

TABLE III
WALLACH REARRANGEMENT OF NATURAL AZOXYBENZENE
IN 95% SULFURIC ACID AT 25°^a

Time, sec	Absorbance at 464 nm	
	Obsd	Calcd
0	0.000	0.000
180	0.045	0.043
480	0.113	0.109
840	0.184	0.179
1260	0.253	0.253
1800	0.328	0.332
2520	0.411	0.416
3480	0.494	0.500
22,320	0.776	0.757
77,640	0.846	0.853

^a $A_0 = 20.0 \mu M$; $\epsilon_1 = 34,700 M^{-1} \text{ cm}^{-1}$; $\epsilon_2 = 45,900 M^{-1} \text{ cm}^{-1}$; $k_1 = 3.58 \times 10^{-4} \text{ sec}^{-1}$; $k_2 = 1.67 \times 10^{-5} \text{ sec}^{-1}$.

TABLE IV
WALLACH REARRANGEMENT OF AZOXYBENZENE-*d*₁₀ IN
95% SULFURIC ACID AT 25°^a

Time, sec	Absorbance at 464 nm	
	Obsd	Calcd
0	0.000	0.000
120	0.022	0.024
300	0.055	0.059
540	0.103	0.102
800	0.161	0.161
1380	0.230	0.233
1800	0.282	0.281
2340	0.338	0.336
3360	0.421	0.419
4140	0.469	0.466
5700	0.541	0.530
6900	0.579	0.562
11,880	0.664	0.624
18,300	0.699	0.650
85,500	0.779	0.753

^a $A_0 = 17.5 \mu M$; $\epsilon_1 = 3.47 \times 10^4 M^{-1} \text{ cm}^{-1}$; $\epsilon_2 = 4.59 \times 10^4 M^{-1} \text{ cm}^{-1}$; $k_1 = 3.42 \times 10^{-4} \text{ sec}^{-1}$; $k_2 = 1.67 \times 10^{-5} \text{ sec}^{-1}$.

natural azoxybenzene, respectively. A 2% change in either A_0 or k_1 gives noticeably poorer fits. This gives $k_H/k_D = 1.05 \pm 0.05$ which was experimentally indistinguishable from unity. In 80.5% sulfuric acid at 75° k_H/k_D was found to be 1.00 ± 0.05 . The probable absence of a primary isotope effect is thus demonstrated.

The observations reported here therefore show that nucleophilic attack during or before a rate-limiting step cannot be excluded as a mechanistic possibility for the Wallach transformation, but the rate-limiting step does not seem to include loss of an aromatic proton.

Experimental Section

Materials.—4- and 4'-bromoazoxybenzene were prepared by previously described methods.¹² Azoxybenzene-*d*₁₀ (mp 36°) was prepared by reduction¹³ of nitrobenzene-*d*₅ which in turn had been prepared from benzene-*d*₆ (Merck Sharpe and Dome Ltd.). Deuterium content was estimated as 98+ % for the azoxybenzene by comparison of pmr peak areas with those of dilute solutions of natural azoxybenzene. The spectrum of the deuterated azoxybenzene above 300 nm and the pK_a of its conjugate acid were the same as for natural azoxybenzene.

Bromide Displacement.—Portions (10 ml) of 0.036 *M* solutions of the bromine compounds were sealed in ampoules after nitrogen flushing. The ampoules were heated in boiling water for several minutes and then placed in a 117° oven. After heat-

ing, the ampoule contents were diluted with water, the alcohols were removed with the water pump, and the residue was acidified to pH 5 with standard perchloric acid and titrated for halide ion by Mohr's method. Blank samples containing only solvent and base were run for each solvent system and found to be stable.

Wallach Reaction Kinetics.—Approximately 20 μM solutions of the azoxybenzene were placed in a jacketed tube with water thermostated at the desired temperature circulated through the outer jacket. The tube was placed in a calibrated Coleman Jr. spectrometer set at 464 nm. In Tables III and IV the background absorbance of 0.136 has been subtracted from the observed absorbances. The runs in 80.5% sulfuric acid were performed as described previously.³

Registry No.—4'-Bromoazoxybenzene, 16054-48-1; 4-bromoazoxybenzene, 16109-68-5; azoxybenzene, 495-48-7; azoxybenzene-*d*₁₀, 25244-28-4.

