

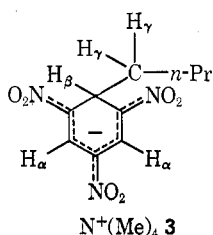
TABLE III
ANALYTICAL DATA^a

Compd	Found, %			Calcd, %			Mp, °C
	C	H	N	C	H	N	
N ⁺ (Me) ₄ (TNB-butyl) ⁻	48.46	6.87	15.99	48.83	7.02	16.27	206.5-207.5
As ⁺ (Ph) ₄ (TNB-butyl) ⁻	61.98	4.87	6.16	62.48	4.94	6.34	120-122
As ⁺ (Ph) ₄ (TNB-methyl) ⁻	61.24	4.42	6.95	60.89	4.29	6.87	166-167

^a Analyses were performed by Baron Consulting Co., Orange, Conn. 06477.

pattern observed for the ring protons are typical for "Meisenheimer" complexes.²⁻⁴ The fact that the γ -methyl protons are shifted slightly downfield from the methyl resonance frequency of methylcyclohexane is probably due to the anisotropy of the nearby NO₂ groups. The observed coupling constants and chemical shifts do not change significantly in other solvents. Addition of TNB to an acetonitrile-*d*₃ solution of **2** does not affect the nmr spectrum of the complex, indicating exchange of methyl anion between the complex and TNB must occur slowly (if at all!) at 40°.⁷

B. Tetramethylammonium Butyl-2,4,6-trinitrocyclohexadienate (3).—The nmr spectrum of this compound shows absorptions which can be assigned to the protons in **3** (see Table II).⁶ The proton resonances of



the anion do not change significantly when tetraphenylammonium is substituted for tetramethylammonium.

Ir Spectra.—The most significant features of the infrared spectrum of the (TNB-butyl)⁻ complex in deuteriochloroform are the presence of two very strong bands at 1219 and 1159 cm⁻¹ and the complete absence of bands at 1550 and 1345 cm⁻¹, the characteristic stretching frequencies of the NO₂ group in TNB.⁸ In analogy with Norris' investigation of the TNB-cyanide complex, we assign the intense bands at 1219 and 1159 cm⁻¹ to the antisymmetric and symmetric NO₂ stretching frequencies of the complex.⁸ This assignment is consistent with Norris' suggestion that the effect of delocalization of negative charge is to decrease the NO bond order, thus shifting the NO₂ stretching frequencies to lower energy.

Support for this point of view is provided by the following experiment: on acidification (HCl gas) of a deuteriochloroform solution of the (TNB-butyl)⁻ complex the purple color fades to yellow; new intense bands at 1545 and 1350 cm⁻¹ appear in the infrared spectrum of the acidified solution; and in addition, the previously observed NO₂ stretches are now completely absent. The nmr spectrum of the acidified solution indicates 2,4,6-trinitrobutylbenzene is a decomposition product. Similar color changes are obtained if the (TNB-methyl)⁻ complex is studied.

Experimental Section

Nmr spectra were recorded at 60 and 100 MHz on Varian spectrometers. Chemical shifts relative to internal tetramethyl-

(7) This result is quite general for "Meisenheimer" complexes.^{2,3}

(8) A. R. Norris and H. F. Shurvell, *Can. J. Chem.*, **47**, 4267 (1969).

silane were determined by the usual side-band techniques. Visible spectra were recorded using matched 1-cm quartz cells in a Cary 14 spectrometer, and infrared spectra were measured in 0.1-mm path length sodium chloride cells in a Beckman IR-12 spectrometer.

Preparation of Compounds.—The preparation of **3** is illustrative of the general synthetic procedure; a solution of TNB (0.60 g, 2.8 mmol) in 10 ml of acetone was added dropwise with stirring to a solution of tetramethylammonium tetrabutylboride⁹ (0.34 g, 1.1 mmol) in 10 ml of acetone under nitrogen. After addition was completed the resulting purple solution was stirred for 0.5 hr. Excess ether (~100 ml) was added to the reaction mixture, which was subsequently stored at 0° for 4 hr. The precipitated purple solid (0.29 g, 70%) was filtered, washed with ether, and recrystallized from an ethanol-ether mixture.

