of about two parts water to one part methanol, the metal salt of the surfactant would precipitate out. The solution was allowed to stand overnight in order to complete precipitation and then filtered by suction filtration. The resulting product, which still contained appreciable amounts of solvent, was then dissolved in 300-400 milliliters of benzene and allowed to stand until the solution was clear. Any aqueous phase which separated was removed by means of a separatory funnel. The volume of the benzene was then reduced to approximately 250 milliliters by boiling. This treatment (which was possible because the catalysts are stable in boiling benzene) also helped to remove any dissolved water in the benzene. When the initial benzene volume was small, more benzene was added in an attempt to insure that as much dissolved water as possible would be removed. The benzene solution was then freeze-dried to remove the solvent.

The freeze-dryer trap which had a central tube forty millimeters in diameter was attached to a half inch vacuum line. Freeze-drying produced the catalyst in a dry porous form which was easy to dissolve. The elemental analyses of the aluminum and cerium salts are presented in Table III. The analyses were performed by Baron Consulting Co. (Orange, Conn.). It is obvious that these salts are not pure. The analysis for the cerium salt indicates that the composition most nearly matching the experimental analysis is $CeNa_{0.2}(C_{20}H_{37}SO_7)_{3.2} \cdot 0.75\ H_2O$. This indicates that some of the sodium salt probably coprecipitated when the cerium salt was formed. The resulting material is 94 percent by weight cerium salt. The low aluminum value can probably be attributed to the same cause. The analysis of the sodium salt indicates that the sodium content is too high. This is probably due to the presence of a small amount of excess sodium hydroxide. This analysis is of the batch of sodium salt which had properties which indicated that it was more basic than the other samples of sodium salt used.

Indicators. Dibutylphosphate, and indicator grade phenylazodiphenylamine, N,N-dimethyl-p-phenylazoaniline (Butter Yellow), and 1,9-diphenyl-1,3,6,8-nonatetraen-5-one were obtained from Eastman Kodak and used without further purification. Purified 4-phenylazonaphthylamine was generously provided by Dr. H. Benesi of Shell Development Corp.(Houston, Texas).

TABLE III

Analysis of Aluminum Salt

	Calculated $Al(H_2O)_6(E)_3$	Measured
C	51.48	51.49
H	8.86	8.69
Al	1.93	1.72

Analysis of Cerium Salt

	Calculated $Ce(E)_3$	Calculated $CeNa_{0.2}(E)_{3.2} \cdot 0.75\ H_2O$	Measured
C	51.30	51.00	50.99
H	7.96	7.92	7.99
S	6.85	6.81	6.49
Ce	9.97	9.30	9.35
Na	--	0.31	0.37

Analysis of Sodium Salt

	Calculated Na(E)	Calculated (Na(E) ·0.047 NaOH)	Measured
C	54.04	53.81	53.86
H	8.39	8.35	8.36
S	7.21	7.18	7.09
Na	5.17	5.39	5.39

$E = C_{20}H_{37}SO_7$

PROCEDURES:

Decomposition of Benzyl Chloroformate

The rate of the decomposition of benzyl chloroformate was determined by measuring the amount of carbon dioxide gas evolved as a function of time, using the apparatus shown in Figure 1. The temperature of the reaction was controlled by immersing the reaction flask in an oil bath which was kept at a constant temperature by means of a Cole-Parmer (Chicago, Ill.) Magnetic "6x6" stirrer with hot plate equipped with a temperature control probe. This held the bath temperature constant to within ±0.5 degrees.

The catalyst was dissolved in fifty milliliters of the solvent and placed in the reaction flask. The flask was placed in the oil bath overnight to achieve temperature equilibrium. The reaction was commenced by introducing one milliliter of benzyl chloroformate into the flask through its side arm with a syringe.

Measurements of the volume of gas evolved were then made at constant time intervals. For most reactions the interval was thirty minutes but for very fast or slow reactions it was varied from five minutes to two hours. Whenever possible the reaction was allowed to proceed until it was essentially complete and the volume of gas evolved at completion (V_∞) determined.

The rates were calculated in one of two ways. When a measured value for V_∞ was available the simple first order rate equation

$$k_p = \frac{1}{t} \ln \frac{V_\infty}{V_\infty - V} \qquad (6)$$

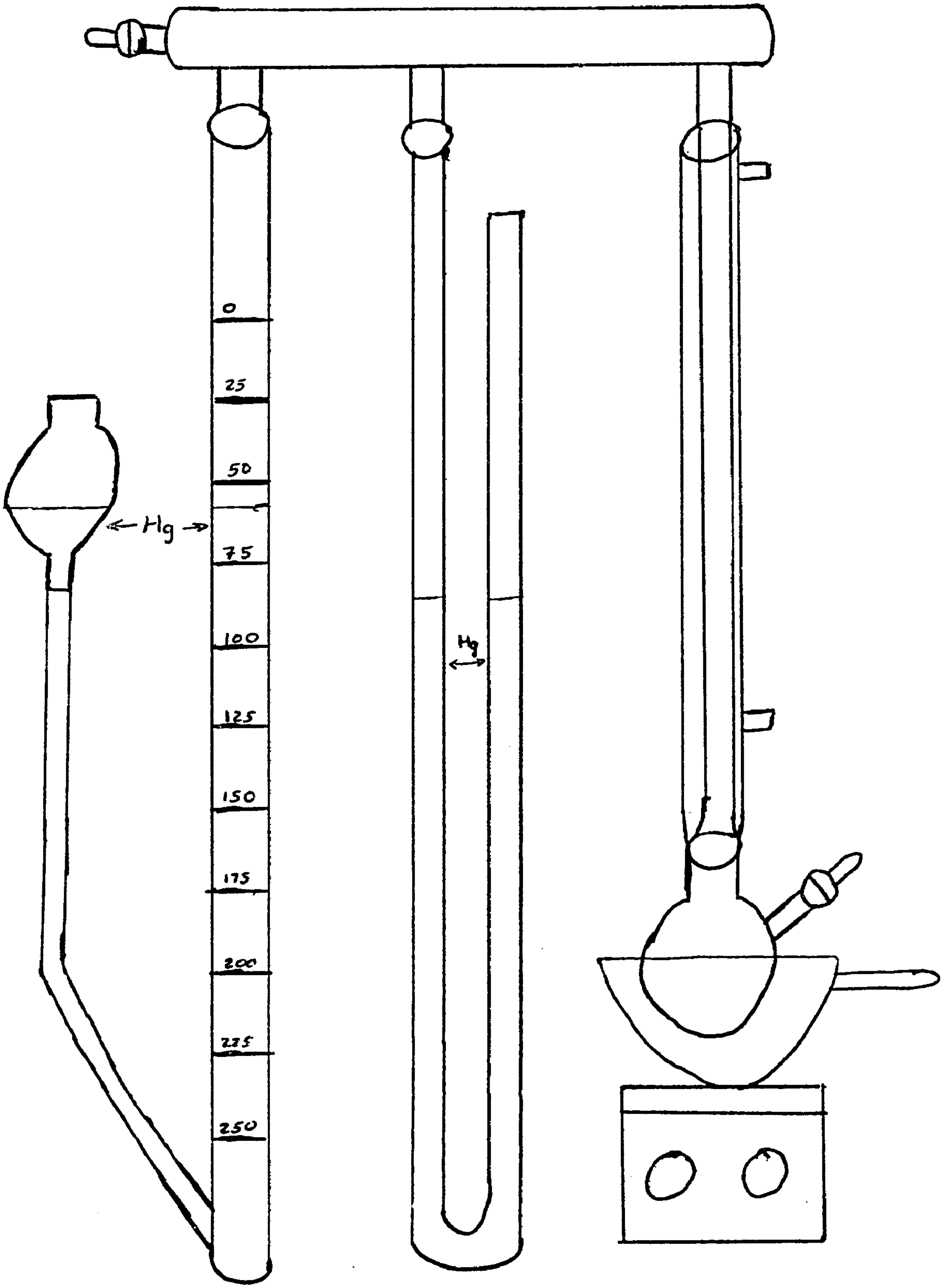


Figure 1. Gas volume apparatus

was used, where k_p is the pseudo-first order rate constant and V is the volume of gas evolved at time t. This gave k_p values with an error of about five percent.

In those cases where, owing to very long half-lives or instrumental difficulties, a good value of $V\infty$ was not available, the rate constant was calculated by the Guggenheim method[46] using the equation:

$$\ln(V_2 - V_1) = - k_p t + \ln V\infty(1-e^{-k_p \Delta t}) \qquad (7)$$

where V_1 is the volume evolved at time t and V_2 is the volume at time t + Δt. If one plots $\ln(V_2-V_1)$ versus t for a fixed Δt the slope of the resulting line will be $-k_p$ with an error of about ten percent. In cases in which both methods of calculation were used the values generally agreed fairly closely, which leads to the conclusion that the Guggenheim method should also give reasonable results when used alone.

Diels-Alder Reaction

The rates of the Diels-Alder reaction were determined by following the concentration of the benzoquinone spectrophotometrically at 454 nm with a Perkin-Elmer Model 402 ultraviolet-visible spectrophotometer. The spectrophotometer was equipped with a sample holder block which was maintained at a constant temperature by circulating through it water from the bath of a Forma Scientific Co. (Marietta, Ohio) Forma Temp Jr. constant temperature bath.