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Critical Micelle Concentrations of Optically Active and Racemic 2-Octylammonium and 2-Octyltrimethylammonium Ions

ROBERT A. MOSS AND WARREN L. SUNSHINE¹

Wright Laboratory, School of Chemistry,
Rutgers University, The State University of
New Jersey, New Brunswick, New Jersey 08903

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Our demonstration that the stereochemical course of alkanol formation *via* the classical amine-nitrous acid deamination reaction can be moderated by the presence of alkylammonium ion micelles² forms part of a rapidly growing interest in the control of organic reaction chemistry by micellar phases.³ The rational design of micellar agents now assumes special importance.

The dependence of the critical micelle concentration (cmc), defined as "the saturation concentration of singly dispersed species,"⁴ on such parameters of molecular structure as chain length and branching, number, type, and location of ionic "head" groups, chain unsaturation, gegenion identity and charge type, and related factors, has been well studied.⁵ Studies of chiral micellar agents, and especially of the effect of possible diastereomeric and enantiomeric interactions on the cmc are, however, not common. Beckett and coworkers reported that the cmc's of some racemic and optically active *N*-alkyl-*N,N*-dimethylalanine hydrobromides were identical.⁶ In a preliminary trial we had found apparent differences in the cmc's of racemic and optically active 2-octylammonium perchlorate in 1.5 *M* aqueous sodium perchlorate at pH 4.⁷

It did seem possible that micellar agents composed of a single enantiomer might "fit" together more or less

(1) NDEA Fellow, 1968-1970.

(2) R. A. Moss and D. W. Reger, *J. Amer. Chem. Soc.*, **91**, 7539 (1969).

(3) See E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 339 (1969).

(4) See K. Shinoda, T. Nakagawa, B-I. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963, p 4.

(5) Reference 4, particularly Chapter 1.

(6) A. H. Beckett, G. Kirk, and A. S. Virji, *J. Pharm. Pharmacol., Suppl.*, **19**, 71 (1967).

(7) Reference 2, Note 14.

(12) L. C. Behr, *J. Amer. Chem. Soc.*, **76**, 3672 (1954).

(13) A. Lachman, *ibid.*, **24**, 1180 (1902).

readily than the corresponding racemic modification. D and L amino acids apparently differ in their "fit" to the surface of D-N-alkyl-N,N-dimethylalanyl betaines.^{8,9} The likelihood that many investigations of micellar control of organic reaction stereochemistry will be forthcoming, impelled us to give further scrutiny to our preliminary observation and to report the results at this time.

Cmc's of racemic and optically active (89–94% optically pure) 2-octylammonium bromide (at pH 1.5) and 2-octyltrimethylammonium bromide were determined in water and in 1.5 M aqueous sodium bromide. The cmc of 2-octylammonium perchlorate was determined in 1.5 M and 2.0 M aqueous sodium perchlorate at pH 1.5. Cmc's were taken as the "break points" of graphs of log (micellar agent concentration) vs. observed surface tension obtained with a DuNouy tensiometer. All measurements were made on solutions in a thermostatted cell at 31° and were reproducible to ± 0.3 dynes/cm. The cmc values recorded in Table I each represent the average of at least three

TABLE I

CMC'S OF RACEMIC AND OPTICALLY ACTIVE 2-OCTYLAMMONIUM AND 2-OCTYLTRIMETHYLAMMONIUM IONS				
Case	Micellar agents ^a	Solvent	Cmc (mol/l.)	% avg dev
1	2-OTA-Br	H ₂ O	0.325	6.8
	2-OTA-Br*	H ₂ O	0.362	2.5
2	2-OTA-Br	1.5 M aqueous NaBr	0.148	2.7
	2-OTA-Br*	1.5 M aqueous NaBr	0.146	6.1
3	2-OA-Br	1.5 M aqueous NaBr ^b	0.129	1.6
	2-OA-Br*	1.5 M aqueous NaBr ^b	0.128	2.4
4	2-OA-ClO ₄	1.5 M aqueous NaClO ₄ ^b	0.0499	1.8
	2-OA-ClO ₄ *	1.5 M aqueous NaClO ₄ ^b	0.0516	1.9
5	2-OA-ClO ₄	2.0 M aqueous NaClO ₄ ^b	0.0417 ^c	0.2
	2-OA-ClO ₄ *	2.0 M aqueous NaClO ₄ ^b	0.0427 ^d	0.7

