[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE CATHOLIC UNIVERSITY OF AMERICA]

The Dimethylamino Radical[1]

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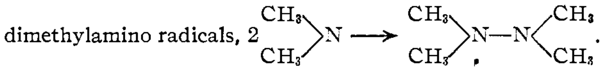
RECEIVED DECEMBER 26, 1956

A paramagnetic violet solid is obtained by passing dilute vapors of tetramethyltetrazene ($(CH_3)_2N—N{=}N—N(CH_3)_2$) over a tungsten filament heated to about 1300° and then quickly condensing the products onto a liquid nitrogen-cooled surface. This material changes suddenly and irreversibly to a white solid when warmed to about −160°. The resulting mixture contains substantial quantities of tetramethylhydrazine which presumably results from the condensation of two dimethylamino radicals,  $2\,(CH_3)_2N \longrightarrow (CH_3)_2N—N(CH_3)_2$. These results strongly suggest that the violet material is the dimethylamino radical. The violet material also was prepared by irradiating the vapors of tetramethyltetrazene with intense ultraviolet light and quickly freezing the products with liquid nitrogen.

Audrieth and Ogg[2] have reviewed the chemistry of hydrazine and point out that tetra-substituted tetrazenes exhibit thermal instability and when heated yield nitrogen gas and tetra-substituted hydrazines. For example, azyl radicals have been postulated[3] as the intermediate which condenses to form the substituted hydrazine as

$$R_2N—N{=}N—NR_2 \longrightarrow 2R_2N\cdot + N_2$$

$$2R_2N\cdot \longrightarrow R_2N—NR_2$$

Our experiments were designed to stabilize the intermediates formed during the vapor phase decomposition of tetramethyltetrazene by quickly freezing the products of the reaction with liquid nitrogen. Under the proper conditions we found that it was possible to stabilize a very reactive violet material which appeared to be stable indefinitely at −196° but which changed suddenly to a white solid when allowed to warm up to about −160°.

Experimental

In preparing tetramethyltetrazene the method of Renouf[4] was modified slightly. An ethereal solution of unsymmetrical dimethylhydrazine was oxidized with silver oxide. The powdered silver oxide was added at a rate such that the solution refluxed gently. After the required amount of oxidizing agent had been added, the mixture was cooled and the crude product was obtained by filtering the solution, drying it over anhydrous potassium carbonate and then removing the ether under reduced pressure. The product was distilled *in vacuo* and the fraction boiling at 25° at 12 mm. was collected.

The Thermal Reaction.—Tetramethyltetrazene vapors at low pressure (~0.1 mm.) were passed over a tungsten filament heated to between 1200 and 1300° as determined by an optical pyrometer. The rate of flow was about 10^{-4} moles per minute and after a few minutes, a violet deposit collected on a liquid nitrogen-cooled finger which was about 3 cm. from the hot filament. If the finger was brought closer to the wire, adverse radiation effects were encountered and no violet material was obtained. Preliminary experiments had shown that the violet material is not formed when tetramethyltetrazene is passed through a quartz furnace in the usual way. Indeed, even with a tungsten filament, the geometry of the apparatus is important in obtaining the violet deposit.

The permanent gases formed during this phase of the reaction were removed from the system by means of a high speed diffusion pump and were collected in a gas buret. A sample of these gases was analyzed on the mass spectrometer and the following results were obtained: % N_2, 70.5, 71.5; % H_2, 24.8, 23.6; % CH_4, 4.5, 4.7. In a typical experiment 1.16×10^{-3} moles of tetramethyltetrazene produced 0.74×10^{-3} moles of permanent gas. Thus each mole of tetramethyltetrazene used produced 0.45 mole of N_2. If one makes the reasonable assumption that the nitrogen is produced mainly by the reaction $(CH_3)_2N—N{=}N—N(CH_3)_2 \rightarrow 2(CH_3)_2\text{-}N\cdot + N_2$, then under the conditions of this experiment about half of the tetramethyltetrazene escapes decomposition.

