The ^{15}N nmr shift for $^{15}NH_3$ dissolved in CCl_4 is especially interesting in that it coincides almost exactly with the ^{15}N shift in pure liquid ammonia and is essentially independent of solution composition. This would suggest that either the $^{15}NH_3$ molecules dissolved in CCl_4 tend to remain in aggregates with structures similar to those in pure liquid ammonia (even down to 2 mole % NH_3 in CCl_4) or that the interaction between an $^{15}NH_3$ molecule and surrounding CCl_4 molecules produces an ^{15}N shift (relative to gaseous $^{15}NH_3$) of almost exactly the same magnitude as that due to hydrogen bonding between ammonia molecules in pure liquid ammonia. The fact that the proton shifts in the $^{15}NH_3$–CCl_4 system move to significantly higher fields (relative to liquid $^{15}NH_3$) with decreasing $^{15}NH_3$ concentration indicates that the liquid ammonia structure is being broken. We would thus conclude that the interaction of $^{15}NH_3$ with CCl_4 produces a rather large downfield shift of the ^{15}N resonance. In terms of our model, an interaction between the nitrogen lone-pair electrons and the CCl_4 molecule contibutes $\sigma_{A_{CCl_4}}$ to the ^{15}N shift where $\sigma_{A_{CCl_4}}$ is negative and comparable in absolute magnitude to $\sigma_{A_{NH}}$. Clearly $\sigma_{A_{CCl_4}}$ represents a sizable shift which cannot be ascribed to hydrogen bonding. If we assume that the interaction is of the dipole-induced dipole type, the magnitude of $\sigma_{A_{CCl_4}}$ may be attributable to the large polarizability of the C–Cl bond (four times as large as for the C–H bond) or of the CCl_4 molecule as a whole. This interpretation is, however, purely speculative and other self-consistent interpretations of the experimental observations could, no doubt, be given. In any case, it seems probable that $^{15}NH_3$–solvent interactions other than hydrogen bonding may produce large shifts of the ^{15}N resonance. If this is so, the ^{15}N shift as a measure of hydrogen bonding in amine systems may be of limited utility.

Microcalorimetry. Thermodynamics of the Reaction of an Anionic Detergent with a Cationic Detergent[1]

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Abstract: The heat of reaction of sodium dodecyl sulfate and cetylpyridinium chloride was measured at 37° with a Beckman microcalorimeter. The critical micelle concentration of each detergent was determined in distilled water, 0.0001 *M* NaCl, and 0.145 *M* NaCl, and heats of dilution were measured at several concentrations of each detergent. In all but two cases, this heat of dilution was a composite including the dilution of monomers, the dilution of micelles, and the heat of micellization. Since the product micellizes, the enthalpy reported includes the $\Delta H°$ of interaction plus the $\Delta H°$ of the mixed micelle formation. Two approaches were used in an attempt to interpret the data. The first disregarded the micellization of the product, giving rise to a $\Delta H°$ of ~-18 kcal/mol, an equilibrium constant of 2×10^6, a $\Delta G°$ of ~-9 kcal/mol, and a $\Delta S°$ of ~-30 eu. The second considered the micellized products as a pseudophase and the unmicellized portion as having constant activity. In this instance, an equilibrium constant of $\sim 3 \times 10^{10}$, a $\Delta G°$ of ~-15 kcal/mol, and a $\Delta S°$ of ~-11 eu were obtained. The $\Delta H°$ is the same in both cases. These results are discussed in terms of the nature of the product and precipitate, effect of pH, and the plausibility of the thermodynamic parameters.

This paper describes an attempt to extend the thermodynamic treatment of microcalorimetric data to reactions of the general type $A + B \rightleftharpoons C$. Similar work has already been described by Benzinger[2] for other systems. This system is of interest because certain biological reactions are of this type. It was hoped that this study could serve as an entree to the investigation of such biological interactions.

The use of oppositely charged detergents as reactants was suggested by the paper of vanOss.[3] He demonstrated the reaction by precipitation in an agar double diffusion study.

Although the reaction of charged detergents with one another has been utilized in analytical titrations for some time,[4] there appears to have been little work directed toward the definition of the reaction parameters and the nature of the product. Scowen and Leja[5] have studied the product spectroscopically, and Hua and Chao[6] have measured the surface activity of mixed detergent micelles. Letsinger and Wagner[7] used an anionic detergent to counter the supressor activity of a cationic detergent in a hydrolysis reaction.

In this paper, measurements of the heat evolved during the interaction of sodium dodecyl sulfate (DSS) and cetylpyridinium chloride[8] (CPC) are described. The reaction is expected to be of the type $A + B \rightleftharpoons C$, but complicated by aggregation of the monomers and the product.

