Inorg. Chem. **1994,** *33,* 1388–1391

Direct Detection of Aqueous Diazene: Its UV Spectrum and Concerted Dismutation

H. R. Tang and D. M. Stanbury*

Department of Chemistry, Auburn University, Auburn, Alabama 36849

Received June 22, 1993[⊗]

N_2H_2 is an intermediate in the acid-assisted hydrolysis of azodiformate, $(NCO_2)_2^{2-}$. When the hydrolysis is conducted at pH ≈4, the second-order dismutation of diazene occurs on a time scale longer than that of its generation. Due to this property, the intermediate (N_2H_2) and its decomposition can be observed directly in a stopped-flow instrument. The absorption maximum occurs at 355 nm with $\epsilon = 24 \pm 3$ M^{-1} cm^{-1}. The region of absorption (300–430 nm) is in fair agreement with that of the gas-phase spectrum reported by other workers. The rate constant for the second-order dismutation of N_2H_2 is $(2.2 \pm 0.3) \times 10^4$ M^{-1} s^{-1} at 25 °C and 0.11 M ionic strength, which agrees with the previously reported value (2.0×10^4 M^{-1} s^{-1}) obtained by indirect methods. The temperature dependence of this process, over the temperature interval from 283 to 313 K, leads to the activation parameters $\Delta H^{\ddagger} = 13.8 \pm 0.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -116 \pm 2$ J K^{-1} mol^{-1}. The dismutation displays an overall deuterium kinetic isotope effect of 3.3, as determined by conducting the reaction in a fully deuterated medium.

Introduction

Our interest in aqueous 1,2-diazene, N_2H_2, has developed for two major reasons.[1–3] First, the molecule is believed to be an intermediate in certain oxidations of hydrazine, including that by $[IrCl_6]^{2-}$.[4] Second, its characteristic reaction (hydrogenation of π bonds)[5] is believed to entail concerted pericyclic transfer of both hydrogen atoms. Its chemistry, both aqueous and otherwise, has been reviewed,[6] and the evidence for its existence in the gas phase is indisputable. The gas-phase molecule has been extensively characterized, and it has also been characterized in liquid ammonia and in low-temperature matrices. Evidence for the existence of diazene in aqueous media has been based on determination of the products of reactions in which diazene was assumed to be an intermediate. The difficulty in observing this species is tied to its rapid decomposition according to

$$2N_2H_2 \rightarrow N_2 + N_2H_4 \qquad (1)$$

Recently we reported a kinetic study of reaction 1.[1] Millimolar concentrations of diazene were generated in less than 1 ms by subjecting alkaline solutions of the precursor, azodiformate, to a pH jump. The decay kinetics of the diazene so generated was inferred by observing the consumption of azobenzene-4,4′-disulfonate (ABDS) as in

$$(NCO_2)^{2-} + 2H^+ \rightarrow N_2H_2 + 2CO_2 \quad \text{fast} \qquad (2)$$

$$2N_2H_2 \rightarrow N_2 + N_2H_4 \quad k_1 \qquad (3)$$

$$N_2H_2 + \text{ABDS} \rightarrow N_2 + H_2\text{ABDS} \quad k_2 \qquad (4)$$

An important outcome of this study was the realization that millimolar concentrations of aqueous diazene decompose with second-order kinetics on the time scale of several tens of milliseconds. In subsequent publications we have shown that our derived decay rate constant, k_1, is consistent with theoretical predictions,[2] and we have reported ab initio calculations of rate constants for related reactions that have zero driving force.[3]

Despite the kinetic evidence for the existence of aqueous diazene described above, direct detection of this species was not achieved. In the present paper we show that the species can be detected in the UV, we use its absorbance to monitor its decay directly, and we investigate the ionic strength, pH, temperature, and deuterium kinetic isotope effects for this decay process. These results allow us to test our prior measurement of k_1, to assess whether aqueous diazene exists as the cis or trans isomer, and to gain further evidence for a concerted pericyclic reaction mechanism in reactions of diazene.

Experimental Section

Materials. Potassium azodiformate, $K_2[(NCO_2)_2]$, was prepared from azodicarbonamide (Aldrich) and aqueous KOH as according to Thiele.[7] The canary yellow solid was isolated by precipitation from ethanol, washed with methanol and ether, air-dried, and stored in a vacuum desiccator. The material appears to be stable indefinitely unless it is exposed to atmospheric moisture.