The deposit which collected on the filter was a violet, paramagnetic solid and its appearance did not change after standing for several hours at −196°. The liquid nitrogen was removed from the finger and liquid propane at −190° was added and allowed to warm up slowly. When the temperature reached −160° the violet color disappeared quite suddenly and a white deposit resulted. No permanent gas was evolved during this transition.

The deposit was then warmed to −78° and by means of a mass spectrometric analysis, it was found that traces of all three methylamines vaporized at this temperature. When the deposit was finally warmed to room temperature all of the material was in the vapor phase and a representative sample of the vapors was analyzed on the mass spectrometer. The mass spectrum of the products contained a peak at $m/e = 88$ which is characteristic of tetramethylhydrazine. The products also contained a substantial amount of undecomposed tetramethyltetrazene, and the ratio of the peak at $m/e = 116$, which is characteristic of the tetramethyltetrazene, to the peak at $m/e = 88$ was 1.14. The exact concentrations of these two substances cannot be obtained simply by a comparison of these peaks, since the ratio of the ion concentrations need not be the same as the ratio of the concentrations of the two materials present. It can, however, be concluded that both tetramethyltetrazene and tetramethylhydrazine were present in comparable concentrations.

The Photolytic Reaction.—The vapors of tetramethyltetrazene were passed through a quartz tube which was irradiated with a low pressure mercury lamp. The mercury lamp consisted of a quartz tube 12 mm. in diameter and six feet long (the tube was coiled spherically in six coils and was placed concentrically about the reaction chamber which also consisted of a quartz tube 12 mm. in diameter). The two electrodes consisted of tungsten to quartz seals and were sealed to the ends of the spiral. The lamp contained a few drops of mercury and a few mm. of an inert starter gas. The cold finger was located at the exit end of the reaction tube about 2.5 cm. from the last coil of the lamp.

The flow characteristics of the system were the same as in the experiments where the hot tungsten filament was employed, but in the photolytic case a much larger amount of material had to be used before a good colored deposit was obtained. This was because, in the photolytic reaction, only 2-3% of the tetramethyltetrazene, as determined by the amount of nitrogen formed during the reaction, was decomposed.

The deposit appeared to be identical with the product formed during the thermal decomposition on the tungsten filament. The transition to a white solid took place at −160° when the violet deposit was warmed slowly. In a blank experiment where all conditions were the same except that the lamp was not on, the deposit which collected was

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(1) This work was supported in part by Atomic Energy Commission contract No. AT-(40-1)-1305.

(2) L. F. Audrieth and R. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, New York, N. Y., 1951.

(3) Wieland and Fressel, *Ann.*, **392**, 133 (1912).

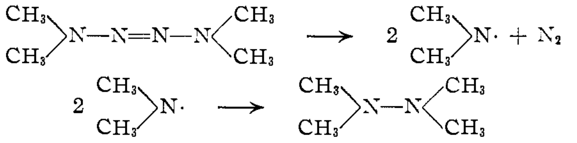
(4) E. Renouf, *Ber.*, **13**, 2173 (1880).

white and no transition could be observed when it was warmed to −160°.

The mass spectrum of the residue at room temperature indicated that a small but definite amount of tetramethylhydrazine was present in the products. The only other material which could be identified definitely was the undecomposed tetramethyltetrazene.

Discussion

The main products of the reaction were found to be nitrogen and tetramethylhydrazine and so it seems reasonable to assume that the following mechanism accounts for the main part of the reaction.



This last reaction occurs at −160° when the transition from violet to white is observed.

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Rate Constants for the Recombination of Iodine Atoms in Liquid Hexane and Decane; Temperature Coefficient for the Recombination in Carbon Tetrachloride

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RECEIVED JANUARY 7, 1957

The rate constants for the combination of iodine atoms in CCl_4, n-C_6H_{12} and n-$C_{10}H_{22}$ at room temperature and in CCl_4 at 50° have been determined using flash photolysis techniques. The value of the constant is not greatly influenced by the chain length of the hydrocarbon solvent. The activation energy of the reaction in CCl_4 is about 3 kcal./mole.