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(1) Presented in part at the 2nd Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., 1968, and at the 23rd Annual Calorimetry Conference, Midland, Mich., 1968.

(2) T. H. Benzinger, *Proc. Natl. Acad. Sci. U. S.*, **42**, 109 (1956).

(3) C. J. vanOss and Y. S. L. Heck, *Z. Immunitaetsforsch.*, **122**, 44 (1961).

(4) W. B. Smith, *Analyst*, **84**, 77 (1959).

(5) R. V. Scowen and J. Leja, *Can. J. Chem.*, **45**, 2821 (1967).

(6) H. Hua and K. Chao, *Chem. Abstr.*, **62**, 7146*b* (1965).

(7) R. L. Letsinger and T. E. Wagner, *J. Am. Chem. Soc.*, **88**, 2062 (1966).

(8) 1-Hexadecylpyridinium chloride.

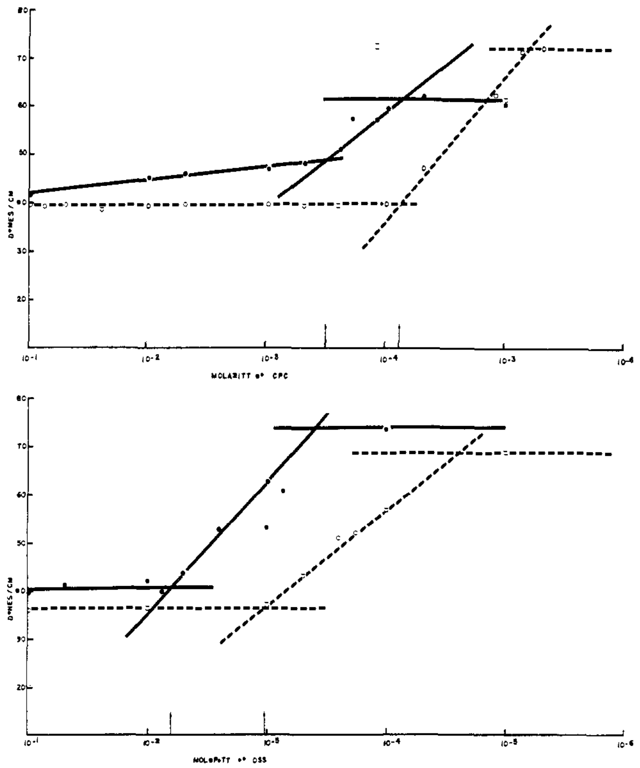

Figure 1. Surface tension as a function of molarity at 37°: solid circles and solid lines, 0.0001 *M* NaCl; open circles and dashed lines, 0.145 *M* NaCl. Arrows indicate cmc's.

Experimental Section

Materials. The detergents used in this study were cetylpyridinium chloride and sodium dodecyl sulfate obtained from Eastman Organic Chemicals. Cetylpyridinium chloride was recrystallized three times, and the two detergents were then dried in an evacuated drying pistol at 56°. A Paar sulfur determination was run on sodium dodecyl sulfate. *Anal.* Calcd for $C_{12}H_{25}NaO_4S$: S, 11.12. Found: S, 11.47. The nitrogen in cetylpyridinium chloride was determined by titration with acetic acid in the presence of mercuric acetate. *Anal.* Calcd for $C_{21}H_{38}ClN \cdot H_2O$: N, 3.91. Found: N, 3.92. Differential thermal analysis and thermogravimetric analysis of sodium dodecyl sulfate indicated 0.5% of a volatile impurity, presumably water. The same two analyses performed on cetylpyridinium chloride indicated 1 mole of water was present. The character of the surface tension *vs.* log concentration curves (Figure 1) also indicated both detergents were reasonably pure.

All other chemicals were reagent grade. Distilled, deionized water was used.

Calorimetry. Calorimetric measurements were made in a Beckman 190B microcalorimeter. It is a differential isothermal calorimeter patterned after the design of Benzinger.[9]

The calibration of the instrument was checked by measuring the heat evolved when 2.00 μmol of hydrochloric acid was neutralized with excess base in "drop" cells. Our results for this measurement were within 3% of the accepted value. The calibration is described by Benzinger.[9] In a typical run (Figure 2), 0.20 ml of a solution containing 0.10–10.0 μmol of sodium dodecyl sulfate was placed in the smaller well of each cell and 15.0 ml of a solution containing 1.00 μmol of cetylpyridinium chloride was placed in the reaction cell. The blank cell contained 15.0 ml of solvent. After the two vessels had reached thermal equilibrium (minimum of 30 min), the solutions were mixed by rotation of the calorimeter. After thermal equilibrium was reestablished, the cell was again rotated. This process was then repeated until small reproducible mixing spikes were obtained (see Figure 2). The mixing spikes measure the thermal disturbances which result from the mixing rotation and occur even when only pure solvent is present. These small values are averaged and subtracted from the heat measured. In most cases, two rotations served to complete the reaction (maximum time 1 hr).

