potassium cyanides is normal for a reaction in a strongly ionizing solvent, in which the anion is able to function independently of the alkali cation attending it.

Reaction 10 above is one of a series of reactions in which a single sulfur atom is transferred from a donor to an acceptor, both reactants being basic in character. Other such reactions might be possible with thiocyanate, thiosulfate or triphenylphosphine sulfide as donors and with cyanide, sulfite or triphenylphosphine as acceptors. Of the nine possible exchange reactions involving these compounds, six have been studied. The exchange of sulfur between thiosulfate and sulfite has been shown to proceed at a measurable rate,[17] while the cyanide–thiocyanate exchange is immeasurably slow.[14] As another example of single-sulfur transfer we have measured the rate of the reaction between sodium cyanide and sodium thiosulfate in water, which proceeds irreversibly and establishes the cyanide ion as a stronger thiophile than the sulfite ion. The results are recorded in Table III; the activation parameters for this reaction, along with those of the sulfur exchange between thiosulfate and sulfite,[17] the reaction of trithionate and sulfite,[18] and the sulfur–cyanide reaction, are given in Table IV. The rate of the reaction between triphenylphosphine and sodium thiosulfate in aqueous methanol has been measured (Table V). The reaction is bimolecular and demonstrates that the phosphine is a stronger thiophilic reagent than sulfite. The reaction of cyanide with triphenylphosphine sulfide is immeasurably slow and only an upper limit on the rate can be estimated. Likewise, there seems to be no reaction between triphenylphosphine and thiocyanate. Therefore, the present data do not indicate the thiophilic order of triphenylphosphine and cyanide ion.

TABLE III

REACTION OF SODIUM CYANIDE WITH SODIUM THIOSULFATE IN WATER, IONIC STRENGTH 0.09

Temp., °C.	k_2, l. m.$^{-1}$ sec.$^{-1}$
25.00	3.9×10^{-5}
69.84	2.94×10^{-4}
90.00	8.62×10^{-4}

TABLE IV

ACTIVATION PARAMETERS AND RATE CONSTANTS AT 25°

Reaction	k_2, l. m.$^{-1}$ sec.$^{-1}$	E_a[a]	$\Delta H\ddagger$[a]	$\Delta S\ddagger$[b]
KCN + S_8[c]	32.0	12.0	11.4	− 4.7
NaCN + S_8[c]	33.6	11.5	10.9	− 5.7
NaCN + $Na_2S_2O_3$[d]	3.9×10^{-5}	13.0	12.4	−38
Na_2SO_3 + $Na_2S_2O_3$[d] [17]	5.0×10^{-5}	14.5	13.8	−32
Na_2SO_3 + $Na_2S_3O_6$[d] [18]	3.5×10^{-4}	11.1	9.5	−43

[a] ±0.5 kcal./mole. [b] Cal./mole degree. [c] Methanol. [d] Water.

TABLE V

SULFUR TRANSFER REACTIONS

$$X + SY \rightarrow XS + Y$$

X	SY	Solvent	Temp., °C.	k_2, l. m.$^{-1}$ sec.$^{-1}$
CN^-	$S{-}SO_3^{-2}$	H_2O	25	3.9×10^{-5}
$(C_6H_5)_3P$	$S{-}SO_3^{-2}$	80% MeOH[a]	25	3.3×10^{-3}
CN^-	$(C_6H_5)_3PS$	90% MeOH[a]	70	$<1 \times 10^{-7}$
$(C_6H_5)_3P$	SCN^-	90% MeOH[a]	70	$<4 \times 10^{-7}$
CN^-	SCN^-	H_2O[15]	25	$< 10^{-6}$
$SO_3^=$	SSO_3^{-2}	H_2O[17]	25	5.0×10^{-5}

[a] Weight per cent. methanol with water.

Table IV shows a great difference in rate between the reaction involving elemental sulfur and the others. This difference resides almost entirely in the entropy of activation which is responsible for a ratio of over six powers of ten between the rates.

CAMBRIDGE, MASSACHUSETTS

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[17] D. P. Ames and J. E. Willard, THIS JOURNAL, **73**, 164 (1951).