By the methods of flash photolysis it is possible to measure directly the rates of atom recombination reactions. This has been done for iodine atoms[2] and bromine atoms[2c,2e] in the gas phase, as a function of temperature,[2b,2e] and for iodine atoms in carbon tetrachloride[2c,3,4] and heptane[3] solutions at room temperature. Values for the recombination rate of iodine atoms in carbon tetrachloride and in hexane have also been calculated[5] by combining photostationary state data[6] with quantum yield data,[5] and with lifetime measurements[7] made by the rotating sector technique. Values for the quantum yields for escape of iodine atoms from their parent molecular partnership have been determined both directly by flash photolysis[3,4] and by the use of a scavenger for iodine atoms.[5] Such data are gradually providing a more quantitative knowledge of the life history of atoms and radicals in solution.

In the present work the rate constants for the recombination of iodine atoms in hexane, decane and carbon tetrachloride at room temperature and in carbon tetrachloride at 50° have been determined by the flash photolysis method, using equipment and techniques similar to those reported elsewhere.[2e,4]

The solvents used were Mallinckrodt "AR low sulfur" carbon tetrachloride, Phillips "pure" grade hexane and Matheson decane. The hydrocarbons were further purified by fractional distillation and prolonged mechanical stirring with concentrated H_2SO_4, followed by washing and drying. They were degassed and transferred to the reaction cell under vacuum, the hexane being distilled through phosphorus pentoxide in the process.[8]

TABLE I

COMPILATION OF RATE CONSTANTS FOR IODINE ATOM COMBINATION IN SOLUTION

	k, l. moles^{-1} sec.$^{-1}$ × 10^{-10}			
Solvent[a]	This work[b]	Marshall and Davidson[3]	Rabinowitch and Wood and Noyes and co-workers[5]	Strong and Willard[4]
CCl_4	0.69 ± 0.06	0.72 ± 0.01	0.84	0.57 ± 0.05[c]
CCl_4(50°)	1.03 ± 0.15			
n-C_6H_{12}	1.8 ± 0.6		1.56	
n-C_7H_{16}		2.2 ± 0.4	1.02	
n-$C_{10}H_{22}$	1.6 ± 0.4			

[a] All at room temperature except for the CCl_4 experiments at 50°. [b] The data are the average of 11 experiments for CCl_4 at 23°, 8 for CCl_4 at 50°, 32 for n-C_6H_{14} and 26 for n-$C_{10}H_{22}$. The limits given are the standard deviation. [c] The difference between this value and that obtained in the present work on the same instrument is of the order of the discontinuous instrumental variations previously described.[2e]

The results of this work and previous determinations of the rate constants (defined as k in $d[I_2]/dt = k[I]^2$) of atom recombinations in solution are given in Table I. Considering the difficulties of such experiments the degree of agreement between different workers and different methods for the carbon tetrachloride solutions and for similar hydrocarbons is gratifying.

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(1) Ravensham College, Cuttack, India. Fulbright Smith-Mundt Scholar (1953–1954), Project Associate (1954–1955), University of Wisconsin.

(2) (a) M. L. Christie, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **A216**, 152 (1952); (b) K. E. Russell and J. Simons, *ibid.*, **A217**, 271 (1953); (c) R. L. Strong and J. E. Willard, Abst. of the New York Meeting of the Am. Chem. Soc., Sept., 1954, p. 26R; (d) M. L. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **A231**, 446 (1955); (e) R. L. Strong, J. C. W. Chien, P. E. Graf and J. E. Willard, *J. Chem. Phys.*, in press.

(3) R. Marshall and N. Davidson, *ibid.*, **21**, 659 (1953).

(4) R. L. Strong and J. E. Willard, THIS JOURNAL, **79**, 2098 (1957).

(5) F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

(6) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

(7) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

(8) To prevent pyrolysis of the hydrocarbon vapor while the reaction cell was being sealed off a plug of the solid was frozen in the side arm with the aid of liquid air on glass wool. This device was necessary to avoid the danger of cracking the optical cell if the bulk of the liquid was frozen in it.