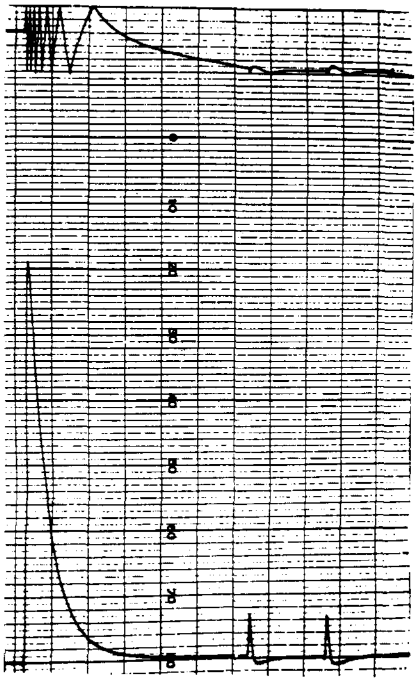

Figure 2. Typical run on the microcalorimeter. The lower curve is the plot of temperature difference *vs.* time, with two mixing spikes. The upper curve is the Disc integrator curve. The value of the heat spike is 10.4 mcal and the mixing spikes are essentially zero.

The values of the mixing spikes and the base-line shift were used to correct the integrated area under the curve. Where the value of the base-line shift correction exceeded 10% of the total, the run was discarded.

The microcalorimeter is equipped with an environmental chamber which maintains the temperature to within ±0.2° of the desired temperature, in this case 37°.

Critical Micelle Concentration (cmc). The cmc's were inferred from the plot of surface tension *vs.* log concentration. Surface tensions were measured using a duNouy tensiometer in a room maintained at 37°.

Calculations. In an attempt to calculate the equilibrium constant (K), it was assumed (as Benzinger[2]) that the amount of heat (Q) is proportional to the amount of product formed (c). Thus

$$c = kQ \tag{1}$$

where k is a constant whose value depends on the reaction. Assuming the reaction is as shown in eq 2, and neglecting the micellization

$$\text{DSS} + \text{CPC} \rightleftharpoons \text{DSS–CPC} \tag{2}$$

of the product, the equilibrium constant can be written as in eq 3 where a is the initial concentration of sodium dodecyl sulfate and b

$$K = \frac{kQ}{(a - kQ)\,b - kQ)} \tag{3}$$

the initial concentration of cetylpyridinium chloride.[10]

The constant k can be evaluated using eq 4. This was done using

$$\frac{kQ_1}{(a_1 - kQ_1)(b_1 - kQ_1)} = \frac{kQ_2}{(a_2 - kQ_2)(b_2 - kQ_2)} \tag{4}$$

all possible pairs of heats from Table II. All calculations were corrected for the mole of water present in the cetylpyridinium chloride. The reaction can be mathematically evaluated using a second approach in which the micellized product is regarded as a

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[9] T. H. Benzinger and C. Kitzinger in "Temperature—Its Measurement and Control in Science and Industry," Reinhold Publishing Corp., New York, N. Y., 1963 p 43.

[10] The activities were assumed to be equal to concentration for the concentrations used. This assumption is reasonable in the case of sodium dodecyl sulfate, the activities of which have been determined by E. J. Clayfield and J. B. Matthews, *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957,* **1**, 172 (1957).

Table I. Checkerboard Diagram Showing Precipitation as a Function of Concentration[a]

	CPC, M				
DSS, M	1×10^{-2}	5×10^{-3}	2.5×10^{-3}	1.2×10^{-3}	6.2×10^{-4}
1×10^{-2}	4100	1400	390	100	27
5×10^{-3}	400	3100	820	230	45
2.5×10^{-3}	190	370	1200	370	140
1.2×10^{-3}	46	80	300	600	220
6.2×10^{-4}	12	25	60	130	270

[a] The solvent was 0.0001 M NaCl. The numbers represent the quantity of light which was seen at 90°.