[18] A. Fava and G. Pajaro, *ibid.*, **78**, 5203 (1956); *Ann. chim.*, **43**, 502 (1953).

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Some Properties of Tetraalkyl-2-tetrazenes[1]

BY WILLIAM E. BULL,[2] JACOB A. SEATON AND L. F. AUDRIETH[3]

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Tetramethyl-2-tetrazene (TMT) and tetraethyl-2-tetrazene in ethanol reveal absorbancy maxima at 277 and 285 mμ with molar absorptivities of 8.3×10^3 and 7.6×10^3, respectively. Changes in absorption spectrum in various solvents have been related to the tendency for 2-tetrazenes to form protonated species in more acidic solvents. The basic nature of TMT has been characterized, using both analytical and titrimetric procedures, by formation of 1:1 compounds with the following protonic and non-protonic acids: $H_2C_2O_4$, $HOC_6H_2(NO_2)_3$, H_2SO_4, $HClO_4$, $CdCl_2$, $CdBr_2$, $HgCl_2$, $HgBr_2$, BF_3 and $AlCl_3$.

The search for a rapid and reliable procedure for the detection and estimation of the 2-tetrazenes led to a study of the ultraviolet absorption characteristics of these hydronitrogen derivatives along with a study of their chemical properties. The absorbancy maxima of compounds containing the azo chromophore generally lie between 240 and 290 mμ.[4] Alcoholic solutions of tetraethyl-2-tetrazene and tetramethyl-2-tetrazene were found to exhibit absorbancy maxima at 284 and 277 mμ, respectively. A linear plot of absorbancy *versus* concentration was obtained for 10^{-4} to 10^{-5} M ethanolic solutions of both tetrazenes measured at the respective wave lengths of maximum absorbancy. The molar absorptivities, a_M, of the tetraethyl- and tetramethyl-2-tetrazenes were found to

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[1] Abstracted in part from the doctoral dissertation submitted to the Graduate College of the University of Illinois by William E. Bull.

[2] Socony–Mobil Research Fellow at the University of Illinois, 1956–1957.

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[4] A. Gillam and E. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1954.

be 7.6 × 10^3 and 8.3 × 10^3, respectively.[5] Values of this magnitude for the molar absorptivities thus afford a simple and a sensitive method for detecting these substances in ethanolic solution.

Variations in the absorbancy maxima of the same substance in different solvents are usually attributed to chemical interaction between the solvent and solute, to the formation of complex species, to dissociation, or to the establishment of a tautomeric equilibrium. For ethanolic solutions of tetraethyl-2-tetrazene an absorbancy maximum is observed at 284 mμ with a perceptible shoulder at 247 mμ. In aqueous solutions, however, the 247 mμ absorption peak is greatly enhanced with the absorption at 284 mμ now appearing as a shoulder. The tetramethyl-2-tetrazene exhibited this phenomenon to a lesser degree in that change from ethanol to water as the solvent shows only a moderate enhancement of the shoulder along with some reduction of the maximum at 277 mμ.

One obvious difference between water and ethanol rests upon their relative acidities, *i.e.*, their respective tendencies to act as proton donors. Since the tetraalkyl-2-tetrazenes are basic in nature and are capable of acting as proton acceptors, the 2-tetrazene peaks with their differing intensities in ethanol and in water may be ascribed to the existence of an equilibrium between the molecular and the protonated or solvated forms of the 2-tetrazenes. Such an equilibrium may be pictured for the tetraethyl-2-tetrazene as

$$\underset{\text{max.} = 284\ \text{m}\mu}{Et_4N_4} + \underset{}{HA} \rightleftharpoons \underset{\text{max.} = 247\ \text{m}\mu}{Et_4N_4HA}$$

Consideration of the respective protolysis constants of water and of ethanol, 10^{-14} and 10^{-19}, respectively, fits such a picture. In ethanolic solution the molecular form would predominate. In aqueous solution there would be a greater tendency toward the formation of a protonated species. By slightly acidifying the ethanolic solution of tetraethyl-2-tetrazene with one drop of concentrated hydrochloric acid, the absorbancy maximum was found to shift to approximately 240 mμ. This shift appeared to verify the conclusion that the absorbancy is a function of the acidic nature of the solvent.