Between 0.4 and 0.5 gram of benzoquinone was weighed into a 50 ml volumetric flask and dissolved in dried benzene. A stock solution of cyclopentadiene was made by diluting 10 milliliters of it to 100 milliliters with benzene in a volumetric flask. A weighed amount of the catalyst, if any, was dissolved in benzene in a 100 ml volumetric flask and 10 milliliters of the cyclopentadiene stock solution was added. The two solutions were then placed in a temperature bath at the reaction temperature for at least fifteen minutes. After the solutions had reached the bath temperature, they were diluted to the mark with dry benzene, also at bath temperature. The spectrophotometer cells were both filled with dry benzene and the base line adjusted to zero absorbance. Twenty-five milliliters was pipetted from each flask and put in a beaker. The solutions were mixed and simultaneously the time drive of the spectrophotometer was started. The cell was filled with the mixed solutions and the benzoquinone concentration was followed as a function of time for twenty minutes.

The overall rate constant k_p was then calculated using the equations:

$$k_p = \frac{1}{t} \frac{1}{(C)_0 - (B)_0} \ell n \frac{(B)\ (C)_0}{(B)_0 (C)} \qquad (8)$$

$$(C) = (B) + (C)_0 - (B)_0 \qquad (9)$$

where B stands for benzoquinone and C for cyclopentadiene and the subscript zero indicates the initial concentrations. The benzoquinone concentrations were determined from the absorbances using a molar absorptivity of 19.7 ± 0.2 (see Fig. 2). The initial cyclopentadiene concentration was calculated from the dilutions. The initial benzoquinone concentration was determined by extrapolation and from the weight of the benzoquinone. The two values generally agreed within two percent. The rates determined by this method were accurate to approximately five percent, based on the reproducability of the uncatalyzed rates.

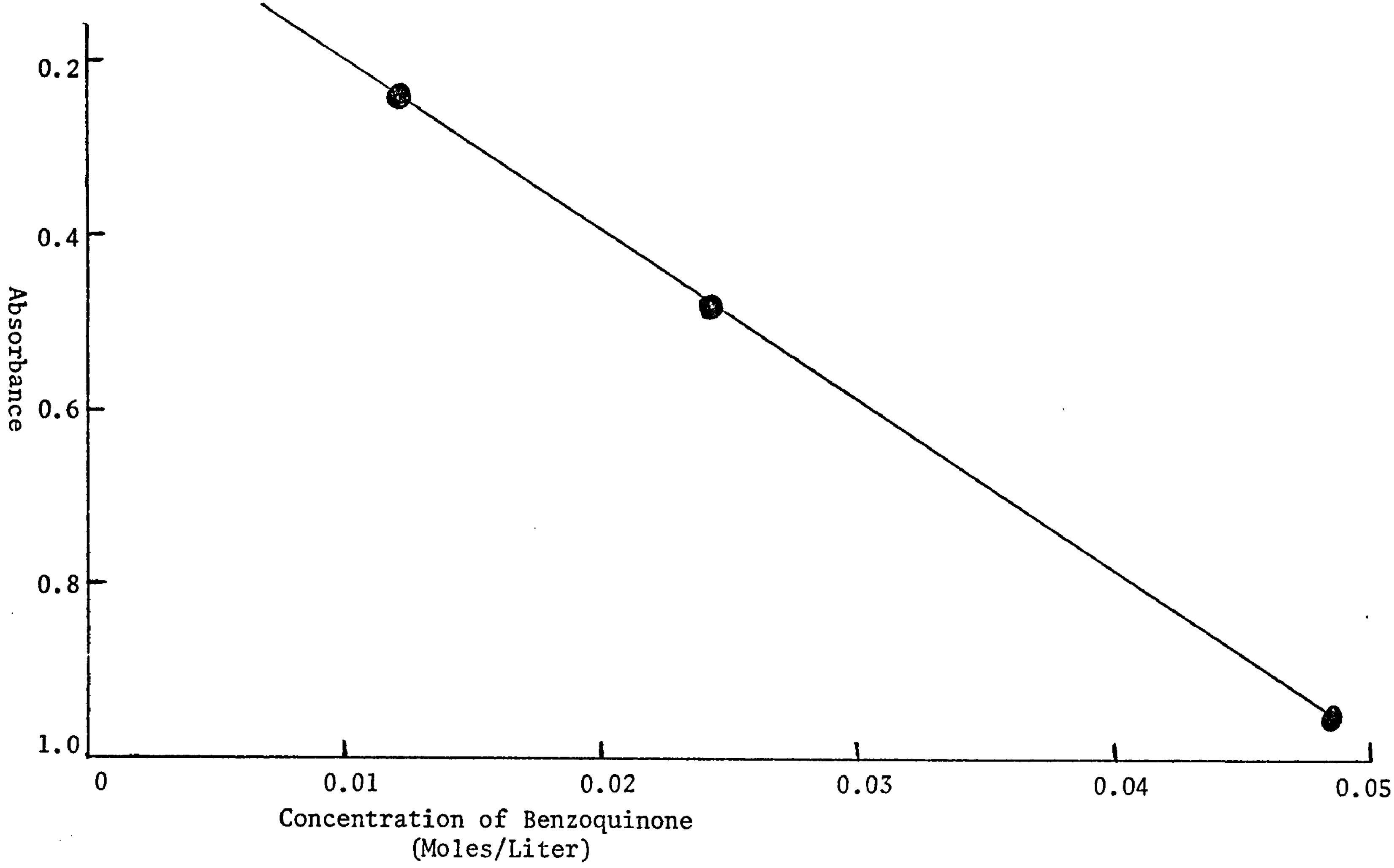
Acidities

The acidities of the catalysts in benzene solution were determined using indicator dyes. The Hammett acidities (H_0) are given by the equation:[47]

$$H_0 = pK + \log \frac{[I]}{[IA]} \qquad (10)$$

where pK is minus the logarithm of the acid-base equilibrium constant in aqueous solution and [I] and [IA] are the spectrophotometrically determined concentrations of the basic and acidic forms of the indicator dyes. The indicators were dissolved in benzene to make stock solutions of approximately 2×10^{-3} molar. Aliquots of the stock solutions were then diluted one hundred times with benzene and the spectra of the basic forms determined. The absorbances of the acidic forms were determined by diluting the indicator stock solutions with a mixed solvent consisting of 10 percent dibutylphosphate and 90 percent benzene. Dibutylphosphate is a strong benzene-soluble acid which completely converted the in-

Figure 2. Beer's law plot for benzoquinone



dicators to the acid form. About 2 grams of catalyst were dissolved in 100 milliliters of benzene to which one or two milliliters of indicator stock solution had been added and the absorbances determined. With these results the acidities were calculated by equation 10.

Catalyst Properties

Vapor pressure osmometry and differential thermal analysis measurements were made on some catalyst samples courtesy of Dr. Paul Becher and ICI United States. The vapor pressure osmometric measurements were performed by Mr. Thomas Harvey and Mr. R. L. Birkmeier using an H-P Model 302B vapor pressure osmometer. The differential thermal analysis was performed by Mr. J. R. Nichols using a DuPont DTA.

RESULTS AND DISCUSSION

Decomposition of Benzyl Chloroformate

The catalytic studies on this reaction were performed in decane because the uncatalyzed rate is very small in it. At 125°C the uncatalyzed rate was determined to be less than 2×10^{-6} $\sec^{-1}$, which is insignificant by comparison with the catalyzed rates.

The dependence of the reaction rate on the catalyst concentration was determined for the aluminum and sodium salts at 126°C. A typical set of data is plotted in Figure 3. The results of these measurements are presented in Table 4 and Figures 4 and 5. Both curves show the non-linear dependence on catalyst concentration and the existence of a critical micelle concentration which are typical of micellar catalysis, although the non-linearity of the curve for the aluminum salt is relatively small. The critical micelle concentrations for the systems were estimated by a linear extrapolation of the five lowest catalyst concentration points to zero reaction rate. Values of 1.5 grams/liter for the aluminum salt and 6.6 grams/liter for the sodium salt were obtained.

The catalytic effectiveness of the other salts at 126°C was determined at a concentration of approximately 40 grams/liter. At that concentration the rate is approximately proportional to the catalyst concentration. The rate constants in Table 5 are, therefore, divided by the catalyst concentration in order to allow for the small variations in the amount of catalyst used. These values show that the acidity of the catalyst is not the determining factor

Figure 3. Typical data for the decomposition of benzyl chloroformate.