Table II. Heats of Reaction[a]

	1 μmol of CPC						1 μmol of DSS					
	0.0001 M NaCl			0.145 M NaCl			0.0001 M NaCl			0.145 M NaCl		
μmol	Measd	Corr	Heat of reaction	Measd	Corr	Heat of reaction	Measd	Corr	Heat of reaction	Measd	Corr	Heat of reaction
0.10	−1.66		−1.66	−1.76		−1.76	−2.01		−2.01	+0.21		+0.21
0.25	−4.53		−4.53	−3.01		−3.01	−3.85		−3.85	−2.52		−2.52
0.50	−9.77		−9.77	−7.64		−7.64	−9.31		−9.31	−3.64		−3.64
0.75	−14.10		−14.10	−13.29		−13.29	−13.45		−13.45	−10.97		−10.97
1.00	−17.58		−17.58	−15.34		−15.34	−16.86		−16.86	−15.32		−15.32
1.50	−17.91	+0.46	−18.37	−10.73	+2.25	−12.98	−20.90	0	−20.90	−16.89		
2.00	−17.21	+0.28	−17.49	−10.98	+9.24	−20.22	−21.64	+0.32	−21.96	−16.76		
10.0	−16.40	+3.18	−19.58	−11.90			−22.41	+1.04	−23.45	−9.21		

[a] Above 1 μmol corrected by allowing an equimolar mixture of detergents to interact with that excess above 1 μmol. Because of the values of the cmc, some of these in saline were not done. All values are in mcal. Quantity of CPC used was not corrected for the 1 mole of water.

Table III. Heats of Dilution in Each Solvent System[a]

Detergent,	CPC in 0.145 M NaCl		CPC in 0.0001 M NaCl		DSS in 0.145 M NaCl		DSS in 0.0001 M NaCl	
μmol	mcal	kcal/mol	mcal	kcal/mol	mcal	kcal/mol	mcal	kcal/mol
1.00	+1.59	+1.59	+4.31	+4.31	+1.14	+1.14	+0.01	[+0.01]
2.00	+2.47	(+1.23)	+6.10	+3.05	+2.11	+1.05	−0.12	−0.06
10.0	+2.64	(+0.26)	+29.30	(+2.93)	+23.52	+2.35	+13.90	+1.39
15.0	+3.95	(+0.26)	+41.70	(+2.78)	+28.91	(+1.92)	+22.30	+1.48

[a] The quantity of CPC has been corrected for the mole of water present. The values in parentheses were above the cmc both before and after dilution, while the value in brackets was below the cmc both before and after dilution.

pseudophase with the unmicellized product at a constant activity. The solubility product-like constant (K') can then be expressed as in

$$K' = \frac{1}{(a - kQ)(b - kQ)} \tag{5}$$

eq 5, and the constant of proportionality calculated using eq 6.

$$\frac{1}{(a_1 - kQ_1)(b_1 - kQ_1)} = \frac{1}{(a_2 - kQ_2)(b_2 - kQ_2)} \tag{6}$$

Precipitation. A precipitation titration was performed using a series of twofold dilutions of each detergent as shown in Table I. Each tube contained equal quantities of the appropriate dilution of both detergents. These were allowed to stand for at least 30 min to ensure complete precipitation. The quantity of precipitate in each tube was measured using light scattering at 90° with an Aminco spectrophotofluorimeter. The measurements were made at 23° immediately after the cuvette was filled and stirred, and before any appreciable settling had occurred.

Results

The precipitation studies (Table I) demonstrate that the heaviest precipitate occurs where equimolar quantities of each detergent are present, while the product is solubilized by an excess of either detergent. This type of precipitation is usually found where the formation of a complex occurs, and differs from most inorganic precipitates where the heaviest precipitate occurs at the greatest total concentration of the respective ions.

Since the heat of precipitation was not known nor was precipitation desirable in the calorimeter, concentrations were chosen where precipitation was not expected to occur at 37°. However, it was necessary to keep the reactants concentrated enough to ensure that the heat was sufficient (minimum measurability of the instrument is approximately 0.4 mcal).

The solvents employed were 0.145 and 0.0001 M NaCl solutions. It was of interest to study the reaction in saline and dilute salt solution to observe what affect the polarity of the medium would have. A dilute salt solution was chosen (instead of water) to eliminate a significant heat of interaction of the chloride ion with the glass vessel as described by Benzinger.[9] The heats measured for the detergent interaction are listed in Table II. In both solvents, the reaction is exothermic, although a greater amount of heat is evolved per mole in the more dilute sodium chloride solution, as expected for a polar reaction.