^a OTA = octyltrimethylammonium, OA = octylammonium. An asterisk denotes the optically active samples. ^b pH 1.5. ^c The cmc is unchanged at pH 4.0. ^d Use of 100% optically pure 2-OTA-Br in cases 1 and 2 gave values within the experimental errors.

measurements on *separately prepared* micellar solutions. The cmc of racemic 2-octylammonium bromide in water (pH 1.5) was determined as 0.34 M. Under these conditions, surface tension–log (concentration) graphs for the optically active salt did not exhibit sharp "breaks." The graphs were satisfactory in the other cases examined, and free of minima, though the "break" became sharper at lower cmc values.¹⁰

Differences, such as they are, between the cmc's of the racemic and optically active ions lie just at the border of combined experimental error (*e.g.*, case 1). Within the accuracy of our measurements, therefore,

(8) A. H. Beckett, G. Kirk, and A. S. Virji, *J. Pharm. Pharmacol.*, **19**, 827 (1967).

(9) This case is obviously not analogous with the title problem, since it involves diastereomeric solubilization interactions rather than enantiomeric micellization interactions. The situations are, nonetheless, conceptually akin.

(10) A recent application of the surface tension cmc determination method, including a sample graph, may be found in L. R. Romstead and E. H. Cordes, *J. Amer. Chem. Soc.*, **90**, 4404 (1968). For other references, see ref 4, p 11.

the racemic and optically active species have essentially identical cmc's. We consider that our earlier, contrary observation⁷ was most likely due to an inadequately purified racemic 2-octylammonium ion sample, which may have exhibited a depressed cmc.¹¹ The present results, together with previous work,⁶ suggest that a continued search for "fit" problems accompanying micellization of racemic, as opposed to optically active micellar agents, might concentrate on molecules in which the center of chirality is located well into the hydrophobic portion of the micellar agent. The effect of chirality at the "head" group (with regard to cmc) is probably mitigated by the water molecules and gegenions which "insulate" the "head" groups from each other in the micelle.

Experimental Section

Materials.—Racemic 2-aminooctane (K & K) was purified by distillation. Distillate was monitored by gas chromatography (gc) on a 10 ft \times 0.25 in., 10% SE-30 on GCR (45–60) column at 122°. When necessary, more rigorous purification was afforded by distillation over a Nester–Faust Teflon annular spinning-band column. Only 2-aminooctane of gc purity (>99%) was used in further work.

Optically active 2-aminooctane was obtained from the racemate by the method of Mann and Porter^{12,13} and had α^{25}_D -2.38° (*l* 0.5 dm, neat), corresponding to an optical purity of at least 89%.¹⁴ A second batch of resolved amine had α^{25}_D -2.51° (*l* 0.5 dm, neat) and was at least 94% optically pure. The two active amine samples were used without distinction in cmc determinations.

2-Octyltrimethylammonium bromide was prepared from 2-aminooctane by the procedure of Clarke¹⁵ (which gave 2-octyltrimethylamine) followed by quaternization with methyl bromide. The 2-octyldimethylamine (bp 37–38°, 1.35 Torr) was produced in 72% yield and showed traces of (presumably) 2-aminooctane and 2-octylmethylamine by gc. It was not further purified, but was converted to the quaternary salt by the following, generalized procedure. 2-Octyldimethylamine, an equal volume of dry ethanol, and 1.75 equiv of methyl bromide (Matheson) were sealed into a pressure tube¹⁷ and shaken overnight at *ca.* 25°. Ethanol and excess methyl bromide were then evaporated. The crystals were washed well with anhydrous ether and then dissolved in the minimum necessary volume of hot methanol. Several volumes of dry ether were added to the cooling methanol solution so as to drive out the salt in a fine form. The salt was collected and triturated with dry ether. The entire process was then repeated twice. Crystals obtained in this way were suitable for cmc determinations, as judged by the absence of minima in their surface tension–log (concentration) graphs.¹⁸ 2-Octyltrimethylammonium bromide was thus obtained in a (purified) yield of 50%. It decomposed at 259–260° (sealed capillary tube) after discoloring above 220°.

