Apparently the ligand remaining after displacement of five of the six ligands in $(CH_3CN)_3W(CO)_3$ with three alkyne ligands depends on the nature of the alkyne. The electronegative CF_3 groups of the hexafluorobutyne-2 ligands may withdraw d electrons from the tungsten atom in $[(CF_3)_2C_2]_3WL$ complexes to the extent that insufficient electron density remains for stabilization of a tungsten–carbonyl bond by partial $p\pi$–$d\pi$ multiple bonding. Thus the ligand remaining attached to the tungsten atom in the hexafluorobutyne complex is the acetonitrile ligand which does not require any $p\pi$–$d\pi$ multiple bonding to form stable bonds with transition metals.

Acknowledgment.—We are indebted to Mr. M. B. Bisnette for assistance with the pressure reactions and other special experiments. We are indebted to the U. S. Air Force Office of Scientific Research for partial support under Grants AF-AFOSR-580-64 and AF-AFOSR-580-66. We also appreciate the generous samples of cyclooctatetraene provided by the Badische Anilin- und Soda-Fabrik, Ludwigshafen, Germany, for this and related research.

CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT,
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Acid Decomposition of Tetraalkyl-2-tetrazenes in Aqueous Solution[1]

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Kinetics for the decomposition of the conjugate acid of tetraalkyl-2-tetrazene homologs was studied, principally by spectrophotometric techniques. Rate data establish the effect of acidity, tetraalkyl-2-tetrazene concentration, temperature, and ionic strength upon the first-order reaction in aqueous solution. A linear free energy relationship was observed between the pK_b values determined for the tetraalkyl-2-tetrazenes and the rate constants for the acid decomposition. Arrhenius constants are nearly the same for the tetraalkyl-2-tetrazenes examined.

Introduction

The reaction for the decomposition of 1,1,4,4-tetraalkyl-2-tetrazenes in acid solution was postulated by Renouf[2] and Fischer and Troschke[3] according to the equation

$$R_2NN{=}NNR_2 + H_2O \xrightarrow{\text{acid}} R_2NH + RNH_2 + R'CHO + N_2 \qquad (1)$$

for the methyl and ethyl homologs, respectively. In eq 1 R′ represents the next lower homolog of R. Overberger and Marks[4] supported the general acid decomposition scheme for 2-tetrazenes described by Wieland and Fressel[5] which considered the initial formation of the secondary amine, nitrogen, and a decomposition fragment which subsequently hydrolyzed to give the primary amine and aldehyde. Although decomposition products were characterized for the above reaction and the stoichiometry established by nitrogen evolution, the kinetics for the acid decomposition has not been reported. Since evidence for the formation of the conjugate acid of a tetraalkyl-2-tetrazene from the corresponding 1,1-dialkyldiazenium ion, $R_2N^+{=}NH$, and its conjugate base in acid solution has been published,[6] we have undertaken a detailed study of the acid decomposition of a homologous series of tetraalkyl-2-tetrazenes, derivatives of an unsaturated hydronitrogen with type formula N_4H_4.[7] In this paper we present the kinetic data for the reaction.

Experimental Section

Materials.—Methods previously described for the preparation and reduction of dialkylnitrosamines[8] with lithium aluminum hydride in ether[9] and the oxidation of the corresponding 1,1-dialkylhydrazines with yellow mercuric oxide or potassium bromate[6] were used to prepare the tetraalkyl-2-tetrazenes. The 2-tetrazenes were purified by vacuum distillation from barium oxide and occasionally by gas–liquid partition chromatography;[6] the purity as estimated by ultraviolet spectra or gas–liquid partition chromatograms was 97–100%. All other materials used were reagent grade chemicals available commercially.

Kinetic Measurements.—The acid decomposition of tetraalkyl-2-tetrazenes in aqueous solution was followed principally by spectrophotometric measurements in the ultraviolet region. Glass-stoppered, 100-ml volumetric flasks nearly filled with the appropriate aqueous solution were equilibrated in a water or oil bath maintained within ±0.05° of the desired temperature. After the appropriate 2-tetrazene in ethanol or water was added to each flask, the solution was diluted to volume and equilibrated at the bath temperature with good agitation for 10–20 min before the initial absorbance, A_0, was measured. During these studies the initial 2-tetrazene concentration was approximately 2×10^{-4} *M* with the pH adjusted to about 2. The limited solubility of the higher homologs of the tetraalkyl-2-tetrazenes in

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[1] Presented in part before the Division of Inorganic Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

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

[3] E. Fischer and H. Troschke, *Ann.*, **199**, 294 (1879).