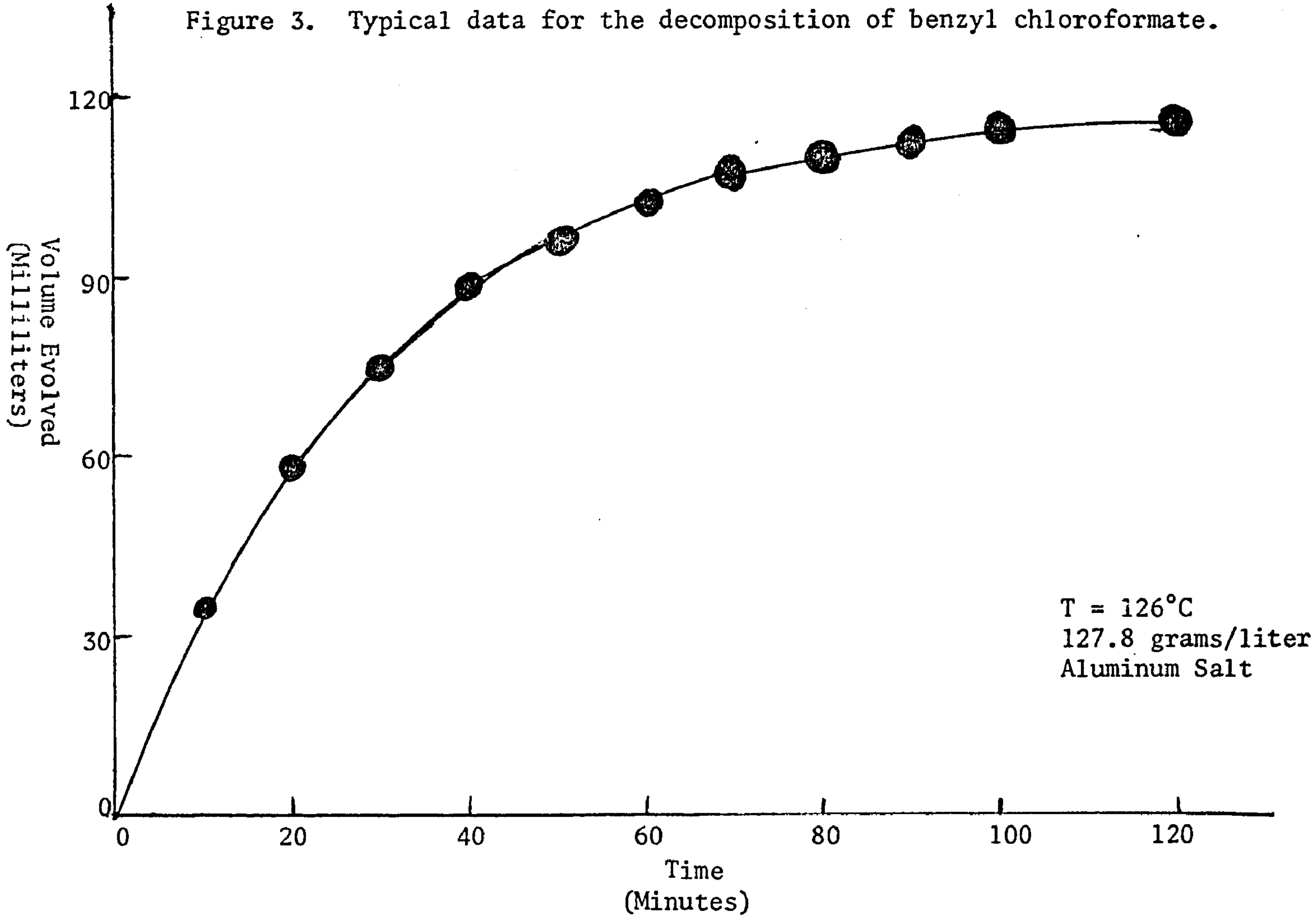


TABLE 4

The Rate of Decomposition of Benzyl Chloroformate in Decane at 126°C at Various Catalyst Concentrations

Sodium Salt

Catalyst Concentration grams/liter	Rate Constant ($sec^{-1} \times 10^5$)
19.2	1.75
25.0	3.28
29.8	4.31
32.8	4.39
36.0	4.44
40.6	6.25
42.4	4.08
47.0	4.69
47.8	5.56
50.6	8.00
59.0	6.47
61.4	6.69
77.8	10.6
81.0	9.69
90.8	8.67
100.0	12.1

Aluminum Salt

Catalyst Concentration grams/liter	Rate Constant ($sec^{-1} \times 10^5$)
12.0	4.58
23.6	11.3
25.4	9.42
31.8	13.6
41.8	18.1
67.4	28.5*
71.0	27.3
86.0	37.4
102.8	49.1
127.8	56.1
151.6	58.5

* Average of two points

Figure 4. The rate of decomposition of benzyl chloroformate as a function of sodium salt concentration at 126°C.

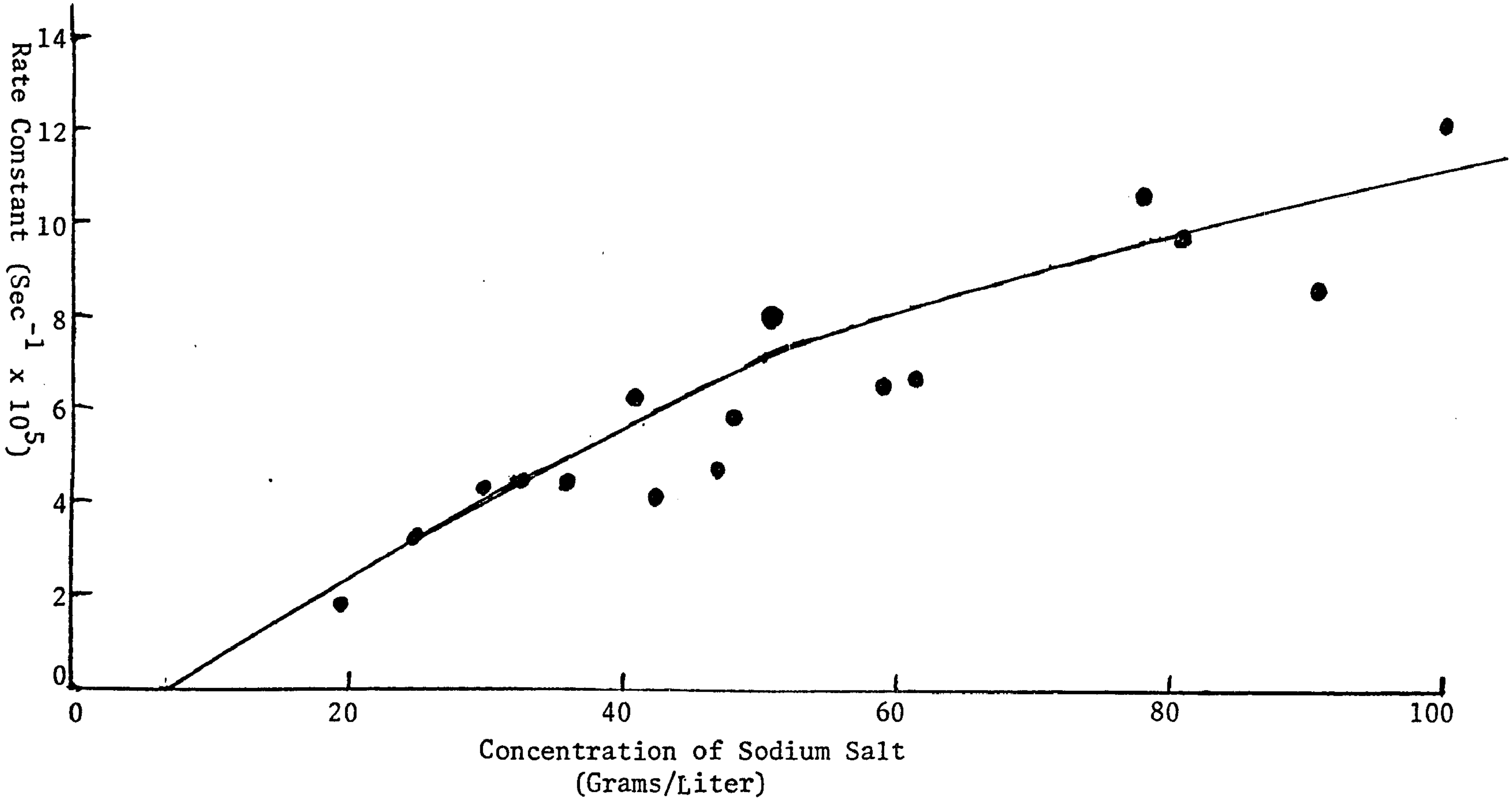


Figure 5. The rate of decomposition of benzyl chloroformate as a function of aluminum salt concentration at 126°C.