Distilled deionized water was obtained from tap water by passage through a Barnstead pretreatment cartridge and subsequent distillation in a Barnstead Fistreem all-glass still. Argon for the deaeration of solutions was purified by passing through a Catalyst Q1 column (Dow) and then through a tower containing the solvent. Other reagents, including glacial acetic acid (Aldrich, 99.99+% purity), KOH, $HClO_4$, ethanol (anhydrous), methanol, and ether, were used without further purification. For the deuterium kinetic isotope effect experiments, acetic-d_3 acid-d (99.9 atom % D), NaOD solution in D_2O (99.9 atom % D), and D_2O (99.9 atom % D) were purchased from Aldrich and used without further purification.

All solutions were prepared with distilled deionized water and were permitted to contact only glass, Teflon, and platinum. Sodium hydroxide (Fisher, ACS Certified) was standardized by titration against 0.070 M potassium biphthalate to a phenolphthalein end point.

Methods. UV–vis absorbance data were obtained by using Cary 210 and Hewlett-Packard 8452A spectrophotometers with quartz cells of 1.00-cm path length. The temperature at the thermostated cell was monitored with a thermistor by using a Digitec digital thermometer, and the condensation, which was caused by using experimental temperature lower than ambient, was driven off by continuously purging the sample chamber with a stream of dry nitrogen gas. Initial concentrations of $(NCO_2)_2^{2-}$ in the stopped-flow experiments were determined by using these spectrophotometers to measure the absorbance of a portion of the stock solutions.

Kinetic data were collected on a Hi-Tech Scientific Model SF-51 stopped-flow apparatus in the 1 cm path length configuration, equipped

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1994.

(1) Stanbury, D. M. *Inorg. Chem.* **1991,** *30,* 1293–1296.

(2) McKee, M. L.; Squillacote, M. E.; Stanbury, D. M. *J. Phys. Chem.* **1992,** *96,* 3266–3272.

(3) McKee, M. L.; Stanbury, D. M. *J. Am. Chem. Soc.* **1992,** *114,* 3214–3219.

(4) Stanbury, D. M. *Inorg. Chem.* **1984,** *23,* 2879–2882.

(5) Pasto, D. J.; Taylor, R. T. *Org. React.* **1991,** *40,* 91–155.

(6) Back, R. A. *Rev. Chem. Intermed.* **1984,** *5,* 293–323.

(7) Thiele, J. *Liebigs Ann. Chem.* **1892,** *271,* 127–137.