[4] C. G. Overberger and B. S. Marks, *J. Am. Chem. Soc.*, **77**, 4097 (1955).

[5] H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).

[6] W. R. McBride and E. M. Bens, *J. Am. Chem. Soc.*, **81**, 5546 (1959).

[7] L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, pp 3–6.

[8] For a review of carcinogenic effects ascribed to nitrosamines see J. H. Weisburger and E. K. Weisburger, *Chem. Eng. News*, **44**, No. 6, 124 (1966).

[9] H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *J. Am. Chem. Soc.*, **77**, 790 (1955).

water required that stock solutions of these 2-tetrazenes be prepared with ethanol. The total amount of alcohol (1.0% maximum) was held constant for a given compound because spectral characteristics of the 2-tetrazenes are known to be dependent upon the solvent. Spectra were taken with a Cary Model 11 instrument at constant wavelength corresponding to the absorption maxima of the 2-tetrazene or by scanning the spectrum from 300 to 220 mμ. Special attention was taken to ensure that during a run the time from withdrawal of the equilibrated solution to the recording of its spectral data was constant. Spectral blanks from solutions prepared in a manner identical with those used in the experiments, except for the omission of the 2-tetrazene, and solutions allowed to decompose for about 12 half-lives were in good agreement.

The validity of the spectrophotometric method was confirmed by independently measuring the rate of nitrogen evolution during the decomposition of tetramethyl-2-tetrazene. In a typical experiment, 0.1097 g of tetramethyl-2-tetrazene was added to 100 ml of 0.02 *M* perchloric acid in a double-jacketed flask connected to an atmospheric hydrogenation apparatus. The acid solution stirred constantly by means of a magnetic stirring bar was maintained at 30.0 ± 0.1° with circulating water from a constant-temperature bath. The volume of gas was measured at room temperature and pressure at regular intervals; a blank was run using 0.02 *M* perchloric acid.

Additional data for the rate of decomposition of tetramethyl-2-tetrazene at 25.5 ± 1.0° were obtained with a Varian A-60 nmr spectrophotometer. In one experiment 0.046 g of tetramethyl-2-tetrazene was dissolved in 5.02 g of deuterium oxide to which 6 *M* sulfuric acid in deuterium oxide was added until the pH of the solution was about 2.0; 0.06 g of sodium 3-(trimethylsilyl)-1-propanesulfonate was used as an internal marker. The decomposition of one portion of this solution was followed spectrophotometrically while the decomposition of the other portion was followed with the nmr spectrophotometer.

Determination of pK_b Values.—The method of Stenstrom and Goldsmith[10] was used to determine pK_b values for the tetraalkyl-2-tetrazenes studied. An aliquot of the stock 2-tetrazene solution was added to a buffer solution,[11] followed by a sodium chloride solution to adjust the total concentration to about 0.16 *M*. Spectra were obtained over the region from 300 to 220 mμ within 3 min after the addition of the 2-tetrazene. A buffer-plus-salt solution was used as a blank for the spectrum; generally, 1-cm cells were used except that 10-cm cells were employed for some of the higher homologs. Immediately after the spectrum was obtained, the pH of the 2-tetrazene solutions was determined with a Beckman Model G or Model H2 pH meter standardized with certified commercial buffer solutions. All measurements were made at room temperature, 24.5 ± 1.0°.