Heats of Dilution. Since one detergent was diluted 76-fold, a significant value for the heat of dilution was expected. The results obtained for the most concentrated solutions are shown in Table III. To interpret these data, we needed to determine the cmc's of both detergents in both solvents at 37°. The values are shown in Table IV. Along with our surface tension values are some literature values at several different salt concentrations. The agreement is quite sufficient for our purposes.

Most heats determined in this study are a composite of three values which include the heat of dilution of the detergent monomer, the heat of dilution of the detergent micelle, and the heat of micellization. A further complication arises from the fact that since the cmc is a

Blank vessel	Test vessel	Enthalpy	
$\mathrm{CPC_{concd} \longrightarrow CPC_{dil}}$	$\mathrm{CPC_{concd} \longrightarrow CPC_{dil}}$	$\Delta H°$ dilution	(7)
$\mathrm{(CPC)_n \rightleftharpoons nCP^+ + nCl^-}$	$\mathrm{(CPC)_n \rightleftharpoons nCP^+ + nCl^-}$	$\Delta H°$ micellization	(8)
	$\mathrm{DS^- + CP^+ \rightleftharpoons DS\text{–}CP}$	$\Delta H°$ interaction	(9)
	$\mathrm{mDS\text{–}CP \rightleftharpoons (DS\text{–}CP)_m}$	$\Delta H°$ mixed micelle	(10)
	$\mathrm{pCP^+ + (CP\text{–}DS)_m \rightleftharpoons (CP_{m+p} + DS_m)^{p+}}$	$\Delta H°$ product–excess interaction	(11)

function of salt concentration, the heat of micellization probably is also. Furthermore, it has been shown[11,12] that the counterions bound to the micelle are also dependent upon the concentration of added salt; therefore, the heat of dilution of the micelle is probably not the same in our two solvents.

Table IV. Cmc Values at 37° Inferred from Surface Tension Measurements[a]

NaCl, *M*	DSS (37°)	DSS[11] (25°)	CPC (37°)	CPC[12] (25°)
0	7.3	8.12	0.47	0.49
0.0001	6.5		0.32	
0.01		5.29		
0.01754				0.12
0.10		1.46		
0.145	1.05		0.076	
0.4382				0.048

[a] The CPC values were corrected for the mole of water present. All values of cmc's below are multiplied by 10^3.

Equations 7–11 represent the processes which we expect to occur. All equations are also appropriate for DSS. Equation 7 includes the dilution of the monomers and the micelles.

The enthalpy of the interaction (eq 9) cannot be measured independently as the product immediately micellizes (eq 10). Thus, the $\Delta H°$ reported here is a combination of the $\Delta H°$ of interaction plus the $\Delta H°$ of the formation of the mixed micelle. In addition, there is a product–excess detergent interaction (eq 11) which was corrected for mathematically and will be subsequently discussed. When the original concentration is above the cmc, it is impossible to separate the heat of dilution from the heat of micellization. However, it would appear from Table III that both the heat of dilution and the heat of micellization are small (<5 kcal/mol).

Effect of pH. The possibility that we were measuring the heat of neutralization instead of, or in addition to, the heat of reaction was considered. Since sodium dodecyl sulfate is a salt of a strong acid and cetylpyridinium chloride of a quaternary base, solutions of these should be neutral. If impurities gave rise to solutions of widely differing pH, heat of neutralization would result upon mixing. However, the pH of sodium dodecyl sulfate solution was 6.96; that for cetylpyridinium chloride 6.16. Calculations based upon this pH difference, assuming the heat of neutralization equal to that value when hydrochloric acid is neutralized by sodium hydroxide, indicate that this heat would be less than 0.1 mcal.

Product–Excess Reactant Interaction. That the product indeed does react with excess detergent was demonstrated in our precipitate studies (Table I). We studied the heat of reaction of each detergent with the product produced in 15.2 ml of solvent. For example, an equimolar solution of the two detergents was allowed to come to equilibrium after reaction. To this was added 0.50 μmol of sodium dodecyl sulfate in the appropriate solvent. An endothermic reaction occurred. The heat of this interaction must be somewhat larger than the value of the correction shown in Table II since the addition of more detergent would drive the reaction further to completion and give off heat due to the reaction with unreacted CPC. The values thus obtained were used to correct the corresponding heats of reaction. These results appear in Table II and are graphically presented in Figure 3. The larger value in saline may be either the further interaction of the counterions or the effect of a more polar solvent.

Four values were not corrected because of problems involved in the reference vessel. In these cases, the detergent being diluted remains above the cmc after dilution. However, in the sample vessel, owing to the presence of the oppositely charged detergent, micelles are being broken up as the result of the reaction. Since we are interested in measuring only the heat of the reaction between monomeric forms of the detergents, and as our reference vessel will not equally cancel the heat of micellization in these four cases, the correction was not determined.