0020-1669/94/1333-1388$04.50/0

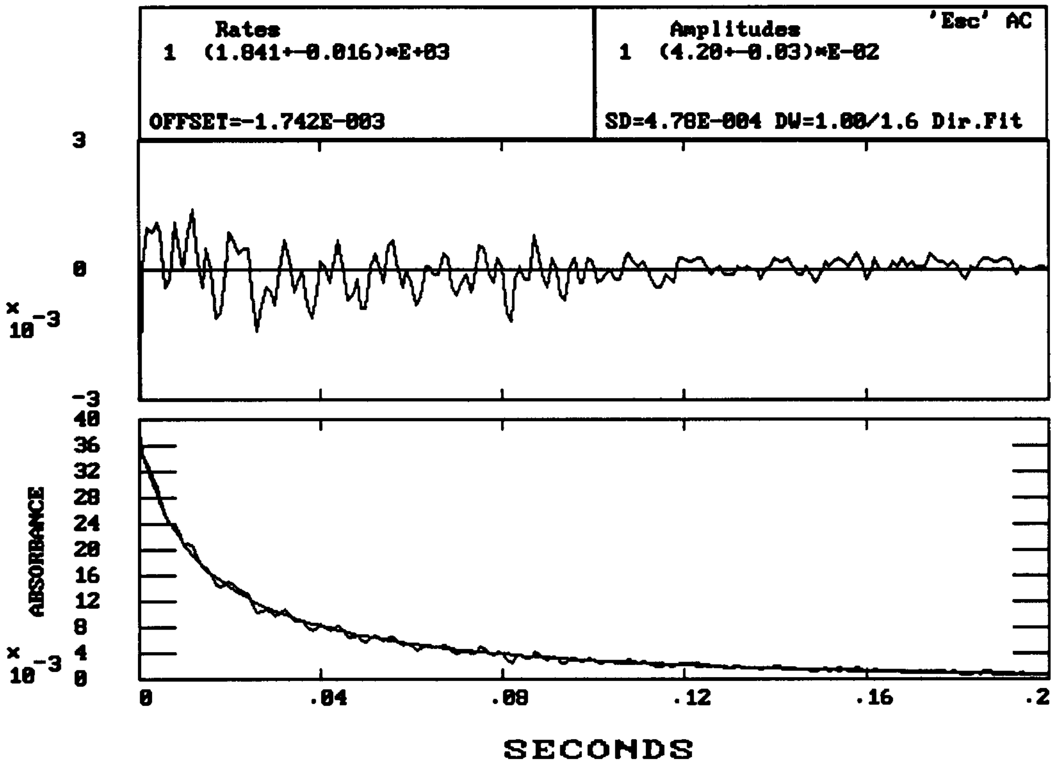

Figure 1. Decay of N_2H_2 at 355 nm, 25 °C, $\mu = 0.11$ M, pH 4.4, $[(NCO_2)_2^{2-}]_0 = 1.7$ mM, [NaOH] = 0.10 M, and [HOAc] = 0.21 M. Fitted function is a homogeneous second-order decay.

with an SU-40 spectrophotometer unit and a C-400 circulating water bath. The reactions were performed under anaerobic conditions at 0.1 M ionic strength. The thermostated water bath surrounding the flow circuit was continuously deaerated with nitrogen. The output from the SU-40 unit was digitized by an On line Instruments System (OLIS) Model 4300s data acquisition system running on a Zenith 248/12 computer. OLIS software was used to obtain the second-order fits to the time-dependent data.

pH measurements were performed at room temperature on a Corning 130 pH meter equipped with as Ross combination electrode (Orion No. 8103) filled with 3 M NaCl.

Numerical Methods. Uncertainties in k_1 and ϵ_{max} for N_2H_2 were calculated by taking into account propagation of error. A modified version of the Los Alamos nonlinear least-squares program running on a Macintosh II computer was used to obtain the activation parameters.[8] The data were weighted as the inverse square of the dependent variable. Uncertainties are expressed as one standard deviation.

Results

We have reported previously[1] that the acid-catalyzed hydrolysis of azodiformate, $(NCO_2)_2^{2-}$, obeys the rate law

$$-d[(NCO_2)_2^{2-}]/dt = k[H^+][(NCO_2)_2^{2-}] \qquad (5)$$

The proposed mechanism was

$$(NCO_2)_2^{2-} + H^+ \rightarrow [X] \qquad k \qquad (6)$$

$$[X] + H^+ \rightarrow N_2H_2 + 2CO_2 \qquad \text{(fast)} \qquad (7)$$

$$2N_2H_2 \rightarrow N_2H_4 + N_2 \qquad k_1 \qquad (8)$$

with $k = 1.2 \times 10^8$ M^{-1} s^{-1}. A value of 2×10^4 M^{-1} s^{-1} for k_1 was inferred from a study of competition kinetics in which azobenzene-4,4′-disulfonate was used as the competitor.[1]

From the rate constants noted above, 1.6 mM $(NCO_2)_2^{2-}$ undergoes hydrolysis with a half-life of 0.15 ms at pH 4.4, whereas the N_2H_2 so generated decomposes with a half-life of 14 ms. Therefore, a significant concentration of N_2H_2 can be prepared within the dead time of the instrument (~3 ms), and it will decompose on a time scale suitable for stopped-flow observation. Thus, solutions of $K_2(NCO_2)_2$ in aqueous NaOH were mixed with appropriate buffer solutions in the stopped-flow instrument. As is shown in Figure 1, when such experiments were performed, a weak absorbance signal was indeed observed that decayed to zero on the predicted time scale. Rather poor results were obtained when a first-order fit to these data was attempted; on the other hand, when the data were fit with the function

$$A = \frac{A_0}{1 + A_0 k_{obs} t} \qquad (9)$$

which is the integrated form of the rate law $-dA/dt = k_{obs}A^2$, the fits were excellent. If it is assumed that the absorbance is due to N_2H_2 and that N_2H_2 decomposes according to the rate law

$$-d[N_2H_2]/dt = 2k_1[N_2H_2]^2 \qquad (10)$$

then $k_{obs} = 2k_1/\epsilon b$ where b is the path length, 1 cm. The value of A_0 derived from the fits can be converted to ϵ by dividing by $b[N_2H_2]_0$, the value of $[N_2H_2]_0$ being taken as $[(NCO_2)_2^{2-}]_0$. Such experiments were conducted over the wavelength range from 300 to 430 nm, and the data are shown in Figure 2 as the UV–vis spectrum of aqueous N_2H_2.