Results

Comparable data for the decomposition of tetramethyl-2-tetrazene in acid solution were obtained to at least 30% decomposition by methods involving evolution of nitrogen gas, nmr resonance, and ultraviolet absorption. First-order kinetics was indicated in all cases. Typical rate constants for tetramethyl-2-tetrazene at 30.0° were 2.08×10^{-5} and 2.02×10^{-5} sec^{-1} based on gasometric and spectrophotometric data, respectively. Area measurements associated with dimethylamine and tetramethyl-2-tetrazene from several nmr experiments confirmed the 1 to 1 correspondence between the formation of the dimethylamine salt and the decomposition of the conjugate acid of the 2-tetrazene. Reasonably satisfactory first-order rate constants were obtained from the nmr data; concentration effects precluded fully quantitative results. In addition to the formation of the dimethylamine salt and nitrogen from the decomposition of tetramethyl-2-tetrazene, the presence of an unidentified intermediate was observed from nmr spectra; after 3 days at room temperature, salts of dimethylamine and methylamine were the only major products. Formaldehyde was identified from the decomposed solution by the isolation of its 2,4-dinitrophenylhydrazone.[12] No positive test for formaldehyde using Schiff's reagent[13] was observed for a hydrochloric acid solution of tetramethyl-2-tetrazene after 30 and 120 min unless the acidic solution was first made basic and then reacidified; qualitatively, the formaldehyde increased with decomposition time. The analysis of aliquots from the decomposition of tetramethyl-2-tetrazene in a hydrochloric acid solution gave negative results for active chlorine by a colorimetric procedure.[14] Subsequently, absorbance measurements at 263 mμ[15] of an N-chlorodimethylamine solution at 25.0° and a pH of about 2 indicated a rate of decomposition several times faster than tetramethyl-2-tetrazene under comparable conditions. Since results obtained by nmr, gas evolution, and spectrophotometric techniques were generally in agreement, detailed rate data presented hereafter were obtained only by the spectrophotometric method.

Relevant spectral data for the conjugate acid of most tetraalkyl-2-tetrazenes studied are summarized in Table I. Absorbance values at wavelengths characteristic of both the 2-tetrazene and its conjugate acid were employed for determining the pK_b values at 25.0°.[10] The maximum difference in the two values was 0.04 unit for the 2-tetrazenes listed; average pK_b values are reported in Table I.

TABLE I

SPECTRAL DATA FOR TETRAALKYL-2-TETRAZENES

2-Tetrazene	λ_{max}, mμ	log ε	pK_b at 25.0°
Tetramethyl	236	3.950	7.78
1,4-Diethyl-1,4-dimethyl	233	3.823	7.21
1,1-Diethyl-4,4-dimethyl	235	3.976	6.95
1,4-Diisopropyl-1,4-dimethyl	234	3.989	6.92
Tetraethyl	238	3.957	6.45
Tetra-*n*-propyl	242	3.948	6.30

Typical results for the decomposition of tetramethyl-2-tetrazene at various temperatures are presented in Figure 1. Relative absorbance, A/A_0, is plotted *vs.* time. In many cases the first-order relationship was observed for more than 90% decomposition of the 2-tetrazenes. Numerically, the data were treated by the method of least squares with the equation: $\log (10A_0/A) = St + Y$; every point was given equal weight. The theoretical intercept, Y, at time $t = 0$ is 1.000;

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[10] W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

[11] Universal buffer solutions of phosphoric, acetic, and boric acids with sodium hydroxide: H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 1456 (1931).

[12] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 171.

[13] J. F. Walker, "Formaldehyde," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1964, pp 468, 469.

[14] I. Weil and J. C. Morris, *J. Am. Chem. Soc.*, **71**, 1664 (1949).

[15] I. Weil and J. C. Morris, *ibid.*, **71**, 3123 (1949).

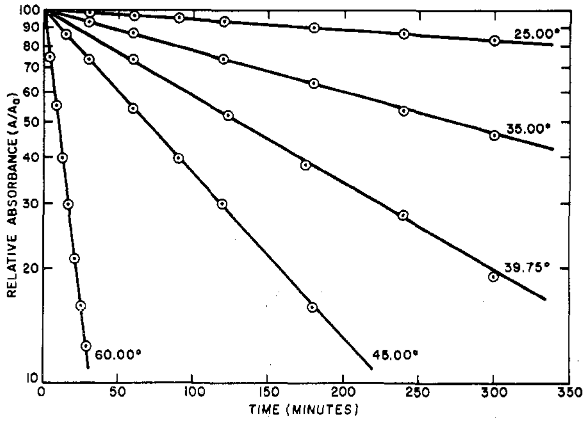

Figure 1.—Typical first-order data for the acid decomposition of tetramethyl-2-tetrazene at various temperatures.

the rate constant, k, in sec^{-1} is determined from the slope S. The calculated rate constants and intercepts, together with standard deviations[16] (in parentheses) associated with the least significant figure or figures and the number of data points, n, are given in Table II. No significant difference in rate data for aqueous solutions and those with up to 1% alcohol was observed for tetraethyl- and tetra-*n*-propyl-2-tetrazenes, those compounds for which comparable data were available. Data in Tables III–VI are treated numerically in the same manner as described above.