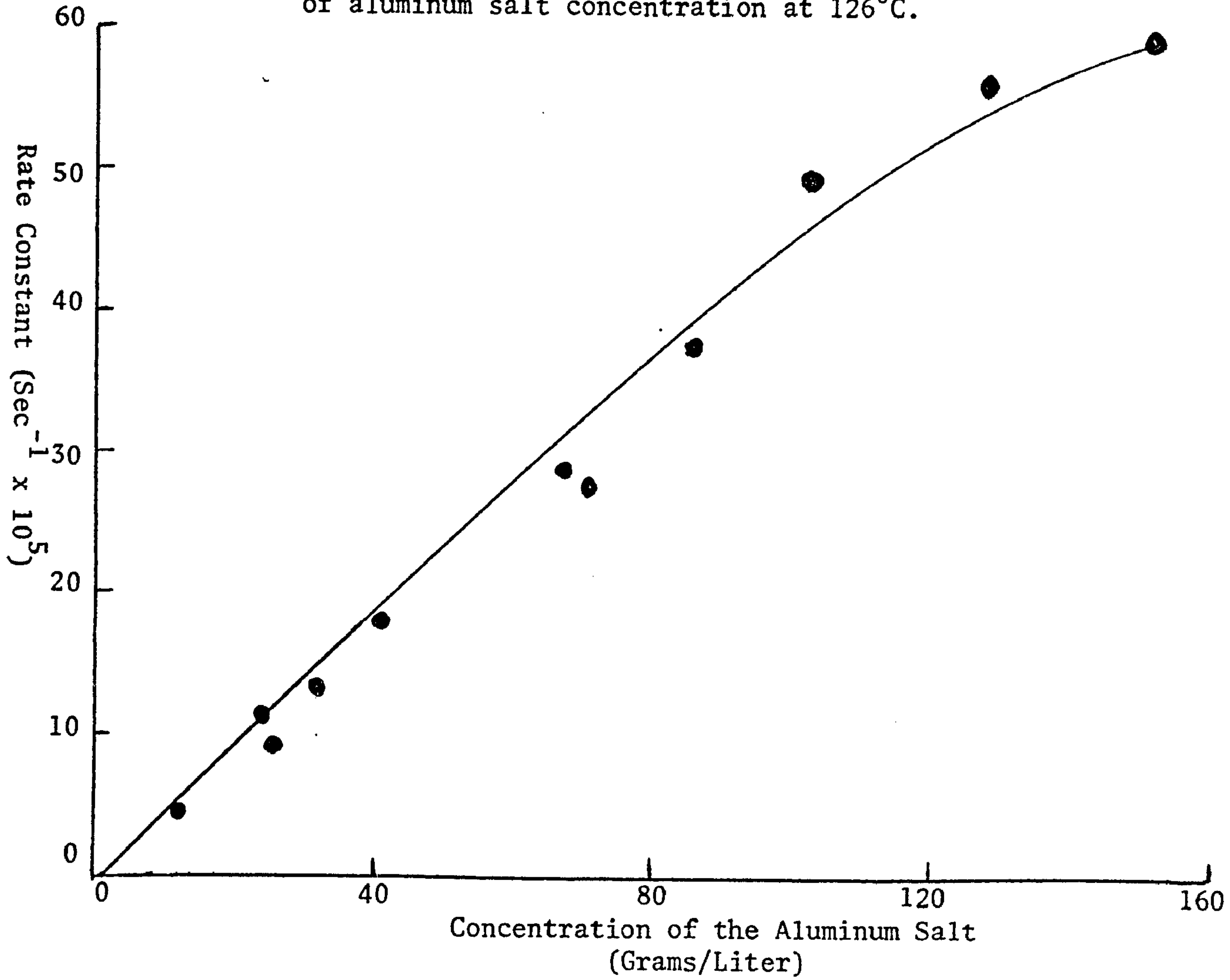


TABLE 5

The Variation of the Catalytic Activity with the Cation

Cation	Acidity	Rate Constant (liters-gram^{-1}-sec^{-1}x 10^6)
Zn^{+2}	0.7	131.
Cr^{+3}	-2.3	6.60
Al^{+3} (from the nitrate)	0.1	5.56
Al^{+3} (from the chloride)	0.7	4.31
Na^{+}	5.3	1.39
Ce^{+3}	3.1	1.04

in the catalytic activity for this reaction. The zinc salt, which is no more acidic than the aluminum salt, gives an order of magnitude higher catalysis, while the cerium salt is a less effective catalyst than the sodium salt. The aluminum salt made from aluminum nitrate was a somewhat more effective catalyst than that made from the chloride. This may be due to the retention of a small amount of chloride ion in the product or to differences in dryness. All the values for the aluminum salt, except the one in Table 5, are for the salt made from the chloride.

For the zinc, cerium, aluminum, and sodium salts the temperature dependences of the rate constants were determined. The results are presented in Table 6 in a form similar to that used in Table 5. Figure 6 is the Arrhenius plots of these values and Table 7 contains the calculated constants from the Arrhenius equation. It is obvious that except for the cerium salt the activation energies are unusually large. The values reported for the activation energies for the decompositions of chloroformates in the literature[40,42] are close to the value observed for the cerium salt. The much larger values for the other three catalysts must indicate a change in the mechanism.

As mentioned in the introduction, Kevill and Weitl[42] proposed two possible mechanisms for this reaction, a cyclic covalent mechanism and an ionic mechanism. It seems probable that in nonpolar solvents the cyclic covalent mechanism predominates and that in view of the similarity in activation energies this is also the

TABLE 6

Temperature Dependence of the Rate Constants for the Decomposition of Benzyl Chloroformate

Catalyst	Temperature	Rate Constant (liters-gram^{-1}-sec^{-1} x 10^6)
Sodium Salt	126	1.39
	116	0.514
	107	0.169
	95	0.055*
Aluminum Salt	126	4.31
	115	1.30
	114	0.99
	108	0.53
	108	0.47
Cerium Salt	126	1.04**
	106	0.27**
Zinc Salt	126	131.
	112	6.55
	104	1.19

* From Marmo[44]

** Average of two points

Figure 6. Arrhenius plots for the catalyzed decompositions of benzyl chloroformate.