The region of absorption is in fair agreement with that of the gas-phase spectrum reported by Back, Willis, and Ramsay.[9] The absorption maximum occurs at 355 nm with $\epsilon = 24 \pm 3$ M^{-1} cm^{-1}. The values of k_1 were wavelength independent and had an average value of $(2.2 \pm 0.3) \times 10^4$ M^{-1} s^{-1} at 25 °C and 0.11 M ionic strength. This rate constant for the second-order dismutation of N_2H_2 in aqueous solution is in excellent agreement with the previously reported value (2.0×10^4 M^{-1} s^{-1}) obtained by competition kinetics.[1]

---

(8) Moore, R. H.; Zeigler, R. K. *LSTSQR*; Los Alamos National Laboratory: Los Alamos, NM, 1959.

(9) Back, R. A.; Willis, C.; Ramsay, D. A. *Can. J. Chem.* **1974**, *52*, 1006–1012.

Table 1. Kinetic and Activation Parameter Data for Dismutation of N_2H_2[a]

	T, K						
	283.15	288.15	293.25	298.15	303.25	308.25	313.25
$10^{-3}k_{obs}$, s^{-1}	1.66	1.82	2.11	2.31	2.54	2.98	3.21
$10^{-4}k_1$, M^{-1} s^{-1}	1.56	1.71	1.98	2.16	2.38	2.79	3.01

$\Delta H^{*} = 13.9 \pm 0.6$ kJ mol^{-1} [b] $\Delta S^{*} = -116 \pm 2$ J mol^{-1} K^{-1} [b]

[a] Data obtained at pH 4.4, 0.11 M ionic strength, and 380 nm, with $[(NCO)_2{}^{2-}]_0 = 0.89$ mM and $\epsilon = 18.7$ M^{-1} cm^{-1}. [b] The standard deviations are calculated by the Los Alamos nonlinear least-squares computer program.[8]

Effect of pH. The pH dependence of the dismutation of diazene was investigated by mixing the stock solution with acetic acid and perchloric acid solutions of appropriate concentration. This procedure generated reaction mixtures at pH 5.1 and 1.5, respectively, with $\mu = 0.11$ M, for which the rate constants were $k_1 = 2.35 \times 10^4$ and 2.21×10^4 M^{-1} s^{-1}, respectively, at 380 nm with $\epsilon = 18.7$ M^{-1} cm^{-1}. It is thus seen that the decomposition rate law for N_2H_2 is independent of pH between pH 5.1 and 1.5.

Ionic Strength Effect. The ionic strength dependence of the decay of N_2H_2 was investigated by preparing stock solutions of azodiformate in 0.2, 0.1, and 0.05 M NaOH and mixing them with acetic acid solutions of appropriate concentration. This procedure generated reaction mixtures at pH 4.4 with $\mu = 0.11$, 0.06, and 0.03 M, for which the rate constants were $k_1 = 2.24 \times 10^4$, 2.18×10^4, and 2.08×10^4 M^{-1} s^{-1}, respectively, at 355 nm with $\epsilon = 24.3$ M^{-1} cm^{-1}.

These data were analyzed by plotting log k_1 versus $2A\mu^{1/2}/(1 + \mu^{1/2})$ as suggested by the Davies equation

$$\log k = \log k_{ref} + 2z_a z_b A\mu^{1/2}/(1 + \mu^{1/2}) \qquad (11)$$

where μ is the ionic strength and A is a collection of physical constants with the value 0.509 for water at 298 K. The plot has a slope of 0.29. Ideally, the slope of such a plot would be zero for reactions involving uncharged species and unity if they both bear a charge of 1 (or −1). Our slope of 0.29 implies that the reactants are uncharged, the deviation from zero reflecting the small influence of electrolytes on the activities of nonelectrolytes.