Arrhenius constants were calculated by the method of least squares using the rate data from Table II. These results are presented in Table III. No correlation of ΔE or log A with the member of the homologous series is evident from the data.

The influence of tetramethyl-2-tetrazene concentration on its rate of decomposition in acid solution was also investigated. These results are summarized in Table IV. The pH of the solution was about 2 at all 2-tetrazene concentrations except 2.00×10^{-1} M, where the acidity was 0.703 M (corrected to a pH of about 2, $k = 6.18 \times 10^{-5}$ sec^{-1}). At tetramethyl-2-tetrazene concentrations greater than 2×10^{-3} M, the solutions often became yellow to red,[17] accompanied by an increase in decomposition rate. In these cases the rate was calculated from the initial slope.

Sodium chloride and sodium perchlorate were added to solutions of tetramethyl-2-tetrazene in order to investigate the effect of ionic strength on the rate of decomposition. Typical data are included in Table V for low ionic strength; results for high ionic strength are given in Table VI.

Figure 2 illustrates the influence of pH on decomposition rate of tetramethyl-2-tetrazene at 25.00°. In the range from 1.0 to 5.0 the rate constants are independent of pH. At lower pH values the decomposition rate of tetramethyl-2-tetrazene was increased substantially. A linear relationship was obtained if rate constants were plotted *vs.* an acidity function, H_0. These results are given in Figure 3. The molar absorptivity of the conjugate acid of tetramethyl-2-tetrazene was constant at these acid concentrations.

TABLE II

RESULTS FOR THE ACID DECOMPOSITION OF TETRAALKYL-2-TETRAZENES

Temp, °C	10^5k, sec^{-1}	Intercept	n
	Tetramethyl		
24.75	0.968 (10)	1.003 (1)	7
25.00	0.976 (3)	1.001 (<1)	14
25.00	0.996 (7)	1.003 (1)	11
25.00	1.003 (5)	1.002 (<1)	14
35.00	4.26 (3)	1.002 (1)	8
35.00	4.34 (2)	1.002 (2)	11
35.00	4.41 (7)	1.000 (2)	7
39.75	9.15 (7)	1.009 (4)	12
45.00	17.00 (7)	1.002 (2)	9
50.00	34.2 (3)	1.015 (4)	13
55.00	64.0 (6)	1.012 (5)	11
60.00	119.8 (7)	1.007 (4)	9
60.00	122.6 (7)	1.007 (3)	7
	1,4-Diethyl-1,4-dimethyl		
25.00	2.08 (2)	1.000 (3)	12
35.00	9.25 (10)	0.996 (5)	12
45.00	38.1 (4)	0.999 (5)	9
	1,1-Diethyl-4,4-dimethyl		
35.00	18.7 (1)	0.997 (3)	12
40.00	37.1 (2)	0.997 (2)	12
45.00	76.0 (3)	1.004 (2)	12
50.00	142.0 (7)	0.997 (3)	8
	1,4-Diisopropyl-1,4-dimethyl		
25.00	5.46 (2)	0.998 (1)	11
30.00	11.59 (2)	0.997 (<1)	10
35.00	23.8 (<1)	0.999 (<1)	11
45.00	93.2 (7)	0.997 (3)	6
50.00	158.8 (14)	0.993 (4)	6
	Tetraethyl		
24.75	7.65 (2)	1.001 (<1)	13
35.00	32.5 (2)	0.998 (3)	9
45.00	112.8 (8)	1.001 (4)	8
	Tetra-*n*-propyl		
15.00	3.73 (3)	0.997 (2)	10
25.00	17.16 (3)	0.999 (<1)	11
35.00	69.3 (3)	0.998 (2)	10
	Tetraisopropyl		
20.00	32.7 (<1)	0.998 (<1)	12
22.50	46.0 (3)	0.993 (2)	11
25.00	62.6 (8)	0.994 (4)	9
27.50	97.1 (3)	0.998 (2)	11
30.00	135.8 (7)	0.991 (3)	10
32.50	195.4 (5)	1.000 (1)	7
	Tetra-*n*-butyl		
30.00	26.5 (3)	0.993 (3)	9
30.00	28.4 (2)	0.997 (2)	11
35.00	60.2 (5)	1.005 (4)	11
40.00	102.0 (10)	0.997 (4)	8