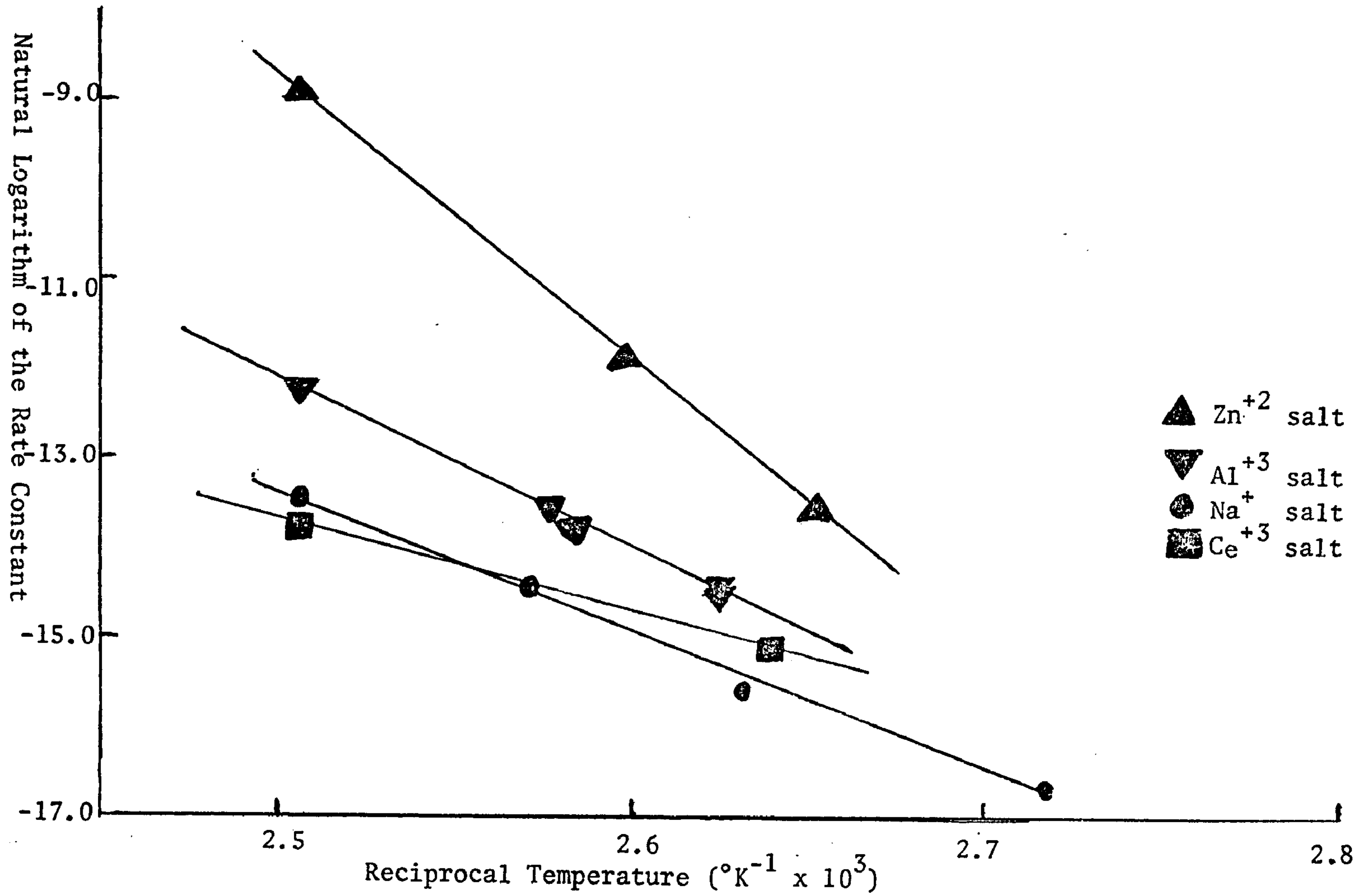


TABLE 7

Activation Parameters for the Decomposition of Benzyl Chloroformate

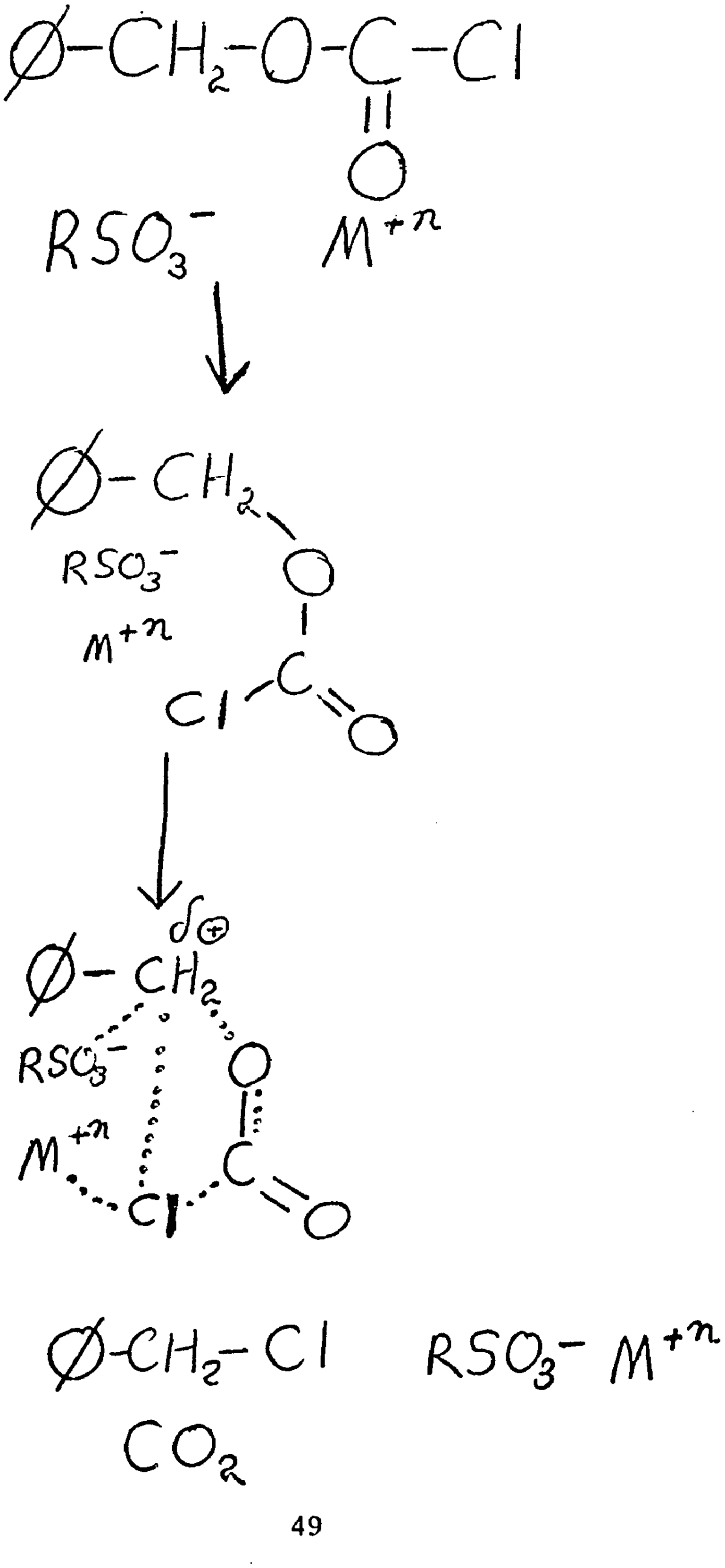
Cation	$\Delta E^{\neq}$ (kjoules/mole)	$\ln A$
Na^+	129±4	25.3±1.2
Al^{+3}	148±7	32.2±2.0
Ce^{+3}	84±4	11.7±1.2
Zn^{+2}	267±4	71.4±1.4

one by which the reaction takes place in the presence of the cerium salt. The much higher activation energies of the reaction when it is catalyzed by the other salts, however, suggests that the ionic character of the transition state is increased. The higher activation energy is reasonable for the ionic mechanism since energy is required to cause the charge separation. The increase in the ionic nature of the transition state can be explained by postulating that the reactant and catalyst interact in the micelle as shown in Figure 7.

The inability of the cerium salt to strongly catalyze the reaction can be explained as being due to its large size which does not allow the sulfonate group and the metal ion both to be close to the reactant molecule at the same time. The balance between the pre-exponential factors and the activation energies is interesting.

If everything else was equal the higher the activation energy the slower the reaction would be, but in this case the pre-exponential factor increases even more quickly. This can be explained by the dependence of the factor on the activation entropy. The higher the activation energy the greater the ionic character of the transition state, and the greater the ionic character of the transition state the freer the carbon dioxide group in the transition state. It appears that the increased freedom of the carbon dioxide group more than balances the greater energy required at the temperatures at which this study was carried out.

Figure 7. Decomposition of benzyl chloroformate proposed mechanism for micellar catalysis.



The differences between the individual cations appear to depend on both their acidity and geometry. Certainly the more strongly positively charged (more acidic) the cation ion is the more strongly it will interact with the partial negative charge on the chloride, but the results show that this is not a sufficient explanation. The proposed mechanism introduces, in addition, a geometric factor which arises from the necessity of having the cation and the sulfonate group simultaneously interact with the reactant molecule. These results are interesting, as they suggest the possibility of studying the internal geometry of the micelles and also give some interesting insight into the mechanism of the reaction.

Diels-Alder Reaction

Before the effects of the catalysts could be determined it was necessary to accurately measure the rate of the uncatalyzed reaction. The results of a typical experiment are shown in Figure 8. The catalyzed runs appeared similar. The uncatalyzed rates at a number of temperatures are presented in Table 8. In Figure 9 the logarithms of the rates are plotted versus the reciprocals of the temperatures. The activation energy calculated from a linear least squares fit of these results is 34.9±1.3 kjoules/mole and the natural logarithm of the Arrhenius pre-exponential term (A) is 9.4±0.4. These values do not agree particularly well with the ones calculated from the values reported by Wassermann;[37] $\Delta E = 48.5 \pm 1.7$, $\ell nA = 15.0 \pm 0.7$. Wassermann's values give rate

