PHOTODECOMPOSITION OF HYDRAZINE FUELS

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UV photometric measurement at 253.65 nm of hydrazine (N_2H_4) concentration in the gas phase has been used to study its 248.3-nm laser-photodissociation at 296 K. H-atoms, the major product in the photolysis, were directly detected by cw-resonance fluorescence. The primary quantum yield of $H(^2S)$ formation was measured to be 0.85 ± 0.15. The reaction, $H + N_2H_4 \rightarrow$ products; (k_1), that is initiated by the laser-flash was studied in the temperature range 296-222 K. The Arrhenius temperature dependence was determined to be $k_1 = (7.57 \pm 1.55) \times 10^{-12} \exp[-(1150 \pm 50)/T]$ cm^3 molec^{-1} s^{-1}.

INTRODUCTION

Hydrazine (N_2H_4), methylhydrazine (CH_3NNH_2), and unsymmetrical dimethylhydrazine ((CH_3)$_2$NNH$_2$), are an important class of nitrogen-based compounds that have positive standard enthalpies of formation. Decomposition of these compounds offer a wide variety of industrial applications such as in electrical power cells, fuels for thruster engines aboard the Space Shuttle and the Titan launch vehicles, as a mono-propellant, and in explosives. In addition to the above immediately practical reasons of studying hydrazine chemistry, the understanding of its laboratory photochemical decomposition is relevant to combustion because both processes can involve common reaction intermediates.[1-4] In this study we report the nature of the near ultraviolet absorption spectrum of N_2H_4 in the region 191-291 nm, the dissociation modes in the laser-photolysis at 248.3 nm, and the kinetics of the elementary reaction, $H + N_2H_4 \rightarrow$ products, which is an important reaction in the pyrolysis of hydrazine fuels. Several previous studies on this reaction have all reported a different temperature dependence for this atom-molecule reaction. Our carefully chosen experimental conditions indicate that all but one previous study had interference from secondary reactions. Using our data and that of Stief and Payne[5], it is now possible, for the first time, to make a recommendation for the Arrhenius activation energy and the pre-exponential factor for this reaction.

EXPERIMENTAL TECHNIQUE

The apparatus used to measure the ultraviolet absorption spectrum of N_2H_4 vapor is similar to that previously employed by *Vaghjiani and Ravishankara*,[6] and the present experimental procedures are fully described elsewhere.[7] The relative UV absorbance spectrum of a column of slowly flowing mixture of N_2H_4/helium was monitored in a 100-cm-long Pyrex absorption cell using a diode-array spectrometer. The relative absorbance data was converted to absolute cross sections by using the 253.65 nm absorption cross section value determined in a separate experiment. In this experiment, as before, the 253.65 nm absorbance was monitored in a column of N_2H_4/He, and the hydrazine

concentration in the experiment quantified by passing the eluting mixture through a series of Pyrex traps maintained at 77 K, and titrating the collected N_2H_4 with standard KIO_3 solution in 6 M HCl acid solution. The Beer-Lambert law, $A_{253.65} = 1\sigma_{253.65}[N_2H_4]$, where $A_{253.65}$ is the measured absorbance at 253.65 nm, and 1 the cell path length, was used to calculate the absorption cross section, $\sigma_{253.65}$, from the volumetrically determined hydrazine concentration, $[N_2H_4]$. The spectrum determined in this work together with data from previous work is shown in Figure 1.