The preparation of the (TNB-methyl)⁻ complex was similar, except in order to achieve good yields it became necessary to stir the solutions for a much longer period (~12 hr) prior to the addition of ether.¹⁰

The salts appear to be relatively stable in air but were stored under nitrogen as a precautionary measure. The color of dilute solutions of the complexes fades in about 1 hr when they are exposed to light. Spectroscopic measurements were made on freshly prepared solutions and reproducibility was excellent. Analytical data are recorded in Table III.

Registry No.—**1**, R = *n*-C₄H₉, cation = As⁺(Ph)₄, 25448-31-1; **2**, 25448-32-2; **3**, 25448-33-3.

Acknowledgments.—The author gratefully acknowledges the interest and support of Professor I. D. Kuntz throughout the course of this study. Thanks are also due to Professor P. von R. Schleyer and Mr. M. Hendrick who read and commented on the manuscript of this paper.

(9) R. Damico, *J. Org. Chem.*, **29**, 1971 (1964).

(10) Trialkylboron compounds, which burn spontaneously in air, appear to be side products of these reactions. It is advisable to carry out these syntheses in a well-ventilated hood.

Mechanistic Aspects of the Wallach Transformation of Azoxybenzenes

EDWARD C. HENDLEY¹ AND DONALD DUFFEY

Department of Chemistry, Mississippi State University, State College, Mississippi 39762

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In strong sulfuric acid solutions, azoxybenzenes are converted to *p*-hydroxyazobenzenes in a process known as the Wallach transformation.² The exact dependence of the reaction rate on the acidity of the medium is unknown and appears to differ measurably for differently substituted azoxybenzenes,³ but it is evident that more than one proton is transferred to the azoxybenzene

(1) Deceased.

(2) E. Bunce in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968.

(3) D. Duffey and E. C. Hendley, *J. Org. Chem.*, **33**, 1918 (1968).

prior to or during a rate-limiting step most probably involving N–O bond scission.

Mechanisms proposed for the Wallach reaction differ mainly in whether nucleophilic attack at a *para* position occurs before or after the rate-limiting step. If bisulfate ion or another suitable nucleophile attacks before the N–O bond cleaves, then evidence is needed for an equal probability of attack at the nonequivalent *para* positions to explain the nearly equal appearance of hydroxyl at either position in the product.^{4,5}

Miller and Parker⁶ have reported Hammett σ parameters of 0.769 and 0.595 for the displacement of chloride by hydroxide at the 4 and 4' positions⁷ where both substrates were activated toward nucleophilic attack by a nitro group *ortho* to the chlorine. With *p*-bromoazoxybenzenes the relative ease of nucleophilic displacement of bromide from the 4 and 4' positions is found to depend on the reaction conditions, and, under some conditions, the two positions are equally susceptible to attack.

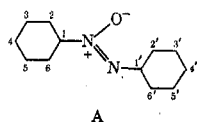
In Table I it is seen that both 4- and 4'-bromoazoxybenzene are considerably less reactive in butanol than in ethanol, and a considerably greater difference between the reactivities of the two isomers is also observed in butanol than in ethanol. In aqueous ethanol the order of reactivity is apparently reversed although the difference is probably not significant. A trend of decreasing difference in reactivity with increasing ion-solvating power or polarity is thus evident. This trend indicates a likelihood that in aqueous sulfuric acid solution the nonequivalent *para* positions in azoxybenzene may be equally susceptible to nucleophilic attack.