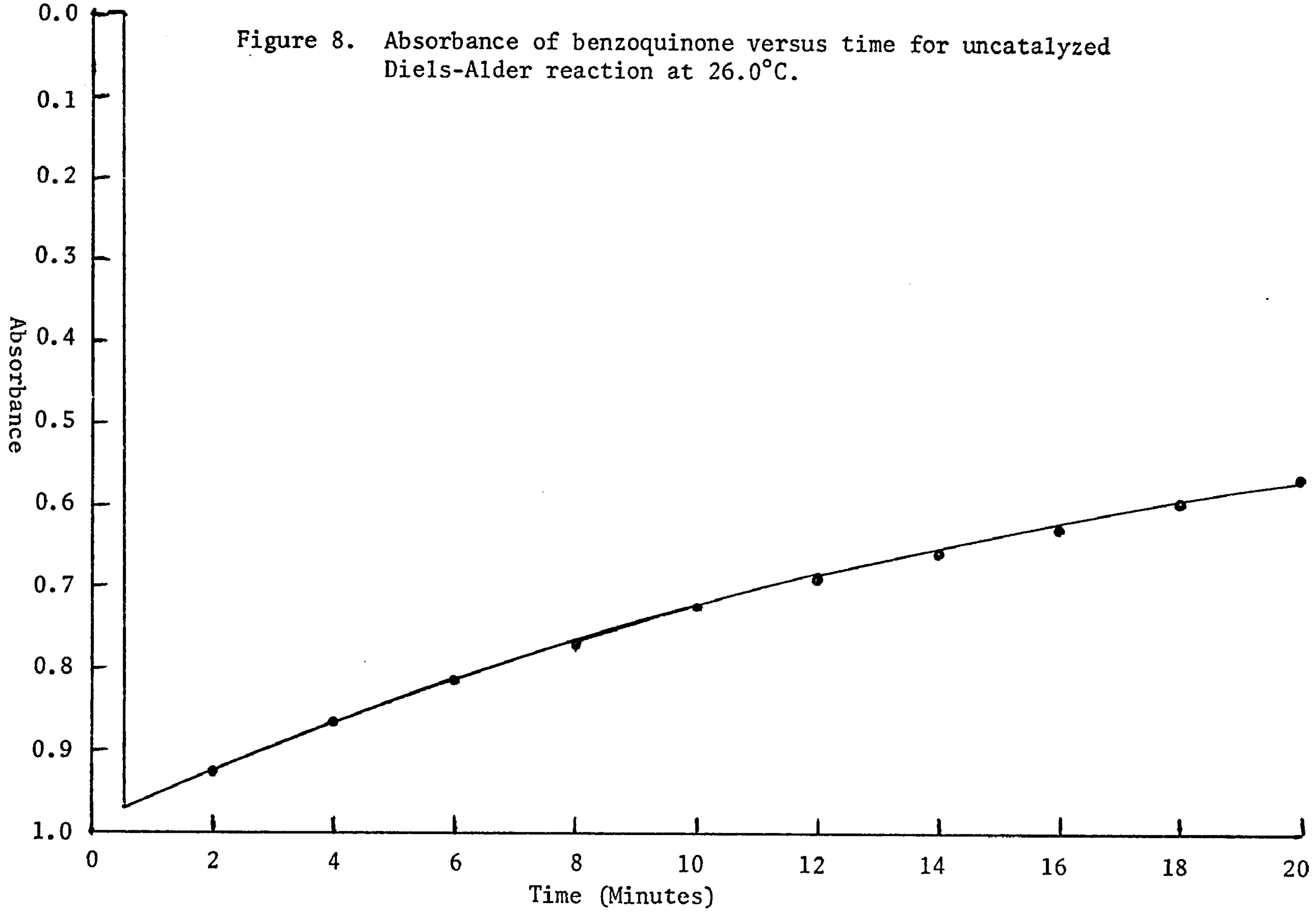


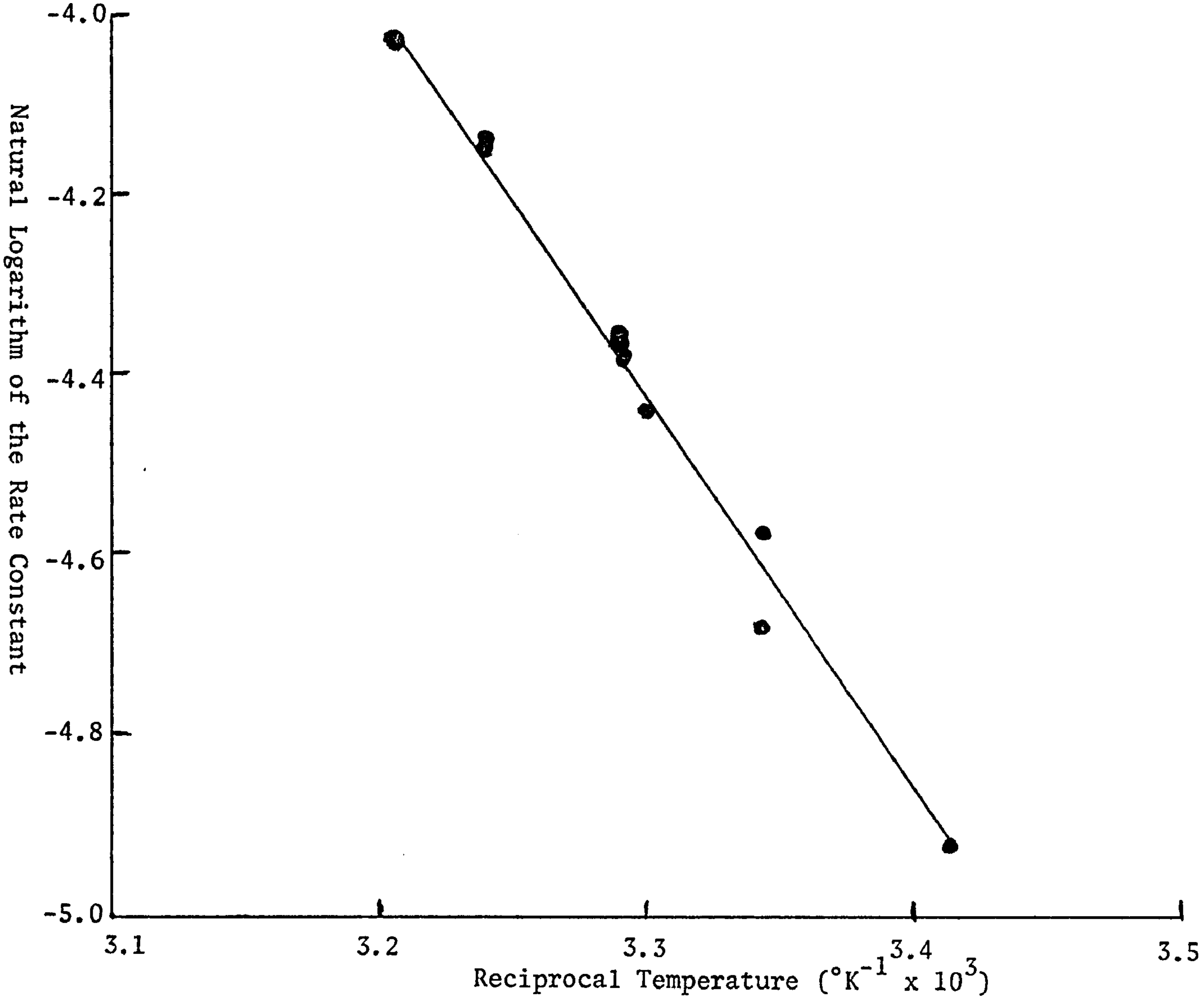
Figure 8. Absorbance of benzoquinone versus time for uncatalyzed Diels-Alder reaction at 26.0°C.

TABLE 8

Rate of the Uncatalyzed Diels-Alder Reaction at Various Temperatures

Temperature °C	Rate (liters-mole^{-1}-sec^{-1} x 10^3)
20.0	7.3
20.0	7.3
26.0	9.3
26.0	10.3
30.0	11.8
30.8	12.5
31.0	12.7
31.0	12.8
35.8	15.8
35.8	16.0
39.8	17.8
39.8	17.8

Figure 9. Arrhenius plot for the uncatalyzed Diels-Alder reaction



constants which agree with the experimental values at 20°C but are 50 percent too large at 39.8°C. The reason for this disagreement is unclear. The measured values were used in all the calculations.

Once the uncatalyzed rates had been determined, the catalytic effectiveness of the surfactants could be determined. The sodium, cerium, and aluminum salts were used to catalyze the reaction, the rates at 30.0°C are presented in Table 9 and plotted in Figures 10, 11, and 12, in terms of the ratio of the total measured rate constant (k_p) from equation 8 and the uncatalyzed rate (k_o). The curves show the characteristics typical of micellar catalysis; i.e., a non-linear dependence of the reaction rate on the catalyst concentration and the existence of a critical micelle concentration.

Values for the critical micelle concentration can be estimated by linearly extrapolating the points at low catalyst concentrations to zero catalysis (i.e. $k_p = k_o$). The values determined and the number of points used are presented in Table 10. Interestingly, if one uses the value for cerium which is obtained from only three points, the values of the intercepts are approximately equal. The cerium value, however, is very dependent on the number of points taken, due to the large amount of scatter in the cerium results. The results, considering the inaccuracy of the extrapolations used to determine them, are in reasonably good agreement with the values of Muto and Meguro.[15]

The large amount of scatter in the values appears to be due to variations in the catalyst activity rather than inaccuracies

TABLE 9

The Effect of Catalyst Concentration on the Rate of the Diels-Alder Reaction at 30.0°C

Aluminum Salt

Concentration (grams/liter)	Rate Constant Ratio
4.50	1.07
4.75	1.11
7.75	1.28
10.95	1.30
10.95	1.38
14.00	1.24
15.35	1.37
16.70	1.65
16.90	1.69
17.40	1.41
23.60	1.62
24.70	1.87
26.60	1.52
27.20	1.54
27.55	1.87
28.40	1.92
28.60	1.83
32.60	1.70
36.10	1.69
39.50	2.10
40.20	1.86
40.45	1.76
44.70	2.18

Cerium Salt

Concentration (grams/liter)	Rate Constant Ratio
3.10	1.04
5.10	1.18
7.55	1.28
9.25	1.32
9.30	1.20
10.15	1.21
10.80	1.34
11.10	1.18
13.40	1.25
13.45	1.31
14.35	1.55
15.30	1.28

TABLE 9 (Continued)

Cerium Salt (Continued)

Concentration (grams/liter)	Rate Constant Ratio
15.60	1.65
15.95	1.52
16.75	1.21
20.15	1.52
20.50	1.44
24.60	1.48
27.45	1.45
29.10	1.72
34.70	1.44
35.60	1.54
40.50	1.76
45.40	1.69

Sodium Salt - Batch 1

Concentration (grams/liter)	Rate Constant Ratio
7.60	1.10
9.95	1.08
11.20	1.13
15.45	1.18
17.00	1.25
17.70	1.18
19.75	1.25
21.80	1.34
22.85	1.31
26.00	1.21
28.55	1.25
32.65	1.30
35.60	1.17
49.00	1.37

TABLE 9 (Continued)

Sodium Salt - Batch II

Concentration (grams/liter)	Rate Constant Ratio
18.70	0.93
23.05	0.85
30.70	0.99

Sodium Salt - Batch III

Concentration (grams/liter)	Rate Constant Ratio
22.25	1.04
27.45	1.08
27.45	1.11
39.95	1.01
41.05	1.12
45.95	1.11
49.25	1.11

Figure 10. The rate of the Diels-Alder reaction as a function of sodium salt concentration at 30°C.

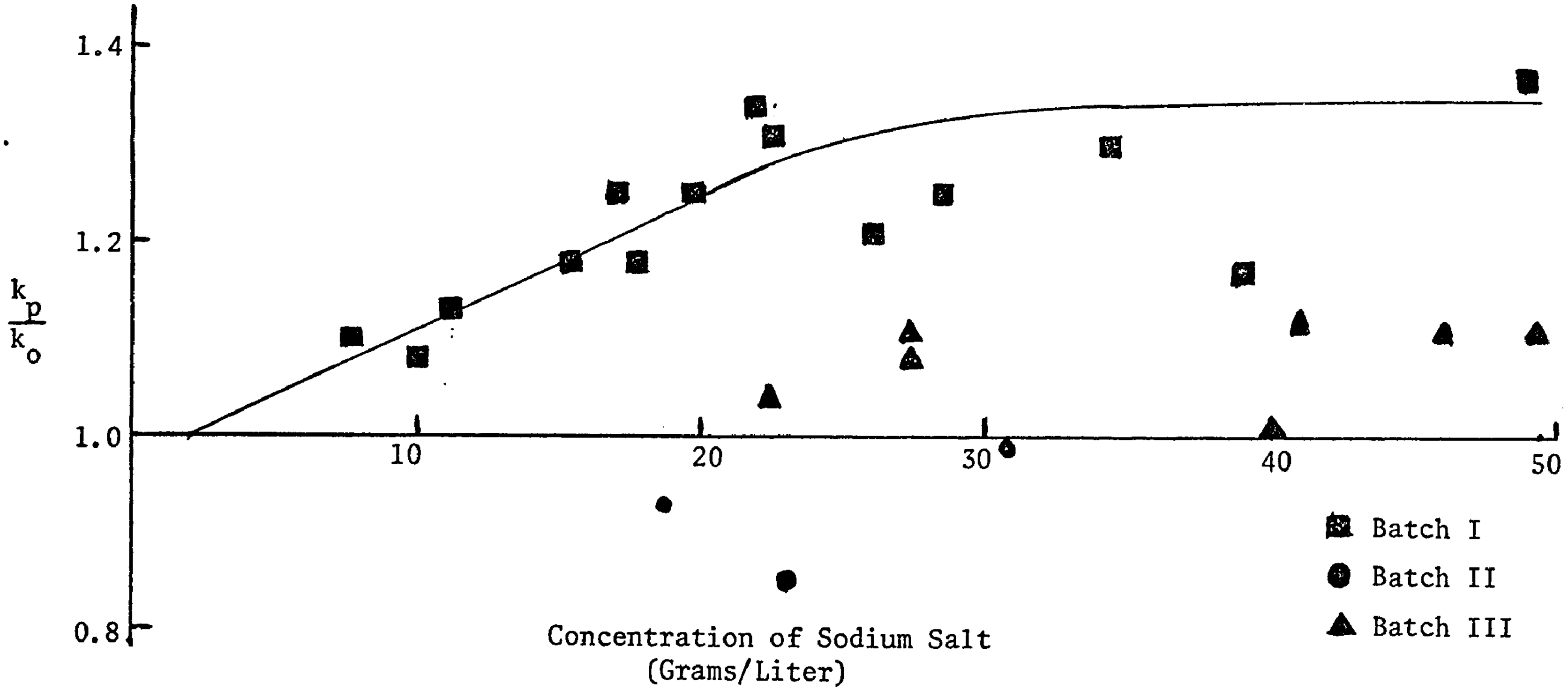


Figure 11. The rate of the Diels-Alder reaction as a function of cerium salt concentrations at 30°C.