Activation Parameters. Temperature-dependent data on the kinetics of N_2H_2 decomposition were collected over the range from 10 to 40 °C. The data are presented in Table 1. These data were analyzed according to the Eyring equation

$$k_1 = \frac{\kappa RT}{Nh} \exp\left(\frac{\Delta S^{*}}{R}\right) \exp\left(\frac{-\Delta H^{*}}{RT}\right) \qquad (12)$$

The plot of $\ln(k_1/T)$ as a function of inverse temperature is linear. The activation parameters were obtained by fitting eq 12 to the values of k_1, which led to the following values: $\Delta H^{*} = 13.9 \pm 0.6$ kJ mol^{-1} and $\Delta S^{*} = -116 \pm 2$ J mol^{-1} K^{-1}.

Kinetic Isotope Effect. In order to investigate the deuterium kinetic isotope effect for the dismutation of N_2H_2, the reaction was conducted in a fully deuterated medium. It was monitored at 355 nm at pH 4.4. The initial concentration of N_2D_2 was calculated by assuming that it was formed with 100% yield from the starting $(NCO_2)_2{}^{2-}$; the starting concentration of $(NCO_2)_2{}^{2-}$ was determined from the UV spectrum of its stock solution under the assumption that its peak molar absorptivity was 33 M^{-1} cm^{-1}, i.e., that it was not affected by deuteration of the medium. The kinetic isotope effect so obtained, $k_1{}^H/k_1{}^D$, was 3.3 ± 0.5.

Discussion

As is shown by the UV spectrum in Figure 2, an intermediate is generated in the acid hydrolysis of azodiformate. There are several lines of evidence that point to the assignment of this species as N_2H_2. (1) It has long been inferred that N_2H_2 is an intermediate in this reaction on the basis of product yields. (2) The UV spectrum is similar to the gas-phase spectrum of N_2H_2. (3) The pH and ionic strength dependences of the decay of the intermediate are consistent with its formulation as an uncharged species. (4) The rate constant and activation parameters for decay of this intermediate are in agreement with those obtained from ab initio calculations. (5) The deuterium kinetic isotope effect for its decay is consistent with the decay being a hydrogen atom transfer process. Details of these arguments are presented below.

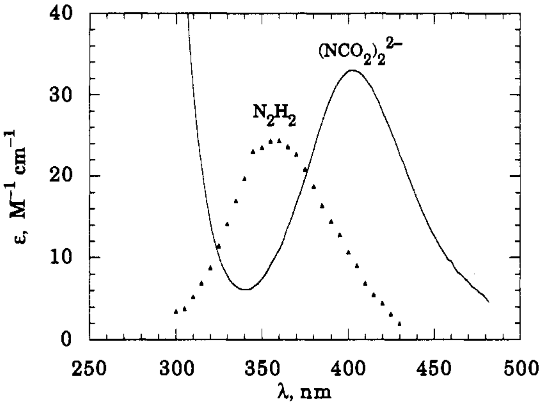

Figure 2. UV–vis absorption spectra of azodiformate and diazene in aqueous solution. Spectrum of diazene obtained at 25 °C, 0.11 M ionic strength, and pH 4.4 with $[(NCO_2)_2{}^{2-}]_0 = 1.7$ mM, [NaOH] = 0.10 M, and [HOAc] = 0.21 M. Spectrum of azodiformate obtained at 25 °C, $\mu = 0.05$ M ($NaClO_4$), pH 11.7, and $[(NCO_2)_2{}^{2-}] = 0.8$ mM.

UV Spectrum of N_2H_2. The gas-phase UV spectrum of N_2H_2 was first reported in 1968 by Trombetti.[10] It appeared as a weak and broad continuum centered around 350 nm. A higher resolution spectrum, which showed strong vibronic structure, was reported by Willis and Back in 1973.[11] An analysis of this vibronic structure was published in 1974, which confirmed that the species is *trans*-N_2H_2.[9] A spectrum at yet higher resolution and with a modestly revised interpretation was published in 1978.[12] These publications are consistent in showing spectra that are centered around 360 nm. In contrast to this, a spectrum attributed to N_2H_2 in liquid ammonia is centered around 420 nm, the red shift having been attributed to hydrogen-bonding effects;[13] The unusual biphasic decay kinetics reported in this study renders these results somewhat dubious. Our spectrum resembles that of gas-phase N_2H_2, and it shows no indication of a solvent-induced red shift.