The photodissociation of N_2H_4 was studied in a flash-photolysis apparatus of a design similar to that of *Vaghjiani and Ravishankara*.[8] The formation of $H(^2S)$ in the pulsed-laser photolysis (under optically thin conditions) of N_2H_4 was directly monitored by cw-resonance fluorescence detection of the $(2\ ^2P^o \rightarrow 1\ ^2S)$ transition in H-atoms at 121.6 nm. All experiments were carried out under slow-flow conditions, and under pseudo-first-order conditions in [H] with the photolyte in an excess such that the temporal profile of $[H]_t$ immediately after photolysis followed an exponential relationship:

$$[H]_t = [H]_0 e^{-kt} \tag{1}$$

$[H]_t$ and $[H]_0$ are the concentrations of H-atoms at time t and zero, respectively. $k = k_1[N_2H_4] + k_d + \Sigma_i k_i[i]$, and is the pseudo-first-order rate coefficient for loss of [H] in the gas mixture. k_1 is the second-order rate coefficient for the reaction $H + N_2H_4$, k_d is the first-order rate coefficient for diffusion of [H] out of the detection zone, and k_i is the second-order rate coefficient for the reaction of H with minute impurities, i, in the gas mixture. Typical [H] temporal profiles obtained are shown in Figure 2. The slopes of the decays give values for the pseudo-first-order rate coefficient, k, and the intercepts, S_{oN} (at time zero), a measure for the initial amount of H-atoms produced in the photolyses. The intercept in a given hydrazine photolysis is compared to the intercept, S_{oR}, obtained in a back-to-back photolysis of a known amount of CH_3SH under similar experimental conditions. The $[CH_3SH]$ is determined from the measured flow rates and the measured cell pressure. The $[N_2H_4]$ was directly determined by photometry at 253.65 nm. The observed initial signals, S_{oN} and S_{oR} need to be corrected for the attenuation of the detected 121.6 nm resonance fluorescence by the presence of the excess photolyte, and normalized by the photolytic energies, E_N and E_R, employed, respectively, in the two experiments.[9,10] The plots in Figure 3 show how the observed signals, when normalized for the amount of photolyte present and photolysis energy employed, vary with the concentration employed. It can be shown that the primary $H(^2S)$ quantum yield, Φ_N, in hydrazine photolysis is given by:

$$\Phi_N = \Phi_R \times \sigma_R/\sigma_N \times \exp(I_N)/\exp(I_R) \tag{2}$$

Φ_N, Φ_R, σ_N, σ_R, I_N, and I_R are the primary quantum yields for $H(^2S)$ production, the absorption cross sections at 248.3 nm, and the intercepts in Figure 3, respectively, for each of the photolytes, N_2H_4 and CH_3SH. The values of the absorption cross sections used in this work are summarized in Table 1. Any revision in these values will directly affect the $H(^2S)$ quantum yield computed in this study.

The kinetics of the reaction, $H + N_2H_4 \rightarrow$ products; (k_1), was studied by measuring the pseudo-first-order rate coefficient, k, as a function of $[N_2H_4]$. A typical result at 296 K is shown in Figure 4. The straight line is a linear-least-squares fit to the data points whose slope yields a value for k_1(296 K). k_1 was also measured at 273, 250, 232, 230, and 222 K.[11,12] The Arrhenius temperature dependence of k_1 is shown in Figure 5. The straight line is a linear-least-squares fit to the data points. The temperature dependences obtained in previous studies are also shown in Figure 5.

RESULTS AND DISCUSSION

The absorption cross section at 253.65 nm, $\sigma_{253.65}$, was calculated to be $(2.86 \pm 0.17) \times 10^{-20}$ cm^2 molec^{-1} at 296 K. The normalized absorption spectrum in the region 191-291 nm is shown in Figure 1. The relative shape and the absolute values of this work and that of Biehl and Stuhl[13] are in reasonable agreement to within $\pm$ 20% in the wavelength region 195-230 nm. Becker and Welge's, discrete values in the vacuum-UV are also in good agreement.[14] We are therefore confident that our photometric measurements at 253.65 nm give accurate absolute N_2H_4 number densities, to within $\pm$ 6 % (where the error is 1-sigma, precision plus systematic), in the photodissociation and kinetics experiments.