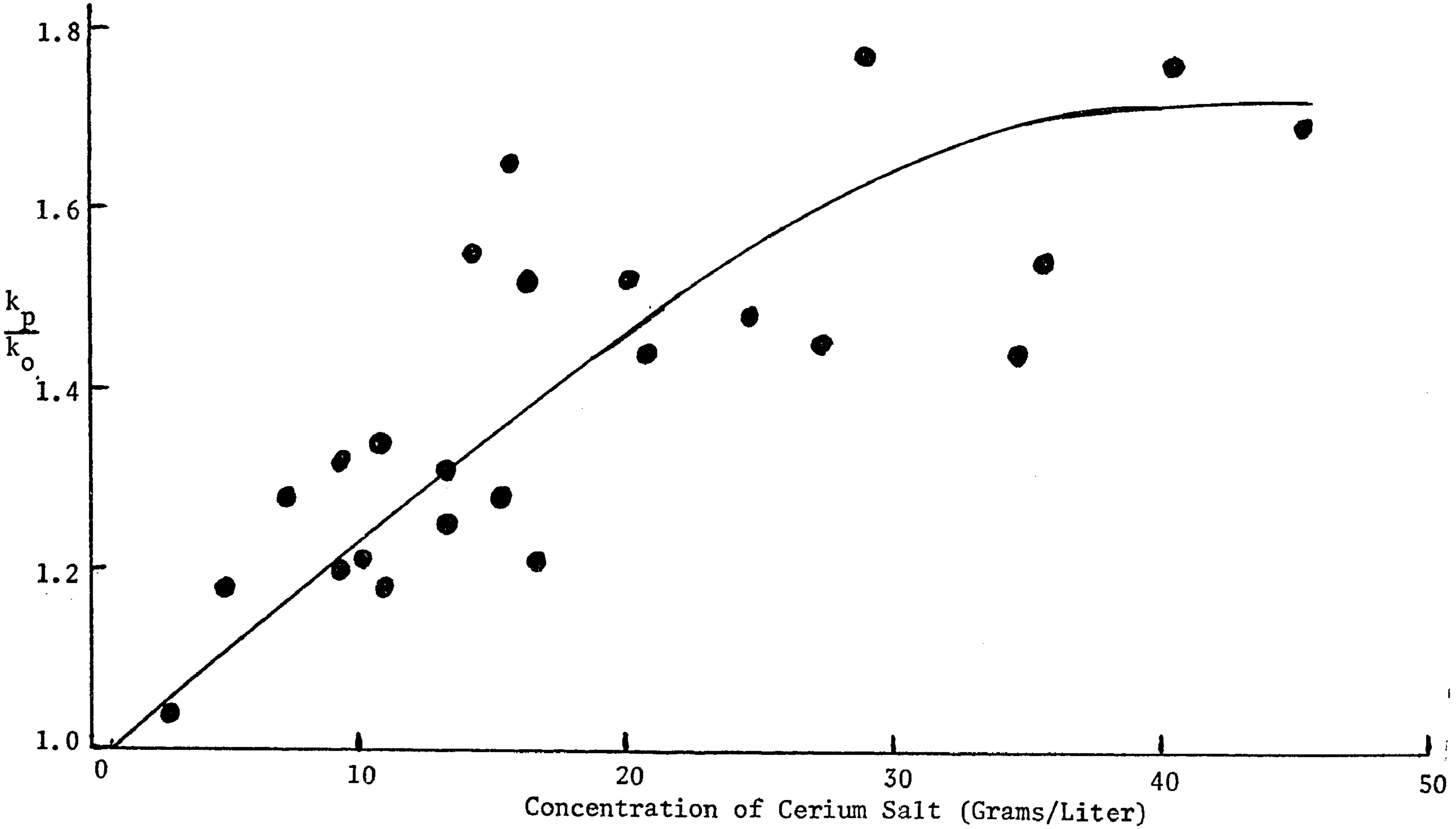
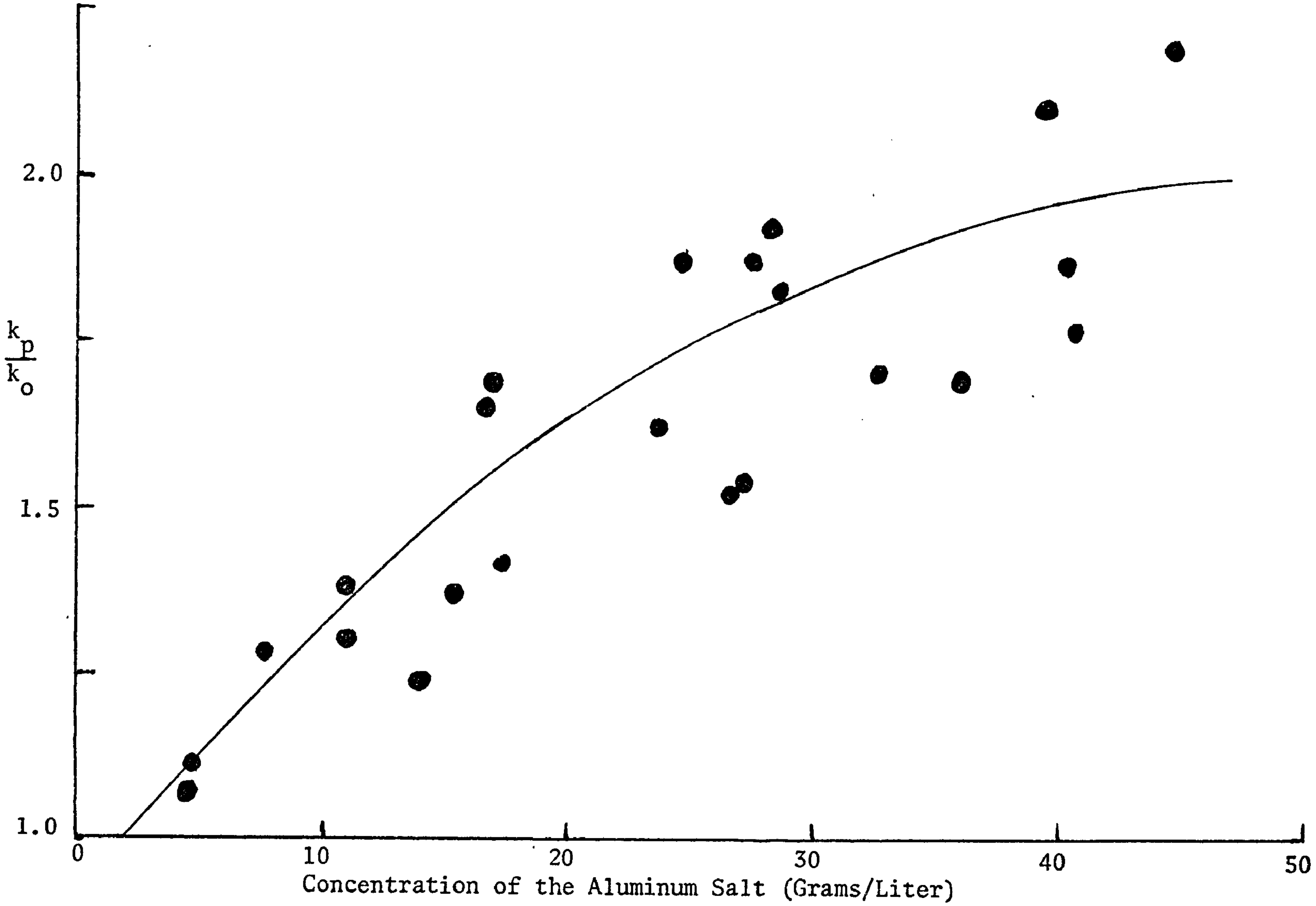


Figure 12. The rate of the Diels-Alder reaction at various aluminum, salt concentrations at 30°C.



in the measured rates themselves. This is indicated, for instance, by the sodium results. One bottle of catalyst (squares) catalyzed the reaction, samples from another bottle from the same source (circles) inhibited it and a third sample (triangles) gave intermediate results. Similar variations were observed between different batches of the other salts. In general, samples from the same batch gave results which agreed with each other more closely than with those obtained with samples from different batches. This can be attributed to variations in purity and dryness from batch to batch. Table 11 shows the results of attempting to study the variation of the amount of catalysis with temperature for the aluminum salt. The rates are expressed as the increase over the uncatalyzed rate ($k_p - k_o$) because, of course, the ratio k_p/k_o depends on the value of k_o, which changes with temperature. While the large scatter in the values makes analysis difficult, it appears that, similarly to the literature results for trichloroacetic acid discussed in the introduction,[39] the activation energy of the catalyzed reaction is close to zero. If one takes the average value of k_p/k_o at the aluminum salt concentration of 25 grams/liter to be 1.75 and assumes as an approximation that the uncatalyzed rate is independent of the presence of the catalyst; then the catalyzed rate is 0.46 liters^2-mole^{-2}-sec^{-1}. If in addition, however, one takes into account the fact that the surfactant is present in the form of micelles with an aggregation number of about 15, then the rate becomes 6.9 liters^2-mole^{-2}-sec^{-1}

TABLE 10

Critical Micelle Concentrations for the Diels-Alder Reaction System at 30°C

Catalyst	Number of Points	CMC (grams/liter)
Aluminum Salt	5	2.0
Cerium Salt	3	2.1
Cerium Salt	5	0.8
Sodium Salt	7	1.9
Sodium Salt	Ref. 15 (20°C)	1.1

TABLE 11

Variation of the Catalysis with Temperature of the Diels-Alder Reaction by the Aluminum Salt

Catalyst Concentration (grams/liter)	Temperature	$k_p - k_o$
10.30	20.3°C	0.20
10.30	25.0°C	0.16
10.30	30.0°C	0.27
12.30	20.5°C	0.16
12.45	29.8°C	0.24
12.35	34.5°C	0.25
12.35	38.9°C	0.18
12.30	39.0°C	0.25

where the rate expression now contains the concentration of micelles. This rough value is twice as large as the rate constant for catalysis by trichloroacetic acid. Since the aluminum salt catalyzes the reaction even more strongly than the trichloroacetic acid, the zero activation is not unreasonable.