Anal. Calcd for C₁₁H₂₆BrN: C, 52.38; H, 10.39; Br, 31.68; N, 5.55. Found: C, 52.21; H, 10.57; Br, 31.56; N, 5.32.¹⁹

(11) The argumentation and conclusions of ref 2 are unaffected by the present findings.

(12) F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 456 (1944).

(13) We thank Mr. C. Talkowski for the amine resolution.

(14) F. G. Mann and J. Reid, *J. Chem. Soc.*, 3384 (1950), report α^{15}_D -2.86° (*l* 0.5 dm, neat) for scrupulously dried amine. Traces of water are known to depress this value to α^{15}_D -2.55° .¹⁶ Our amine samples were dried by distillation from sodium just prior to polarimetry and optical purities are therefore based on the former value.

(15) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **78**, 5597 (1956).

(16) H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

(17) Methyl bromide was introduced as a liquid at -70° . The reaction is exothermic. Reagents should be mixed at low temperature and allowed to warm after the pressure tube has been sealed.

(18) Alternative purification methods such as recrystallizations from acetone, ethylacetate, or alcohol–ether did not yield material satisfactory for cmc determinations.

(19) Analysis by Micro-Tech Laboratories, Skokie, Ill. Infrared and nmr spectra were in accord with structure.

Optically active 2-octyltrimethylammonium bromide was prepared from resolved 2-aminooctane in an identical manner. From 2-aminooctane, $\alpha^{25}_D -2.377^\circ$ (88.6% optically pure), the optically active salt obtained had $\alpha^{25}_D +3.18^\circ$ (c 1.0 M in methanol, 0.5 dm).

Cmc Determinations.—All solutions of the ammonium salts were prepared in "Lecktrostill Steam Distilled Water," resistivity $>1.5 \times 10^6$ ohm cm (Electrified Water Co., Newark, N. J.). Stock solutions were water, 1.5 M aqueous NaBr, 1.5 M aqueous NaBr (acidified to pH 1.5 with HBr solution which had been preadjusted to 1.5 M in bromide ion), and 1.5 M and 2.0 M aqueous NaClO₄ (acidified to pH 1.5 with HClO₄). Solutions of the amine or the ammonium salt were prepared (above the cmc) using these stock solutions. 2-Octylamine solutions were preadjusted to pH 1.5 with aqueous HBr (1.5 M in bromide) before bringing to dilution with bromide stock solution. A similar procedure was used in the perchlorate experiments.

Surface tension was determined in a cell thermostatted at 31° by a Haake constant-temperature circulating pump. An aliquot of the amine or the ammonium ion solution (at a concentration above the cmc) was successively diluted by addition of 0.50-ml portions of the appropriate stock solution from an accurate buret (± 0.01 ml). Stirring was accomplished after each dilution with a micro stirring bar and the surface tension corresponding to the then present concentration²⁰ was measured with a DuNuoy tensiometer.²¹ Cmc values were then determined from graphs of observed surface tension vs. log (concentration). Average cmc values, determined from at least three separately prepared micellar solutions appear in Table I.

Registry No.—(±)-2-OA-Br, 25474-24-2; (−)-2-OA-Br, 25474-25-3; (±)-2-OTA-Br, 25474-26-4; (+)-2-OTA-Br, 25474-27-5; (±)-2-OA-ClO₄, 25474-28-6.

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(20) The volume additivity demanded by this procedure was demonstrated to ± 0.01 ml by parallel control experiments for cases 1, 2, and 4 of Table I.

(21) The average deviation from the mean of a series of 12 surface tension readings taken either on water or a micellar solution was ± 0.3 dynes/cm.