Organic azo compounds (RN=NR) can be prepared as cis and trans isomers. They show characteristic n → π* transitions in the near UV, and because of symmetry selection rules, these transitions are much stronger for the cis isomers than the trans isomers.[14] Cis isomers have molar absorptivities in the range 127–420 M^{-1} cm^{-1}, while for the trans isomers these values are closer to 15 M^{-1} cm^{-1}. Since our measured value for aqueous N_2H_2 is 24 M^{-1} cm^{-1}, we infer that it is the trans isomer. This inference is consistent with the fact that gas-phase N_2H_2 is in the trans configuration,[6] with ab initio calculations that predict the

---

(10) Trombetti, A. *Can. J. Phys.* **1968**, *46*, 1005–1011.
(11) Willis, C.; Back, R. A. *Can. J. Chem.* **1973**, *51*, 3605–3619.
(12) Back, R. A.; Willis, C.; Ramsay, D. A. *Can. J. Chem.* **1978**, *56*, 1575–1578.
(13) Back, R. A.; Willis, C. *Can. J. Chem.* **1974**, *52*, 2513–2515.
(14) Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973**, *6*, 275–280.

cis isomer to be significantly higher in energy,[2,15] and with calculations which show that solvation does not significantly affect the energy difference between the two isomers.[16]

Medium Effects. The rate of decomposition of N_2H_2 is only weakly dependent on ionic strength, as is expected for an uncharged species. Moreover, since the decomposition is pH independent over the range from pH 5.1 to 1.5, substantial amounts of charged species such as N_2H^- or $N_2H_3^+$ must not be formed under these conditions. This is in agreement with expectations that N_2H_2 should be a very weak acid and the observation that azo compounds, in general, are very weak bases and are not protonated in aqueous solution except when other groups in conjugation markedly affect the nature of the system.[17] Further support for this can be found in the work of McKee, in which a pK_a of -1.5 was calculated for $N_2H_3^+$.[16]

N_2H_2 Decay Mechanism. The detailed mechanism of decay of aqueous diazene is believed to be

$$trans\text{-}N_2H_2 \rightleftarrows cis\text{-}N_2H_2 \qquad K_{t\text{-}c} \qquad (13)$$

$$cis\text{-}N_2H_2 + trans\text{-}N_2H_2 \rightarrow N_2 + N_2H_4 \qquad k_{2H} \qquad (14)$$

The first step shows the high-energy cis isomer to be formed in a rapid preequilibrium, and the double hydrogen atom transfer occurs in the next step. By this mechanism, the measured rate constant, k_1, is given by $K_{t\text{-}c}k_{2H}$. The detailed mechanism of trans to cis isomerization has been a matter of some debate, because both theory and experiment agree that in the gas phase this process is very slow.[2,18–22] We recently proposed that the process is solvent catalyzed.[1] McKee has refined this proposal by considering a mechanism in which *trans*-N_2H_2 is protonated and then deprotonated to give *cis*-N_2H_2, and he has shown that such a process could occur rapidly enough under our conditions.[16]

The second step is a concerted orbital-symmetry-allowed pericyclic process, and we have previously reported that the overall rate constant, k_1, is consistent with ab initio treatments of such a transition state.[2] In this prior report the experimental aqueous rate constant was compared to the ab initio results by converting the rate constant from units of $M^{-1}\ s^{-1}$ to $atm^{-1}\ s^{-1}$, calculating the corresponding value of $\Delta G^\ddagger$, and comparing it to the ab initio value. Note that this procedure is based on the assumption of negligible specific solvation effects. Unfortunately, a minor error was committed in converting units. The correct values should have been a rate constant of $8.2 \times 10^2\ atm^{-1}\ s^{-1}$ and a $\Delta G^\ddagger$ of 13.5 kcal mol^{-1}. This is to be compared with an ab initio value for $\Delta G^\ddagger$ of 14.9 kcal mol^{-1} (obtained as the sum of ΔG° for reaction 13 plus $\Delta G^\ddagger$ for reaction 14). The correction actually improves the agreement between experiment and theory.