Further consideration of these findings led to the study of the ultraviolet absorption spectra of the tetraalkyl-2-tetrazenes in solvents of varying acidic and basic character. As the acidic nature of the solvent decreases the ratio of the absorbancy at the higher wave length to the absorbancy at the lower wave length increases. The data are summarized in Table I. The absorbancy ratio was found to be independent of the tetrazene concentration in water and in ethanol.

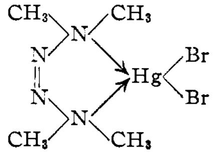
The ultraviolet absorption spectra of salts and of coördination compounds of tetramethyl-2-tetrazene lend support to this hypothesis. The ultraviolet absorption spectrum of the tetramethyl-2-tetrazene–mercuric bromide complex in ethanol was found to be identical to the spectrum of the acidic form of tetramethyl-2-tetrazene, *i.e.*, identical to the spectra of salts of tetramethyl-2-tetrazene.

TABLE I

VARIATION OF THE ABSORBANCY RATIO WITH CHANGE OF SOLVENT

Solvent	$\frac{A(\lambda = 284\ \text{m}\mu)}{A(\lambda = 247\ \text{m}\mu)}$ of Et_4N_4	$\frac{A(\lambda = 277\ \text{m}\mu)}{A(\lambda = 250\ \text{m}\mu)}$ of Me_4N_4
Water	0.508	1.22
Ethanol	1.54	1.71
Chloroform	1.45	1.69
Diethyl ether	..	2.03
Cyclohexane	..	2.01
n-Hexane	2.21	..

The fact that the mercuric bromide complex has a molecular weight corresponding to a monomer and is a non-conductor in ethanol suggests that its structure may be represented as



This structure retains the formal coördination number of four for the mercury(II) ion and also suggests that a *cis* modification is a more logical structure for the 2-tetrazenes than is a *trans* form. A Fisher–Taylor–Hirschfelder model of the above structure can be constructed readily and shows very little molecular strain.

Experimental

Materials.—Technical 1,1-dimethylhydrazine was used for the preparation of tetramethyl-2-tetrazene.

The procedure first described by Renouf[6] for the preparation of tetramethyl-2-tetrazene by the oxidation of 1,1-dimethylhydrazine using mercuric oxide was modified in several important details. One hundred-fifty grams of 80% 1,1-dimethylhydrazine (2.0 moles) was diluted with 750 ml. of ether in a 2-l. three-necked round-bottomed flask. The flask was fitted with a stirrer and a reflux condenser, and immersed in an ice-bath. Yellow mercuric oxide was added slowly through the reflux condenser to the constantly stirred solution over a period of two hours. The first 20 g. of mercuric oxide reacted relatively slowly. Subsequent quantities of the mercuric oxide were found to react almost instantly with evolution of sufficient heat to cause the ether solution to reflux. Addition of mercuric oxide was continued until a yellow color persisted in the reaction mixture. A total of 450 g. of mercuric oxide (2.02 moles) was required. Another two hours of continued rapid stirring was allowed for the completion of the reaction. The reaction mixture was filtered to remove the unreacted mercuric oxide and the free mercury, and this residue was washed with ether. The ethereal solution was separated from the aqueous layer which had formed during the reaction. The aqueous layer was extracted with ether and the combined ether solutions were dried with anhydrous sodium sulfate. The dry ether solution was concentrated by evaporation under reduced pressure. Seventy-six grams (0.65 mole) of product corresponding to a 65% yield was collected with a boiling range of 31–34° at 15 mm. This material was used directly to prepare many of the derivatives described below. Further purification was accomplished by redistilling from fused barium oxide. Pure tetramethyl-2-tetrazene was found to boil at 32 ± 0.5° at 15 mm. (reported b.p. 130° (760 mm.),[6] 44° (30 mm.)[7] and 25° (12 mm.)[8]).

Anal. Calcd. for $C_4H_{12}N_4$: C, 41.35; H, 10.42; N, 48.23. Found: C, 41.41; H, 10.28; N, 46.47.

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[5] W. R. McBride and H. W. Kruse, THIS JOURNAL, **79**, 572 (1957), recently reported a molar absorptivity of 7156 for tetramethyl-2-tetrazene in alkaline solution.