The Structure of the Adduct from Diphenylketene and Triethyl Phosphite

J. E. BALDWIN¹ AND J. C. SWALLOW

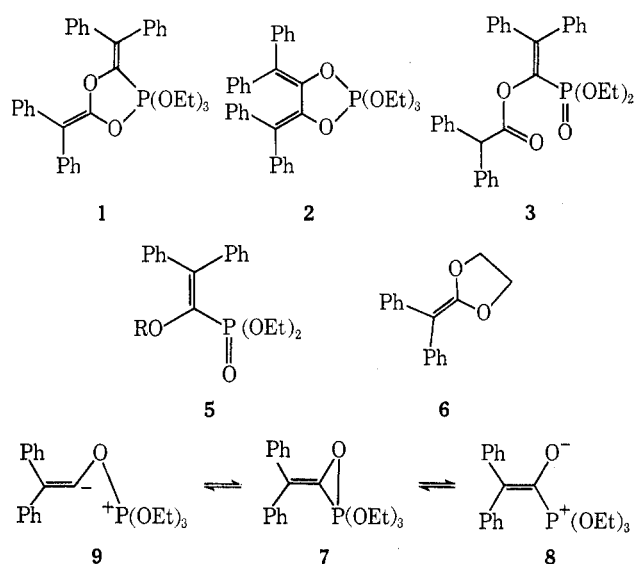
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 23, 1970

During the course of work on the interaction of trivalent phosphorus with carbonyl derivatives we have examined the 2:1 adduct of diphenylketene and triethyl phosphite.² The structure of this substance, which undergoes a high-temperature deoxygenation rearrangement to diphenylacetylene,² has been the subject of some speculation;³ and we here describe a solution to this problem.

The adduct, C₃₄H₃₅PO₅, prepared as previously described² showed a medium strength band at 1660 cm⁻¹ in the infrared (solid and solution) and the nmr spec-

trum, which contained only phosphorus-bound ethoxyl and aryl protons, underwent an irreversible change at 90°. In accordance with previous speculative suggestions for the presence of pentacoordinate phosphorus atom in this molecule, the ³¹P magnetic resonance spectrum showed a chemical shift of +55 ppm relative to 85% H₃PO₄, without solvent dependence.⁴ However "freezing out" of discrete pseudorotational structures could not be observed in the proton spectrum of the ethoxyl ligands down to -114°. At this stage two structures, 1 and 2, seemed in accord with the evidence, neither of which possessed a carbonyl function, *vide supra*. Distinction between these two possibilities was made on the basis of hydrolytic behavior, for in moist air or in wet ether the adduct was converted into the enol ester (3), ν_{\max} 1760 cm⁻¹, and ethyl diphenylacetate (4). That 4 was a further ethanolysis product of 3



was demonstrated by the observation that methanol, with a trace of sodium methoxide, converted 3 into methyl diphenylacetate. More vigorous hydrolysis of 3 gave almost 2 mol of diphenylacetic acid. Confirmation of the enol ester structure 3 was achieved by synthesis. Thus the Arbuzov product from diphenylacetyl chloride and triethylphosphite was the stable enol phosphonate (5, R = H), from its composition and positive ferric chloride test.⁶ The enolic hydroxyl group of 5 (R = H), exchangeable with deuterium oxide, was acetylated to the acetate 5 (R = COCH₃), ν_{\max} 1760 cm⁻¹, and methylated (diazomethane) to the ether 5 (R = CH₃). Treatment of 5 (R = H) with diphenylketene yielded the phosphonate 3, identical in infrared, ultraviolet and nmr spectra with the originally isolated substance. The hydrolytic conversion of the adduct to 3 then enables the assignment 1 to be proposed for this substance and rejection of alternative 2, since the latter could not readily yield an enol ester 3 under simple hydrolytic conditions. As a close ultra-

(1) Alfred P. Sloan Fellow, 1969-1970.

(2) T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

(3) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 197; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, p 88.

(4) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

(5) F. H. Westheimer, *ibid.*, **1**, 70 (1968).

(6) An analogous enolic compound has recently been described by Richard N. McDonald and Donald G. Hill, *Chem. Commun.*, **12**, 671 (1969).