The continuous spectrum observed is indicative of absorption to one or more dissociative states. A variety of possible primary products can result on absorption of UV light.[7] $H + N_2H_3$, $NH_2 + NH_2$, $NH + NH_3$, $NH_2(\tilde{A}^2A_1) + NH_2$, and $N_2H_2 + H_2$ can energetically form for photolysis wavelengths, λ, < 248.3 nm. We have measured directly, for the first time, an H-atom quantum yield, Φ_N, of 0.85 $\pm$ 0.15 (where the error is 1-sigma, precision plus systematic) at 248.3 nm (Φ_N in CH_3SH is unity).[15] The quantum yield was independent of laser fluences of up to 1.25 mJ cm^{-2} pulse^{-1} employed, and of the linear flow rate of the gas mixture (2-8 cm s^{-1}) through the reaction zone. This indicates that 2-photon processes or subsequent photolyses of the reaction products formed in previous laser pulses, that may produce secondary H-atoms, is unimportant in our experiments. Our result is in excellent agreement with the indirect studies of Schurath and Schindler,[16] who reported a yield of 0.97 $\pm$ 0.10 at 206.2 nm. Ramsay's,[17] and Husain and Norrish's[18] suggestion that $NH + NH_3$ and $NH_2 + NH_2$ are the major primary products in their flash-photolyses experiments is not consistent with our measured H-atom quantum yield. These latter intermediates are thought to be formed in subsequent secondary reactions after the initial flash. Within our experimental uncertainties, unit dissociation of hydrazine is suggested for absorption of 248.3 nm radiation due to a weak electronic transition to the lowest dissociative singlet, $\tilde{A}^1A$, state.

The Arrhenius temperature dependence of the reaction, $H + N_2H_4 \rightarrow$ products; (k_1), is shown in Figure 5, and is given by $k_1 = (7.57 \pm 1.55) \times 10^{-12}$ exp[-(1150 $\pm$ 50)/T] cm^3 molec^{-1} s^{-1}. This is in excellent agreement with $(9.87 \pm 1.17) \times 10^{-12}$ exp[-(1200 $\pm$ 50)/T] cm^3 molec^{-1} s^{-1} reported by Stief and Payne.[5] However, the other three studies of Gehring et al.,[19] Francis and Jones,[20] and Schiavello and Volpi[21] all give different temperature dependences. These are also shown in Figure 5. The interference from secondary reactions at high radical concentrations, and or errors in estimating $[N_2H_4]$ employed in these later studies may be responsible for the differences in the reported values.

In this kinetic investigation of k_1, we have minimized the importance of secondary chemistry by keeping $[N_2H_4]/[H]$ ratio high, typically 5×10^4, and [H] low, typically 1×10^{11} molec cm^{-3}, and have used excess He buffer gas to thermalize the initially produced transnationally hot H-atoms in the photodissociation of N_2H_4. Using our data and that of Stief and Payne,[5] the recommended Arrhenius temperature dependence is derived to be $k_1 = (10.28 \pm 1.22) \times 10^{-12}$ exp[-(1220 $\pm$ 30)/T] cm^3 molec^{-1} s^{-1}. An activation energy of (2.4 ± 0.1) kcal mol^{-1} is obtained for this metathesis reaction in which the products are thought to be $H_2 + N_2H_3$.

We are currently looking at the temperature dependence of k_1 for T > 296 K, and the photodissociation of N_2H_4 at λ < 248.3 nm to get a through understanding of the dissociation mechanism(s) involved in hydrazine photolysis by UV light.

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Table I: Absorption cross section values used in this work

$$\sigma(10^{-20}\ cm^2\ molec^{-1})$$

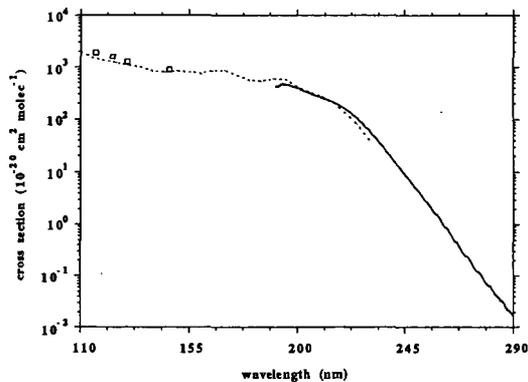| λ (nm)	CH3SH	N2H4
253.65	.....	2.86
248.3	30.0	5.88