[6] E. Renouf, *Ber.*, **13**, 2169 (1880).

[7] J. Watson, *J. Chem. Soc.*, 3677 (1956).

[8] H. Wieland and A. Susser, *Ann.*, **392**, 184 (1912).

The tetraethyl-2-tetrazene used in this investigation was obtained from Dr. Ulrich Scheibler, who had separated it from the mixture obtained by the reduction of diethylnitrosamine with sodium in liquid ammonia. The sample was dried over sodium sulfate and distilled under vacuum, b.p. 79° at 12 mm.

Anal. Calcd. for $C_8H_{20}N_4$: C, 55.75; H, 11.70; N, 32.54. Found: C, 55.86; H, 11.92; N, 32.78.

Spectrophotometric Studies.—All spectrophotometric measurements were made on a Cary double beam recording spectrophotometer model 11, using matched fused silica cells of 1-cm. path length.

A stock solution was prepared by dissolving 1.1898 g. of tetraethyl-2-tetrazene in absolute ethanol and diluting with absolute ethanol to 500 cc. A diluted aliquot of the stock solution was found to exhibit an absorbancy maximum at 284 mμ. The molar absorbancy index of tetraethyl-2-tetrazene in ethanol at the peak of maximum absorption, 284 mμ, is 7.6 × 10^3. Figure 1 illustrates the variation of the absorption spectrum of tetraethyl-2-tetrazene in several different solvents of differing acidic tendencies. The variation of the absorption spectrum as a function of *p*H was applied to the determination of the pK_b of the 2-tetrazene. A value of 5.12 was obtained from measurements of absorbancy in various boric acid-sodium hydroxide buffers in which the ionic strength was maintained constant by the addition of potassium chloride.

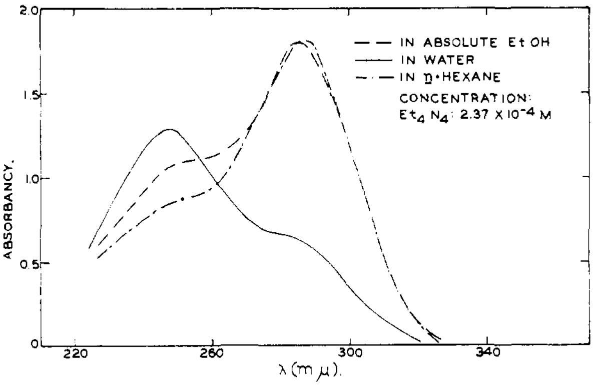

Fig. 1.—Ultraviolet absorption spectrum of tetraethyl-2-tetrazene in water, in ethanol and in *n*-hexane.

The spectrophotometric measurements on tetramethyl-2-tetrazene were made from a stock solution prepared in a similar manner. Variation of the absorption spectrum in water, ethanol and cyclohexane is depicted in Fig. 2.

Basic Derivatives of Tetramethyl-2-tetrazene.—Both the picrate and oxalate salts of tetramethyl-2-tetrazene were isolated. These compounds were prepared by the dropwise addition of the base to a stirred saturated solution of the acid. The picrate, $(CH_3)_4N_4{\cdot}(NO_2)_3C_6H_2OH$, m.p. 80° dec., was prepared by interaction of the components in ether.

(a) **Tetramethyl-2-tetrazene picrate**: *Anal.* Calcd. for $C_{10}H_{15}O_7N_7$: C, 34.78; H, 4.38; N, 28.11. Found: C, 35.01; H, 4.30; N, 27.90.

(b) **Tetramethyl-2-tetrazene hydrogen oxalate**, $(CH_3)_4N_4{\cdot}H_2C_2O_4$: *Anal.* Calcd. for $C_6H_{14}O_4N_4$: C, 34.95; H, 6.80; N, 27.18. Found: C, 34.99; H, 6.91; N, 25.64.