Calculations of Thermodynamic Parameters. Because of the problem encountered due to the lower cmc's in saline, the only values used for the calculations were those in 0.0001 *M* NaCl. Equations 4 and 6 (Experimental Section) were solved for k using each possible pair of heats listed in Table II, column 4, and those listed in Table II, column 10. When the product was considered as a monomeric species (eq 4), $k = 3.39 \times 10^{-6}$ (standard error = 0.09); however, when the micellization of the product is considered as a pseudophase, $k = 3.15 \times 10^{-6}$ (standard error = 0.07).

These values of k were used to calculate the equilibrium constants for each of the equimolar reactions (cationic into anionic and reverse addition). $\Delta H°$ was determined from the slope of our plotted data up to and including the 1:1 ratio of concentration (Figure 3). These values and other thermodynamic parameters appear in Table V.

Table V. Thermodynamic Parameters Calculated from the Average *k*'s and the Heats from Both Equimolar Situations[a]

	Q, kcal/mol	$\Delta H°$, kcal/mol	*K*, mol/l.	$\Delta G°$, kcal/mol	$\Delta S°$, eu
DSS into CPC	−18.51	−18.9	3.1×10^6	−9.20	−31.3
CPC into DSS	−17.75	−17.5	1.2×10^6	−8.61	−28.7
DSS into CPC	−18.51	−18.9	3.0×10^{10}	−14.8	−13.7
CPC into DSS	−17.75	−17.5	3.2×10^{10}	−14.9	−8.7

[a] The upper half of the table contains results obtained when the micellization of the product was neglected. The lower half contains those results obtained when the micellization of the product was treated as a pseudophase.

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[11] D. Stigter and K. J. Mysels, *J. Phys. Chem.*, **59**, 45 (1955).

[12] E. W. Anacker, *ibid.*, **62**, 41 (1958).

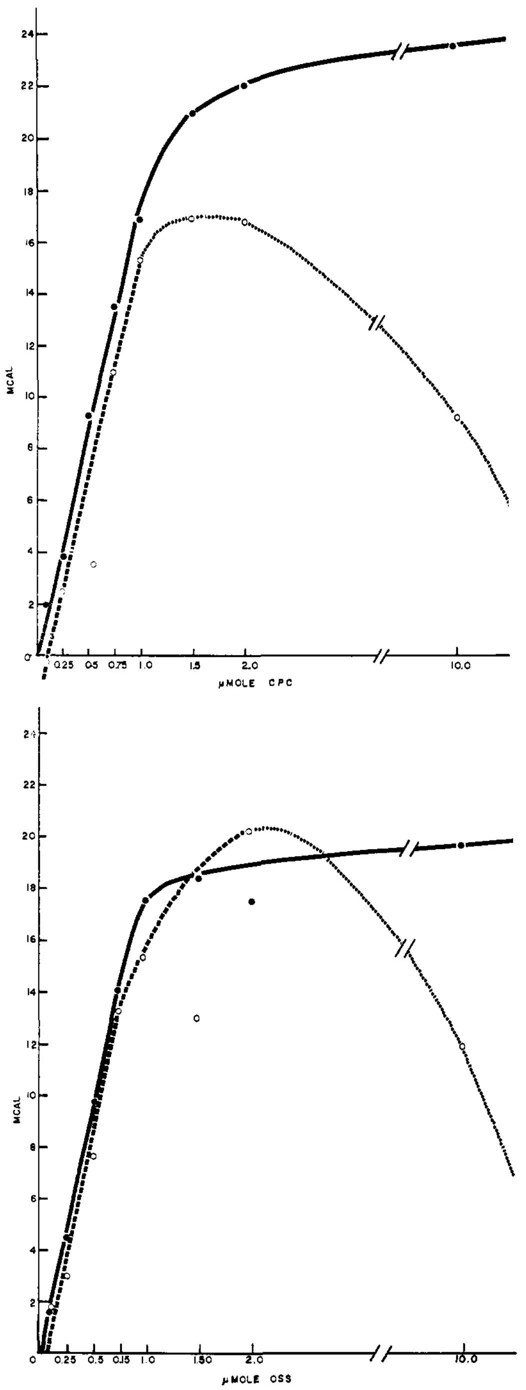

Figure 3. Heat as a function of the quantity of detergent allowed to react with 1 μmol of the opposite detergent. The solid circles and solid lines were done in 0.0001 M NaCl. The open circles were done in 0.145 M NaCl. The light dashes represent the uncorrected points.