Figure 1. UV absorption cross sections of N2H4. Solid line is this work, dashed line is from ref. 13, and squares are from ref. 14.
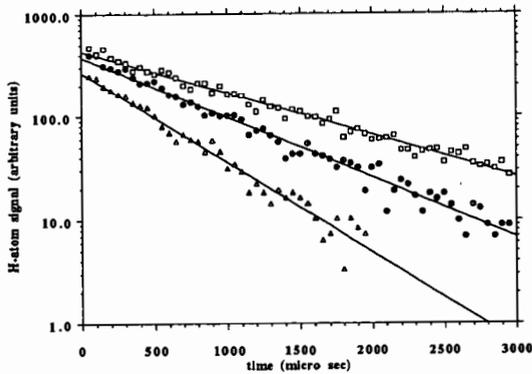
Figure 2. Typical [H] temporal profiles at 296 K. Each data point is the signal collected in 50-μsec dwell-time and co-added over 5000 photolytic pulses. The slopes yield values for k and the intercepts values for S_{oN}.
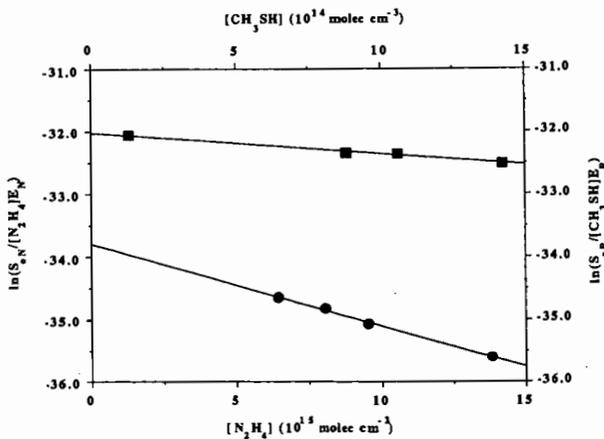

Figure 3. Variation of the log of normalized S_{oN} and S_{oR} signals with $[N_2H_4]$ (circles) and $[CH_3SH]$ (squares), respectively. Intercepts yield values for I_N and I_R, respectively, for the two photolytes.
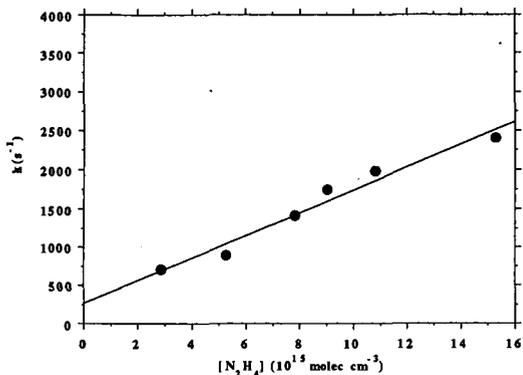
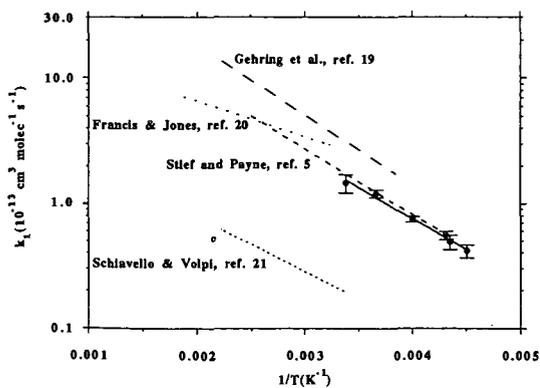**Figure 4.** Plot of k versus [N_2H_4]. The slope yields a value for k_1(296 K).

Figure 5. Arrhenius temperature dependences of k_1. Data points are from this study.