Coördination compounds of cadmium and mercuric halides with tetramethyl-2-tetrazene also were isolated. The cadmium compounds are stable crystalline materials and are only slightly soluble in organic solvents and insoluble in water. The mercuric compounds are much less stable than the cadmium compounds. The chloride was found to have the same solubility characteristics as the corresponding cadmium compound; the bromide was found to be soluble in ethanol and in benzene. Cryoscopic measurements of the tetramethyl-2-tetrazene mercuric bromide complex in benzene gave a molecular weight of 488. An ethanolic solution of the mercuric bromide complex was found to be a nonconductor and to exhibit an absorption spectrum identical to that of the protonated tetramethyl-2-tetrazene.

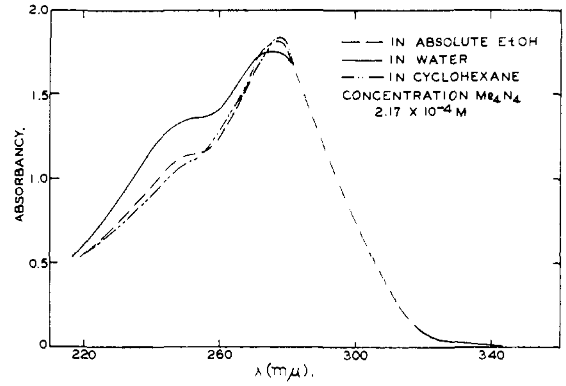

Fig. 2.—Ultraviolet absorption spectrum of tetramethyl-2-tetrazene in water, in ethanol and in cyclohexane.

These derivatives with the exception of the mercuric bromide complex were prepared by adding the crude tetramethyl-2-tetrazene dropwise with stirring to a saturated ethanolic solution of the metal halide. White crystals of the complex formed immediately. The crystals were then isolated by filtration and washed with ethanol. The mercuric bromide complex was prepared by adding a saturated solution of mercuric bromide dropwise to an ethanolic solution of tetramethyl-2-tetrazene. An excess of tetramethyl-2-tetrazene was always maintained. Upon addition of water to the ethanolic solution, a white crystalline material precipitated. The compound was isolated by filtration and recrystallized from warm ethanol.

(a) **Tetramethyl-2-tetrazene cadmium chloride**, m.p. above 250°: *Anal.* Calcd. for $C_4H_{12}N_4CdCl_2$: C, 16.37; H, 4.04; N, 19.04. Found: C, 16.34; H, 3.94; N, 19.08.

(b) **Tetramethyl-2-tetrazene cadmium bromide**, m.p. 138–140° dec.: *Anal.* Calcd. for $C_4H_{12}CdBr_2$: C, 12.39; H, 3.09; N, 13.90. Found: C, 12.10; H, 3.15; N, 14.02.

(c) **Tetramethyl-2-tetrazene mercuric chloride**, m.p. 93° dec.: *Anal.* Calcd. for $C_4H_{12}N_4HgCl_2$: C, 12.42; H, 3.10; N, 14.49. Found: C, 12.15; H, 3.06; N, 13.60.

(d) Tetramethyl-2-tetrazene mercuric bromide,[9] m.p. 87° dec.: mol. wt. calcd. 474, found 488.

An attempt to show the bidentate nature of the 2-tetrazene by replacement of the two coördinated chlorine atoms of *cis*-dichloro-bis-ethylenediaminecobalt(III) chloride was unsuccessful. The only product that could be isolated from the reaction mixture was tris-ethylenediaminecobalt(III) chloride.

By titration of a benzene solution of tetramethyl-2-tetrazene (TMT) with solutions of boron trifluoride etherate in benzene, perchloric acid in acetic acid, aluminum chloride in chloroform and sulfuric acid in acetic acid, it was possible to demonstrate the basic nature of the 2-tetrazene toward both protonic and Lewis acids. Crystal violet was used as an indicator. All titrations gave a sharp, yet fading, color change at a molecular ratio of 1:1, suggesting formation of the following complexes: $TMT{\cdot}BF_3$, $TMT{\cdot}HClO_4$, $TMT{\cdot}AlCl_3$, $TMT{\cdot}H_2SO_4$. The acid solutions were standardized by titration against a known benzene solution of pyridine using the same indicator.

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[9] Although no satisfactory analytical results could be obtained for this compound, the authors have no doubt that an actual compound is formed between mercuric bromide and the tetramethyl-2-tetrazene.