TABLE I
INFLUENCE OF THE MEDIUM ON RATE OF
NUCLEOPHILIC DISPLACEMENT^a

Solvent	90% ethanol	Ethanol	1-Butanol
Initial base concn, <i>M</i>	3.56	0.52	0.08
Reaction time	12 hr	12 hr	10 days
4'-Bromoazoxybenzene	93	55	26 ^b
4-Bromoazoxybenzene	89	67	74
4-Bromonitrobenzene	75 ^c	72	
Bromobenzene	<1		

^a Reported as per cent reacted. ^b After 34 days. ^c After 6 hr.

The expected products of the reaction of 4- and 4'-bromoazoxybenzene with hydroxide in aqueous ethanol, namely, 4- and 4'-hydroxyazoxybenzene, were synthesized by another route⁸ and found to be unstable under the reaction conditions necessitating an estimate of the extent of reaction by the formation of bromide ion and the decrease in base concentration. In Table II the increase in reaction rate for 4'-bromoazoxybenzene that accompanies an increase in initial base concen-



(8) A. Angeli, *Atti Accad. Naz. Lincei*, **23** [I], 557 (1914).

TABLE II
EFFECT OF INITIAL BASE CONCENTRATION ON BROMIDE
LIBERATION FROM 4'-BROMOAZOXYBENZENE^a

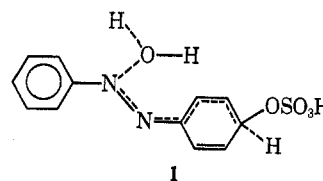
Initial base concn, <i>M</i>	0.89	1.78	3.56
% reacted	19	52	93 ^b

^a Reaction conditions: 90 vol % ethanol, 25 hr at 117°. ^b After 12 hr.

tration is indicative that the initial reaction is bimolecular as expected.

Under normal conditions of the Wallach reaction, *i.e.*, greater than 75% sulfuric acid, most azoxybenzenes exist in the form of their conjugate acids in which the oxygen is apparently protonated.⁹ Whether it is oxygen or nitrogen that is protonated, however, does not alter the high probability that the rings are activated toward attack even by such comparatively poor nucleophiles as bisulfate ion or perhaps water in the less acidic media.

If the Wallach transformation involves nucleophilic attack prior to breaking the N–O bond, there would seem a distinct possibility that the loss of a proton from a phenyl ring, aromatization, and N–O cleavage would be concerted as pictured in the intermediate 1. Such a situation would lead to a primary kinetic isotope effect when the *para* hydrogens are replaced by deuterium.



To test this possibility azoxybenzene-*d*₁₀ was synthesized and its reaction rate compared to that of natural azoxybenzene in the same medium (95% sulfuric acid by weight) and at the same temperature (25°). Calculation of the Wallach reaction rate constants in solvents of 90% or greater sulfuric acid is complicated somewhat by a slower sulfonation reaction undergone by the *p*-hydroxyazobenzene.¹⁰

The reacting system was treated as two consecutive pseudo-first-order reactions¹¹ for which the time dependence of absorbance at a given wavelength is given by

$$\epsilon_1 A_0 \left[\frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \right] + \epsilon_2 A_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]$$

where ϵ_1 and ϵ_2 are the molar extinction coefficients of the conjugate acid of *p*-hydroxyazobenzene and its sulfonation product, A_0 is the initial concentration of azoxybenzene, k_1 is the rate constant of the Wallach reaction, and k_2 is the rate constant for the sulfonation reaction. The parameters ϵ_1 , ϵ_2 , and k_2 were all measured independently, but A_0 was only known as approximately 20 μM . Tables III and IV show reasonably good agreement of the calculated and observed absorbances measured at 464 nm for k_1 values of 3.42×10^{-4} and 3.58×10^{-4} sec⁻¹ for the deuterated and

(9) C.-S. Hahn and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 949 (1962).

(10) P. H. Gore and G. K. Hughes, *Aust. J. Sci. Res., Ser. A*, **3**, 136 (1950). W. M. J. Strachan and E. Bunce, *Can. J. Chem.*, **47**, 4011 (1969).

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 8.

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).