TABLE III

ARRHENIUS CONSTANTS FOR TETRAALKYL-2-TETRAZENES

2-Tetrazene	ΔE, kcal/mole	Log A, sec^{-1}
Tetramethyl	27.1 (1)	14.8 (1)
1,4-Diethyl-1,4-dimethyl	27.4 (1)	15.4 (<1)
1,1-Diethyl-4,4-dimethyl	26.9 (3)	15.3 (2)
1,4-Diisopropyl-1,4-dimethyl	26.0 (3)	14.8 (2)
Tetraethyl	25.0 (2)	14.3 (2)
Tetra-*n*-propyl	25.8 (1)	15.1 (1)
Tetraisopropyl	25.7 (5)	15.6 (4)
Tetra-*n*-butyl	25.2 (12)	14.6 (9)

Discussion

The presence and relative abundance of products from the acid decomposition of tetramethyl-2-tetrazene are

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[16] A. M. Mood, "Introduction to the Theory of Statistics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp 291–294.

[17] The esr spectrum of such a solution was characteristic of that of the tetramethyl-2-tetrazene radical cation: W. M. Tolles, D. W. Moore, and W. E. Thun, *J. Am. Chem. Soc.*, **88**, 3476 (1966).

TABLE IV

EFFECT OF INITIAL CONCENTRATION OF TETRAMETHYL-2-TETRAZENE ON ITS DECOMPOSITION RATE AT 35.00°

Concn, *M*	10^5k, sec^{-1}	Intercept	*n*
2.05×10^{-5}	4.31 (1)	1.000 (1)	12
4.00×10^{-5}	4.33 (2)	1.001 (1)	12
1.24×10^{-4}	4.35 (3)	1.000 (2)	7
2.23×10^{-4}	4.41 (7)	1.000 (2)	7
4.03×10^{-4}	4.56 (2)	1.002 (1)	9
1.00×10^{-3}	4.96 (3)	1.001 (1)	8
2.22×10^{-3}	4.99 (9)	1.010 (4)	8
2.01×10^{-2}	5.21 (7)	1.007 (3)	7
2.00×10^{-1}	7.11 (18)	1.003 (4)	9

TABLE V

EFFECT OF SODIUM CHLORIDE ON DECOMPOSITION OF TETRAMETHYL-2-TETRAZENE AT 35.0°

Ionic strength	10^5k, sec^{-1}	Intercept	*n*
0.0017	4.61 (2)	1.001 (2)	9
0.0097	4.62 (3)	1.005 (2)	9
0.0194	4.68 (3)	1.006 (3)	9
0.0390	4.60 (2)	1.004 (2)	9

TABLE VI

EFFECT OF HIGH IONIC STRENGTH ON DECOMPOSITION OF TETRAMETHYL-2-TETRAZENE AT 25.0°

Ionic strength	10^5k, sec^{-1}	Intercept	*n*
	Sodium Chloride		
0.87	1.06 (<1)	1.004 (1)	9
1.78	1.16 (<1)	1.004 (1)	8
3.73	1.34 (<1)	1.000 (<1)	8
5.79	1.58 (<1)	1.000 (<1)	9
	Sodium Perchlorate		
0.69	1.27 (1)	1.005 (2)	10
2.59	1.83 (1)	1.003 (2)	9
5.36	2.57 (2)	1.001 (3)	9
8.19	3.65 (3)	1.007 (3)	7

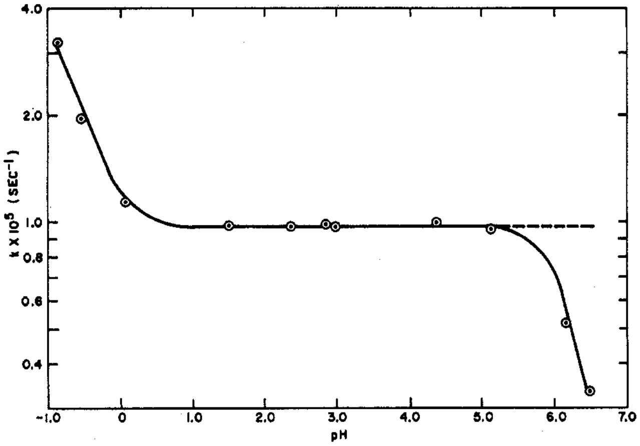

Figure 2.—Influence of pH on the rate of decomposition of tetramethyl-2-tetrazene in aqueous solution at 25.00°.