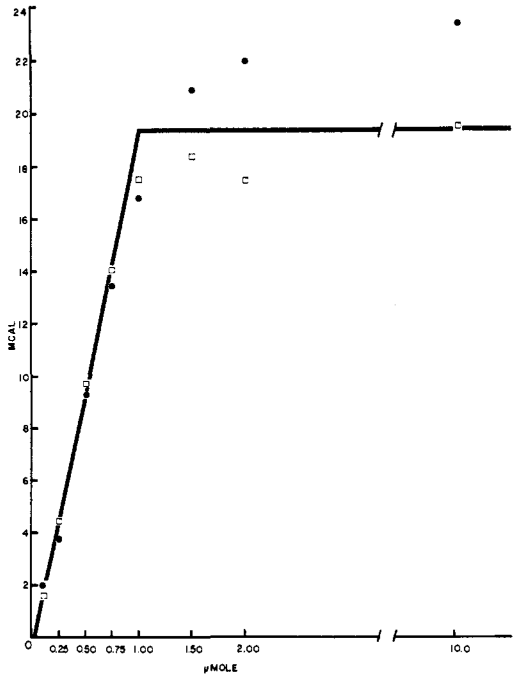

Figure 4. Theoretical line calculated upon the assumption that $K = \infty$. The solid circles are the experimentally determined points when DSS was held constant: the open squares represent those points where CPC was held constant. All heats were determined in 0.0001 M NaCl. The solid line represents the theoretical maximum heat.

Discussion

Nature of Product. The product is probably in the micellar state, but one composed of a mixture of cationic and anionic detergents. This conclusion is suggested by the results of Hua and Chao,[6] who reported the surface activity of mixtures of dodecylpyridinium bromide and sodium dodecyl sulfate to be 650 times greater than that of the cationic surfactant alone. Also, the reaction of monomeric surfactants to produce a micellar product, which is a thermodynamically reversible aggregate of several molecules, would give a negative entropy. Goddard[13] reports a value of −3.2 eu generated in the dissolution of sodium dodecyl sulfate in water at 35° with the value increasing as the temperature rises. Somewhat higher values were reported by Schick[14] who found that the entropy change in the micellization of sodium dodecyl sulfate in 0.2 M sodium chloride from 25 to 55° was −8.3 eu while dodecyltrimethylammonium bromide in 0.2 M sodium bromide gave −5.4 eu in the same temperature range. These calculations were based upon measured enthalpies at equilibrium. In addition to this entropy, the product of our reaction would be a mixed micelle and would have an additional ordering, since to gain the full advantage of the opposite charges, the cationic molecules would have to be surrounded by anionic ones in a situation similar to that on the surface of a crystal.

Plausibility of Thermodynamic Values. The heats measured for this reaction lead to an enthalpy value very near that reported by Lovrien[15] for the binding of anions to albumin. He reported enthalpies that range from −16 to −18 kcal/mol for the interaction of iodide, benzene sulfonate, azobenzene sulfonate, and hexyl sulfate with bovine serum albumin at 25°. Our free-energy values can be compared to those of Steinhardt, *et al.*,[16] who reported a $\Delta G°$ value of −8.2 kcal/mol for the binding of bovine serum albumin to dodecyl sodium sulfate at 23°. Our values are comparable when based on one mathematical approach, and slightly higher when based on the mixed micelle approach. Since the equilibrium constant for this reaction has not been pre-

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(13) E. D. Goddard and G. C. Benson, *Can. J. Chem.*, **35**, 986 (1957).

(14) M. J. Schick, *J. Phys. Chem.*, **67**, 1796 (1963).

(15) R. Lovrien, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967, No. C252.

(16) J. A. Reynolds, S. Herbert, H. Polet, and J. Steinhardt, *Biochemistry*, **6**, 937 (1967).

viously measured, we have no basis on which to compare our values directly. Neither set of values for either mathematical treatment appears, from existing information, to be entirely unreasonable.

The values of k were found to be statistically identical within 99.5% confidence level, and assuming that $K = \infty$, the theoretical maximum amount of heat which could be obtained was calculated and is plotted in Figure 4 along with the experimental points. The values beyond the 1:1 molar ratio when sodium dodecyl sulfate is held constant are too high, and this can possibly be explained as the reaction of the excess cationic detergent with the glass reaction vessels as reported by Blackman and Harrop.[17] When the concentration of cetylpyridinium chloride is held constant, the heat values are low owing to the 1 mole of water present for which no correction has been made. The remainder of the data fits our theoretical curve within experimental error.

