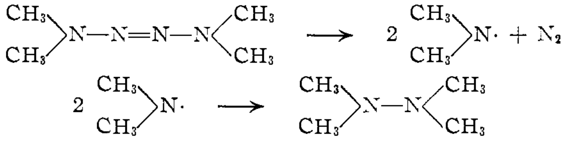
white and no transition could be observed when it was warmed to −160°.

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.



$$(CH_3)_2N{-}N{=}N{-}N(CH_3)_2 \longrightarrow 2\,(CH_3)_2N\cdot + N_2$$

$$2\,(CH_3)_2N\cdot \longrightarrow (CH_3)_2N{-}N(CH_3)_2$$

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

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

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

BY SUKUMAR ADITYA[1] AND JOHN E. WILLARD

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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.

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(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.

Comparison of the rate constants which we have obtained in hexane and decane with each other and with the value of Marshall and Davidson[3] for heptane indicates that there is no large effect of chain length on the rate constant over this range. A small effect may exist within the error limits of these determinations.

Calculation of the apparent activation energy from the rate constants in CCl_4 at 23 and 50° gives a value of 3.2 kcal./mole. This is in the range which would be expected for a diffusion controlled process such as this. The activation energy for the diffusion of iodine molecules in CCl_4 has been found to be 3.3 kcal./mole.[9]

The activation energy found for the gas phase recombination of iodine atoms in the presence of argon is -1.4 kcal./mole,[2e] the negative value being ascribed to the decreasing stability of the two-body complex which is believed to play a role in the "three body" recombination process. In solution "third body" solvent molecules are always present so the rate of diffusion rather than the stability of the two body complex is rate controlling.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetic Studies of Thiourea Derivatives. I. Methylthiourea

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

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The decomposition of methylthiourea in aqueous media has been studied over a wide *p*H range. In acid solutions two parallel first-order reactions were observed and corresponding rate constants evaluated at several temperatures. Above *p*H 7 additional complicating reactions were encountered. The experimental results are compared with those previously reported for urea and thiourea. A possible mechanism is discussed.

Introduction

The isomerization of urea to ammonium cyanate has been investigated previously in this Laboratory.[1] Recently, analogous results were also reported for thiourea,[2] and the marked similarity of the two reaction systems noted. Since both reactions were found to be strictly first-order, presumably unimolecular, decompositions, it seemed desirable to obtain comparable data with related compounds. The present paper is the first in a series to be devoted to the kinetic study of urea and thiourea derivatives.

Although the fundamental organic chemistry of methylthiourea recently has been thoroughly discussed and reviewed by Sahasrabudhey and Singh,[3] no kinetic data on the decomposition of this compound could be found in the literature. Moreover, reasoning based on the mechanism previously postulated for the isomerization of thiourea indicated that the decomposition of the 1-methyl derivative should exhibit several novel features.

Experimental

Methylthiourea was prepared by the addition of ammonia to methyl isothiocyanate.[4] The crude product was recrystallized twice from water, m.p. 118.7–120.4° (lit.[4] m.p. 119–120.5°). Titration of weighed amounts of the purified material with standard mercuric nitrate[5] indicated that the compound was at least 99% pure.

Anal. Calcd. for $C_2H_6N_2S$: C, 26.60; H, 6.70; N, 31.07. Found: C, 26.65; H, 6.69; N, 30.82.

The apparatus and techniques utilized in this investigation were those employed in earlier work[1,2] except as noted below.

Reaction mixtures were analyzed for ammonia and methylamine by the following modification of the ion-exchange method previously described.[1,2,6] Samples of the reacted solutions were adjusted to *p*H 6–7 and passed through ion-exchange columns containing Dowex 50. After careful washing the adsorbed ammonium and methylammonium ions were eluted from the resin with dilute sodium hydroxide. After suitable *p*H adjustment separate aliquots were used to determine ammonia by nesslerization, and methylamine by a colorimetric analysis described in detail elsewhere.[7] The methylamine analysis was not affected by the amounts of ammonia present in the reaction mixtures. In the ammonia analysis, on the other hand, a moderate interference by methylamine was encountered. Suitable corrections could, however, be made by appropriate calibration of the Nessler reagent in the presence of the interfering substance. The average deviation of a set of 8 independent analyses of a 1.11 m*M* methylamine hydrochloride solution was 3.0%. Whereas the average deviation of a set of 8 analyses of 0.148 m*M* ammonium chloride that was also 0.286 m*M* in methylamine sulfate was found to be 4.4%.

Results

As in previous papers the reactions were studied by the method of initial rates. The equation

$$p_1/t = k_1\bar{u} \qquad (1)$$

was used in the analysis of experimental data. In this equation $\bar{u}$ is the average methylthiourea concentration; p_1 denotes the concentration of a particular product, P_1, formed in the reaction time, t; and k_1 is an empirical rate constant based on the rate of formation of P_1. Since very little reactant was consumed during the reaction period, $\bar{u}$ differed from the initial reactant concentration by less than 2%. The rates of formation of three reaction prod-

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