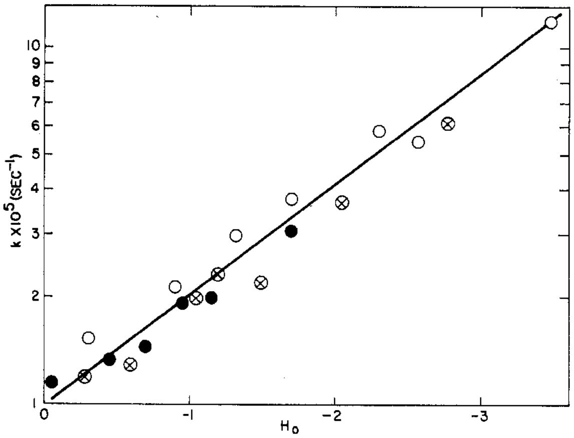

Figure 3.—Correlation of rate constants for the decomposition of tetramethyl-2-tetrazene with acidity function for perchloric acid (○), sulfuric acid (⊗), and hydrochloric acid (●).

in agreement with the previous literature[2-5] and with a recent investigation.[18] In hydrochloric acid solution an N-chloro intermediate may be formed in low concentration which is eventually converted to N-methylmethylenimine through the loss of hydrogen chloride. The conjugate acid of N-methylmethylenimine is almost certainly the unidentified intermediate observed in nmr spectra which hydrolyzes slowly to give methylamine salt and formaldehyde. It has been noted that N-methylmethylenimine polymerizes to a trimer in basic solutions but not in acid solutions.[19] Furthermore, the trimer decomposes rapidly in acid solutions to yield methylamine salts and formaldehyde.[20] These results explain why formaldehyde could not be detected in an acid solution during the first portion of the decomposition of tetramethyl-2-tetrazene but was detected after the solution had been made basic and then acid again and confirm that N-methylmethylenimine is an intermediate during the decomposition.

From spectrophotometric data it is clear that tetraalkyl-2-tetrazenes, T, react with acid, HA, in aqueous media to form conjugate acids

$$T + HA \rightleftharpoons TH^+ + A^- \qquad (2)$$

If the pH of the aqueous solution is such that both 2-tetrazene and its conjugate acid are present, the observed rate will depend upon the fraction of the 2-tetrazene present in each form and their respective rates. Experimentally, rates fall off at pH values higher than 5 as indicated by the points in Figure 2. If the rate is multiplied by the factor $([T] + [TH^+])/[TH^+]$ (this ratio may be estimated from spectrophotometric measurements, Table I), rates continue along the horizontal broken line at high pH values indicating only the conjugate acid is subject to decomposition

$$TH^+ \longrightarrow \text{products} \qquad (3)$$

The first-order constants may be calculated from the equation $k = k_2[H^+]/(K_{TH^+} + [H^+])$,[21] where k_2 is the rate in a sufficiently strong acid solution so that all of the 2-tetrazene is present as the conjugate acid. Calculated constants, k, are given by the solid line in Figure 2 at high pH values, indicating good agreement with the experimental data obtained in this pH range.

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[18] C. Bighi, A. Betti, and G. Saglietto, *Ann. Chim.* (Rome), **56**, 48 (1966).

[19] E. A. Werner, *J. Chem. Soc.*, 844 (1917).

[20] H. Tada, *J. Am. Chem. Soc.*, **82**, 266 (1960).

[21] R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, pp 122–127.