The catalytic effectivenesses of the salts correlate well with their acidities (see Table 15), the more acidic aluminum salt catalyzing the reaction the most and the less acidic sodium salt catalyzing it least. In addition, the batch of the sodium salt which catalyzed the reaction was measurably more acidic than the one which did not. This indicates that for this reaction the catalyst's acidity is a very important factor.

The acidity of the aluminum salt could be notably increased by heating it under vacuum. The salt lost weight on heating and the results suggest that some of the water of hydration of the aluminum was being removed. After this treatment the catalyst was super-active. Some typical results are given in Table 12, but the results were very difficult to reproduce. In addition, while for the untreated catalyst the possible side reactions were insignificant, this was not true for the more active heated catalyst. Apparently the catalyst was causing the reaction of cyclopentadiene and oxygen to form cyclopentadienone and water, which is normally very slow, to become very rapid. The cyclopentadienone then reacted with the other materials in the solution to form a complicated mixture. Bubbling nitrogen through the solution reduced the amount of oxidation but did not prevent it. No further study of the heated catalyst was carried out.

These results indicated that the water content of the solution could affect the reaction rate considerably. To confirm this three identical samples of aluminum salt were treated in three different ways and the results compared, at a concentration of 10.25 grams/liter. One sample was treated in the normal way, one was dried gently by vacuum at about 40°C, and the third was dissolved in benzene saturated with water. The results are in Table 13. This confirms that the amount of water in the system is a critical factor, but does not unfortunately give any way of controlling it reproducibly.

In this reaction the effectiveness of the micellar catalysis is primarily dependent on the acidity and any property which can affect the the effective acidity, such as the water concentration, will affect the catalytic activity.

Catalyst Properties

The pKs and molar absorptivities of the indicators used to determine the catalyst acidities are summarized in Table 14. The acidities of the catalysts are summarized in Table 15. The considerable difference in the two batches of the sodium salt is noteworthy. The lack of a value for the absorbance of the acid form of 1,9-diphenyl-1,3,6,8-nonatetraen-5-one and a consequent larger inaccuracy in the value for the chromium salt is due to the fact that the dibutylphosphate would not convert the indicator

TABLE 12

Effect of Heating on the Catalytic Ability of the Aluminum Salt

Concentration (grams/liter)	Heat Treatment	Temperature of the Reaction	k_p/k_o
17.25	107°C for 20 min.	30.4°C	2.23
14.75	85°C for 30 min.	30.4°C	1.93
14.40	107°C for 1 hr.	30.4°C	3.20
15.95	107°C for 1 hr.	30.4°C	3.27
16.60	113°C for 50 min.	32.0°C	2.73
19.05	112°C for 1 hr.	32.0°C	2.18

TABLE 13

Effect of Water on the Rate of the Diels-Alder Reaction

Treatment	k_p/k_o
Mild drying	1.86
Normal	1.36
Wet Benzene	1.24

to its acid form and so the acid absorbance could not be measured. Owing to the unfortunate fact that many of the acidities fall more or less on the border between two indicators, some of the other values are also less accurate than is desirable but they are sufficient to give a general order.

The vapor pressure osmometry results are summarized in Table 16. These results confirm that these materials do aggregate at elevated temperatures and supports the belief that the catalysis of the benzyl chloroformate decomposition is micellar.

The differential thermal analysis of a sample of the cerium salt showed that at approximately 68°C the sample began to lose water and did so continuously until it decomposed. This indicates that it is probably not possible to dry the catalyst samples reproducibly. This means that it is probably impossible to achieve good reproducability of catalysis for the Diels-Alder reaction.

TABLE 14

Indicator Properties

Indicator	pK	Wavelength (nm)	Molar Absorbtivity Base Form	Acid Form
4-phenylazodiphenylamine	1.5	400	2.88×10^4	-
		544	-	5.77×10^4
N,N-dimethyl-p-phenylazoaniline	3.3	410	2.65×10^4	960
		458	9.22×10^3	9.22×10^3
		520	1536	3.571×10^4
4-phenylazo-1-naphthylamine	4.0	425	2.176×10^4	-
		540	-	4.311×10^4
1,9-diphenyl-1,3,6,8-nonatetraen-5-one	-3.0	378	1.80×10^5	-

pK's are from reference 48

TABLE 15

Acidities of Catalysts

Catalyst	Indicator	Ho
Aluminum Salt	4-phenylazodiphenylamine	0.6,0.7
Zinc Salt	4-phenylazodiphenylamine	0.7,0.9
Cerium Salt	N,N-dimethyl-p-phenylazoaniline	3.1
Chromium Salt	1,9-diphenyl-1,3,6,8-nonatetraen-5-one	-2.3
Sodium Salt (Batch 1)	4-phenylazo-1-naphthylamine	5.3
Sodium Salt (Batch 2)	4-phenylazo-1-naphthylamine	6.2
Heated Aluminum Salt	1,9-diphenyl-1,3,6,8-nonatetraen-5-one	<-3.0

TABLE 16

Micelle Sizes in Decane at 75°C

Catalyst	Aggregation Number (# of sulfosuccinate groups)
Aluminum Salt	6
Cerium Salt	9
Sodium Salt	12

CONCLUSIONS

The most important result of this work is the demonstration of micellar catalysis by the metal salts of bis(2-ethylhexyl) succinate sulfonic acid over a wide range of temperatures. The experiments reported in the literature are limited almost entirely to the vicinity of room temperature. This work, however, demonstrates that micellar catalysis is possible even at much higher temperatures.

The strongest evidence that the reactions are catalyzed by micelles is the existence of critical concentrations for catalysis which can be identified with the critical micelle concentrations. The values from the Diels-Alder reaction agree well with values from the literature which were determined under similar conditions.

The vapor pressure osmometric measurements (which confirm the existence of micelles at 75°C) and the existence of the critical micelle concentrations confirm that, despite the elevated temperature, the benzyl chloroformate decomposition is catalyzed by the surfactant micelles.

The dependence of the reaction rates of both reactions on catalyst concentration appears to be consistent with the type of saturation kinetics discussed in the introduction. In neither case, however, was it possible to evaluate the constants which make up the equations. In the case of the benzyl chloroformate decomposition, this was owing to the impossibility of attaining catalyst concentrations sufficient to make the term K[M], which is the number of micelles containing solubilized reactant, much larger than one. For a reaction such as this one, for which k_o is small, when K[M] is much greater than one, k_ψ is independent of concentration and equal to k_c. Given k_c, K[M] can easily be determined. Since the Diels-Alder reaction has two solubilized reactants, the rate law becomes far more complicated than for a unimolecular reaction. The exact form of the rate law is uncertain because the solubilization of the two reactants cannot be assumed to be independent.

When comparing the effectiveness of the catalysts, it is important to take into account the fact that the number of micelles per gram of catalyst will vary from salt to salt -- depending on the aggregation number. For these reactions this is not an important variable. Under the conditions which were used for the Diels-Alder reaction the micellar weight is relatively independent of the cation (see Table 1), and under those used for the benzyl chloroformate reaction the variation is at most a factor of two (see Table 16) which is too little to affect the qualitative results.

The catalytic effect of the micelles can be divided into two parts. One factor is the increased concentration of the reactant in the micelles which for the unimolecular saturation kinetics is contained in the term K[M]. The other factor is the increased rate constant ($k_c > k_o$) in the micelles. Both the factors should depend on the acidity. The solubilization should because it is an acid-base interaction and the rate in the micelles should because the reactions are acid catalyzed.

While both reactions are acid catalyzed, another factor must affect the catalytic abilities of the metal salts for the benzyl chloroformate reaction. This is clear from the observation that order of catalytic strength is $\mathrm{Zn}^{+2}>>\mathrm{Cr}^{+3}>\mathrm{Al}^{+3}>\mathrm{Na}^{+}>\mathrm{Ce}^{+3}$ while the order of acidities is $\mathrm{Cr}^{+3}<\mathrm{Al}^{+3}\leq\mathrm{Zn}^{+2}<\mathrm{Ce}^{+3}<\mathrm{Na}^{+}$. This other factor presumably depends on the structure of the micelle.

The micelle, also, appears to affect the mechanism of the benzyl chloroformate decomposition. For several salts unusually large activation energies were determined. Despite these large values the reactions were quite rapid owing to the exceptionally large pre-exponential factors. These activation energies, which are far larger than those observed for chloroformate decompositions in bulk solvent, indicate that the mechanism of reaction has changed in the micelles.

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