We now add activation parameters for the k_1 step as results to compare with theory. Our experimental value of 13.8 ± 0.6 kJ mol^{-1} for $\Delta H^\ddagger$ is directly comparable to the ab initio value of 14.2 kJ mol^{-1}, and the agreement is excellent. The experimental entropy of activation, when corrected for the change in standard states, is -143 ± 2 J $K^{-1}\ mol^{-1}$, while the ab initio value is -161 J $K^{-1}\ mol^{-1}$; the agreement here is adequate also. Thus, the enthalpic and entropic details are fully supportive of a model based on a preequilibrium trans–cis isomerization followed by rate-limiting concerted double hydrogen atom transfer. Moreover, the good agreement between the experimental results and the ab initio (gas-phase) calculations indicates that the solvent has virtually no effect other than acting as a catalyst for the trans–cis isomerization of diazene.

It is difficult to formulate a precise interpretation of the deuterium kinetic isotope effect. Necessarily, it is the sum of the primary, secondary, and solvent isotope effects. It may be anticipated that the primary isotope effect will be dominant, and thus the measured value, 3.3, is consistent with a significant degree of hydrogen atom transfer in the transition state. The difficulty in obtaining a more detailed interpretation is that there are two compensating effects to be considered. One effect is that two hydrogen atoms are being transferred (presumably simultaneously), and this should lead to a large isotope effect. The other is that the reaction is highly exothermic ($\Delta H^\circ \approx -300$ kJ mol^{-1}), which should minimize kinetic isotope effects. There are several literature precedents, but they provide little interpretive guidance. Deuterium kinetic isotope effects were reported in an investigation of the gas-phase decomposition of diazene;[18] in this case, however, trans–cis isomerization was apparently the rate-limiting step. In a recent study of olefin hydrogenation by diazene in dioxane–acetic acid, evidence for a kinetic isotope effect was reported but the evidence was only qualitative.[23] Mackenzie et al. have reported large kinetic isotope effects for some double hydrogen atom transfer reactions, but these reactions are intramolecular, are based on hydrocarbons, and are only weakly exothermic.[24] Gerres and Heesing recently reported large kinetic isotope effects for some intermolecular double hydrogen atom transfer reactions, but these too were based on hydrocarbons and were only weakly exothermic.[25] Despite these uncertainties, it is likely that our measured kinetic isotope effect will be typical of other hydrogenations by diazene.

Conclusions

The previous proposal that diazene is an intermediate in the acid hydrolysis of azodiformate is now supported by direct optical detection of the intermediate. This species has a UV spectrum in agreement with that reported for N_2H_2 in the gas phase, and from the intensity of its UV spectrum it can be assigned as the trans isomer.

The decay kinetics of diazene are in agreement with prior indirect measurements. The activation parameters, dependence on pH and ionic strength, and deuterium kinetic isotope effect all support a mechanism involving preequilibrium trans–cis isomerization, followed by concerted transfer of both hydrogen atoms from cis-N_2H_2 to a molecule of *trans*-N_2H_2.

Acknowledgment. This research was supported by a grant from the NSF. D.M.S. is a Sloan Research Fellow. We are grateful to Prof. Mike McKee for helpful discussions.

---

(15) Pople, J. A.; Curtiss, L. A. *J. Chem. Phys.* **1991**, *95*, 4385–4388.

(16) McKee, M. L. *J. Phys. Chem.* **1993**, *97*, 13608–13614.

(17) Smith, P. A. S. *Derivatives of Hydrazine and Other Hydronitrogens Having N–N Bonds*; Benjamin/Cummings: Reading, MA, 1983; p 144.

(18) Willis, C.; Back, R. A.; Purdon, J. G. *Int. J. Chem. Kinet.* **1977**, *9*, 787–809.

(19) Willis, C.; Back, R. A.; Parsons, J. M.; Purdon, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 4451–4456.

(20) Casewit, C. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4057–4062.

(21) Jensen, H. J. A.; Jorgensen, P.; Helgaker, T. *J. Am. Chem. Soc.* **1987**, *109*, 2895–2901.

(22) Andzelm, J.; Sosa, C.; Eades, R. A. *J. Phys. Chem.* **1993**, *97*, 4664–4669.

(23) Saljoughian, M.; Williams, P. G.; Morimoto, H.; Goodlett, D. R.; van Breemen, R. B. *J. Chem. Soc., Chem. Commun.* **1993**, 414–416.

(24) Mackenzie, K.; Gravett, E. C.; Gregory, R. J.; Howard, J. A. K.; Maher, J. P. *Tetrahedron Lett.* **1992**, *33*, 5629–5632.

(25) Gerres, T.; Heesing, A. *Chem. Ber.* **1992**, *125*, 1439–1447.