The rate of decomposition of 2-tetrazenes is increased in strongly acid solutions. Although this increase implies a reaction involving the second conjugate acid TH_2^{2+}, the constant molar absorptivity of the conjugate acids in these solutions may suggest that this increase is due to specific acid catalysis. A line with slope 0.35 is obtained if log k is plotted *vs.* the acidity function H_0 (Figure 3).[22] If log k is plotted *vs.* log $a_{\mathrm{H_2O}}$, a curve with steadily decreasing absolute slope is obtained.[23] A w value of -1.4, well within the range -2.5 to 0.0, suggests that water is not involved in the transformation of the conjugate acid to a transition state.[24] If the frequency factor is kT/h and the activation energies from Table III are used, ΔS^* at 25° is 9.5 eu. This is about the value expected from the known correlation of ΔS^* with w values and may result from solvation changes between reactants and the transition state even though water is not required for the conversion of the conjugate acid to the transition state.[25]

At low ionic strength the rate of decomposition of the conjugate acid of tetramethyl-2-tetrazene was unaltered (Table V). At higher concentrations the logarithm of the rate constant increased linearly with ionic strength for the salts studied. These data in Table VI are in agreement with the known effect of ionic strength.[26]

A linear free energy relationship (correlation coefficient 0.98) is obtained when the rate of decomposition and basicity of tetraalkyl-2-tetrazenes are compared (Figure 4). This would be expected if the conjugate acid of the 2-tetrazene were involved in two similar equilibrium processes such as that represented by eq 2 and one involving the conjugate acid and an activated complex. Under such circumstances the relative free energy changes in the equilibria would be effected similarly by change of alkyl groups on the 2-tetrazene.[27]

The decomposition of dilute aqueous solutions of tetraalkyl-2-tetrazenes, as well as their formation,[6] takes place *via* ionic intermediates in dilute acids. When high concentrations of 2-tetrazenes or acids are employed, side reactions involving radicals may occur during the decomposition. Overberger and Marks[4] noticed that a mechanism different from the one presented in the Introduction was operative during the acid decomposition of 2-tetrazenes in certain nonaqueous media. In solutions of very high acidity, the second conjugate acid of the 2-tetrazene may be formed and may lose nitrogen to form two radical cations.[28] Indeed, the molar absorptivity of the conjugate acid of tetramethyl-2-tetrazene appears to be decreased in 96% sulfuric acid. At the more concentrated 2-tetrazene concentrations radical species are produced.[17] Tetramethyl-2-tetrazene has been pyrolyzed[29] or photolyzed[30] in organic liquids to yield dimethylamino radicals. It seems that a similar reaction involving the conjugate acid may be operative and that the radicals produced can dehydrogenate the conjugate acid[30] to form the tetramethyl-2-tetrazene radical cation.[31] In the region for which values for the Arrhenius constants were obtained in the present work, however, the scheme proposed by Wieland and Fressel[5] accurately represents the acid decomposition of tetraalkyl-2-tetrazenes.

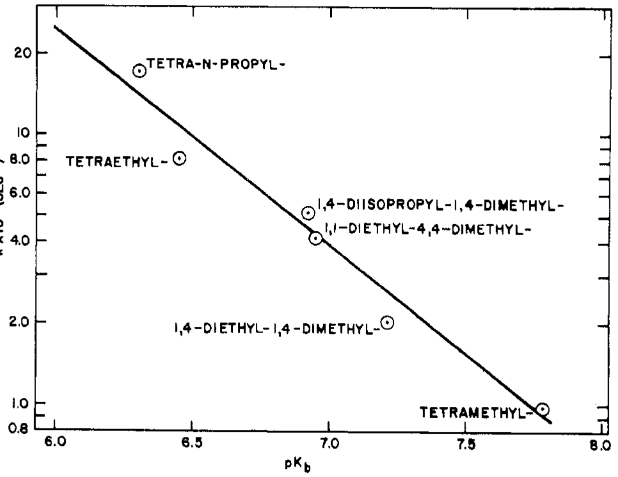

Figure 4.—Correlation of rate constants for the acid decomposition of tetraalkyl-2-tetrazenes with basicity at 25.00°.

Acknowledgment.—We wish to thank Mr. Everett M. Bens and Dr. Wayne R. Carpenter for assistance with gas–liquid partition chromatographic separation of the 2-tetrazenes and Dr. Herman F. Cordes for writing a program to compute the values associated with the acid decompositions.

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[22] F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

[23] J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).

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[25] J. F. Bunnett, *ibid.*, **83**, 4973 (1961).

[26] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, pp 150–155.

[27] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[28] G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, **28**, 3275 (1963).

[29] B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

[30] D. Mackay and W. A. Waters, *ibid.*, *Sect. C*, 813 (1966).

[31] The radical cation is produced more quickly when about 0.1 *M* tetramethyl-2-tetrazene (pH ~2) is irradiated with ultraviolet light than if there is no irradiation.