Application of Calorimetry to Free-Energy Calculations. As an extension of the work of Benzinger[2] where he considered reactions of the type $A + B \rightleftharpoons C + D$, we have explored the reaction $A + B \rightleftharpoons C$. From experimentally measured heat values, thermodynamic parameters have been calculated. The application of calorimetry to this type of system can be a valuable tool in the investigation of other similar systems. Calorimetrically, this could represent a model for many important biological reactions such as antigen–antibody, hemoglobin–haptoglobin, and avidin–biotin.

Acknowledgments. The authors are grateful to Dr. C. L. Sutula for his many helpful suggestions.

(17) L. C. F. Blackman and R. Harrop, *J. Appl. Chem.*, 18, 43 (1968).

Formation of Excited Intermediates in Recoil Carbon Atom Reactions. Pressure-Dependence Studies in the Gas Phase[1]

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Abstract: The variation in yield of carbon monoxide-C^{11}, acetylene-C^{11}, and ethylene-C^{11} from the reaction of recoil carbon atoms with methane, propane, cyclopropane, and neopentane has been studied as a function of the hydrocarbon gas pressure. The hydrocarbons contained 4.5% added oxygen as scavenger. The total gas pressure was varied over a 1000-fold range in all cases except neopentane where the pressure range was varied 100-fold. In all cases studied the yield of carbon monoxide-C^{11} decreased with increasing pressure and yields of acetylene-C^{11} and ethylene-C^{11} increased with increasing pressure. A model is presented which invokes a collision complex being formed prior to carbene formation where the excited carbene then can fragment or react further to give the observed products. The nature of the collision complex is suggested as being responsible for the observed pressure dependency.

The reaction of energetic carbon atoms with hydrocarbons produces acetylene and often ethylene in high yields. Upon addition of oxygen scavenger, carbon monoxide is also formed because the carbon atoms which reach thermal energies react preferentially with oxygen.[2,3] The mechanisms currently proposed for the reaction of carbon atoms involve insertion of either carbon atoms,[4] methyne,[2a,c] or methylene[2a,c] to form excited intermediates. Since phase-effect studies have shown that such intermediates can be stabilized in a solid or liquid matrix,[5,6] pressure-dependence studies on the gas-phase reactions of carbon atoms were initiated[7] to investigate the single collisional deactivation of such intermediates, in systems where the environment of the attacking species is unaltered.[8] For recoil studies the $C^{12}(n,2n)C^{11}$, $N^{14}(p,\alpha)C^{11}$, $C^{12}(\gamma,n)C^{11}$, and $C^{12}(p,pn)C^{11}$ have been the most frequently used nuclear reactions. For pressure dependence studies the $C^{12}(p,pn)C^{11}$ reaction using the 1–3-GeV proton beam at the Brookhaven Cosmotron is ideal. This technique allows accurate monitoring of induced activity[2a,6] as well as low radiation damage to samples.

Experimental Section

Materials. Phillips Research Grade hydrocarbons were used after purification by freezing and melting on a vacuum line. Matheson reagent grade oxygen was used without further purification.

Irradiations. Irradiations were carried out using aluminum (2-S) vessels. All vessels were cylindrical with a 5-cm o.d.; the vessels varied in length from 1.25 to 20 cm. The vessel size used depended on the pressure of the sample. The vessel window thickness varied from 0.76 mm on the low-pressure vessels to 3 mm on the high-pressure vessels. The attenuation of the beam by the thick

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(2) (a) G. Stöcklin and A. P. Wolf in "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna, 1965, pp 121–132; (b) P. Lieberman, Ph.D. Thesis, City University of New York, New York, N. Y., 1967; (c) *cf.* A. P. Wolf, *Advan. Phys. Org. Chem.*, 2, 202 (1964).

(3) *Cf.* R. Wolfgang, *Progr. Reaction Kinetics*, 3, 99 (1965).

(4) C. MacKay, M. Pandow, P. Polak, and R. Wolfgang in "Chemical Effects of Nuclear Transformations," Vol. II, IAEA, Vienna, 1961, pp 17–26.

(5) C. E. Lang and A. F. Voigt, *J. Phys. Chem.*, **65**, 1542 (1961).

(6) G. Stöcklin and A. P. Wolf, *J. Amer. Chem. Soc.*, **85**, 229 (1963).

(7) H. J. Ache and A. P. Wolf, *ibid.*, **88**, 888 (1966).

(8) In a pressure-dependence study the slowing down process of the attacking species is identical at low and high pressures and so the behavior of reaction intermediates can be examined. In mixed systems (*i.e.*, with inert gas added) not only may reaction intermediates be affected but also the energy distribution of the reacting species.