**Table II.** Infrared Stretching Frequencies of [CpFe(CO)$_2$]$_2$, Related Complexes, and Their Radical-Cation Analogues[a]

| compd | parent $\nu_{CO}$ | radical cation $\nu_{CO}$ |
|---|---|---|
| [CpFe(CO)$_2$]$_2$ | | |
| terminal | 1955, 1995 | 2023, 2055 |
| bridging | 1773 | 1934 |
| [Cp*Fe(CO)$_2$]$_2$ | | |
| terminal | 1922 | 1987 |
| bridging | 1747 | 1884 |

[a] Measured in CH$_2$Cl$_2$/TBAH; values in cm$^{-1}$.

all of which proceed through the binuclear radical cation, although no behavior attributable to the generation of this intermediate was observed in their kinetic studies. The mechanisms were (a) direct oxidation of the binuclear radical, (b) initial dissociation followed by oxidation of the resulting 17-electron radical, and (c) a second-order disproportionation of the binuclear radicals. Of these three mechanisms, the current work unambiguously rules out the third. It is, however, more difficult to distinguish between the first two pathways, particularly since their kinetic studies were done in acetonitrile whereas all of our work was carried out in methylene chloride. Nevertheless, we believe that mechanism b best describes the chemical oxidation of [CpFe(CO)$_2$]$_2$, because, as stated earlier, the peak due to the oxidation of the intermediate complex, {[CpFe(CO)$_2$]$_2$(NCCH$_3$)}$^+$, decreases in size, after reaching a maximum value, with higher acetonitrile concentrations. The intermediate is not stable in the presence of excess acetonitrile and, in accord with mechanism b, rapidly dissociates. Mechanism a could be the operative mechanism provided the direct oxidation of the intermediate complex is much faster than the initial oxidation to the binuclear radical cation, which was measured to be ~10$^4$ M$^{-1}$ s$^{-1}$.[11]

### Conclusions

The electrochemistry of [CpFe(CO)$_2$]$_2$ and the related species [Cp*Fe(CO)$_2$]$_2$ was reexamined under a variety of conditions. Both compounds exhibit irreversible net two-electron oxidations in CH$_3$CN/TBAH with $E_{p,a}$ = 0.68 and 0.33 V vs AgCl/Ag, respectively. The complexes are symmetrically cleaved via this process to yield the corresponding 18-electron acetonitrile-adduct cations. These binuclear species also undergo quasi-reversible one-electron oxidations in CH$_2$Cl$_2$/TBAH to generate the cor-

responding binuclear radical cations at 0.68 and 0.34 V, respectively. The radical-cation species were generated and characterized via infrared spectroelectrochemistry. [CpFe(CO)$_2$]$_2$$^+$ exists as a mixture of the cis and trans carbonyl-bridged isomers in solution with $\nu$(CO) at 2023, 2055, and 1934 cm$^{-1}$, while [Cp*Fe(CO)$_2$]$_2$$^+$ with $\nu$(CO) at 1987 and 1884 cm$^{-1}$ exists exclusively as the trans isomer in solution (Table II). The unsubstituted radical cations were further characterized by EPR spectroscopy. [CpFe(CO)$_2$]$_2$$^+$ has $g_\parallel$ = 2.004 and $g_\perp$ = 2.084, while [Cp*Fe(CO)$_2$]$_2$$^+$ has $g_\parallel$ = 1.999 and $g_\perp$ = 2.088. [CpFe(CO)$_2$]$_2$$^+$ has long been invoked as the initial oxidation product of the parent dimer but had never been cleanly generated or characterized prior to this work. The binuclear radical cations are susceptible to rapid ligand-induced disproportionation reactions that were studied via spectroscopic and electrochemical methods. The results of these studies suggest that the mechanisms of these reactions involve the generation and subsequent decomposition of acetonitrile adducts of the binuclear radical-cation species of the form {[CpFe(CO)$_2$]$_2$(NCCH$_3$)}$^+$. For the Cp* compound, the intermediate is short-lived. Stopped-flow measurements of the reaction of [Cp*Fe(CO)$_2$]$_2$$^+$ with CH$_3$CN showed that the reaction is first order in [[Cp*Fe(CO)$_2$]$_2$$^+$ and [CH$_3$CN] with $k$ = 118 (±2) M$^{-1}$ s$^{-1}$. Cyclic voltammetry studies detected the parent intermediate [CpFe(CO)$_2$]$_2$(NCCH$_3$)}$^+$. The initially formed decomposition products of the acetonitrile adduct of the binuclear radical in each case (illustrated for [CpFe-(CO)$_2$]$_2$$^+$) are the 18-electron cationic species [CpFe(CO)$_2$-(NCCH$_3$)]$^+$ and the 17-electron radical CpFe(CO)$_2$•. Subsequent reactions of the 17-electron radical species regenerate [CpFe-(CO)$_2$]$_2$ and lesser amounts of CpFe(CO)$_2$Cl via reaction with the solvent.

**Supplementary Material Available:** Figures showing a cyclic voltammogram and an infrared spectroelectrochemical spectrum of [Cp*Fe-(CO)$_2$]$_2$, EPR spectra of [CpFe(CO)$_2$]$_2$$^+$ and [Cp*Fe(CO)$_2$]$_2$$^+$, and kinetic plots of the reaction of [Cp*Fe(CO)$_2$]$_2$ with acetonitrile (6 pages). Ordering information is given on any current masthead page.

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# Kinetic Behavior of Diazene in Aqueous Solution

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The acid-catalyzed hydrolysis of azodiformate ((NCO$_2$)$_2$$^{2-}$), which has diazene (N$_2$H$_2$) as an intermediate, has been studied by stopped-flow spectrophotometry. When the hydrolysis is conducted at sufficiently low pH ($\approx$6), the second-order dismutation of diazene occurs on a time scale longer than that of its generation. The reduction of azobenzene-4,4'-disulfonate (ABDS) by diazene provides a convenient indicator of these reactions. The consumption of ABDS gives the relative rate constants of dismutation and reduction, and the kinetics study gives the absolute rate constants. At 25 °C these rate constants are 2.0 × 10$^4$ M$^{-1}$ s$^{-1}$ and 1.4 × 10$^3$ M$^{-1}$ s$^{-1}$, respectively. A mechanism is proposed in which *cis*-diazene reduces ABDS and diazene competitively, both reactions proceeding by way of concerted dihydrogen transfer.

### Introduction

Diazene, N$_2$H$_2$, also known as diimide, has a long history, dating back to the work of Thiele in 1892.[1] Presently, it is widely known as a cis-specific reducing agent,[2] although it has been implicated as an intermediate in numerous reactions[2] and may be important

in nitrogen fixation[3] and atmospheric cloud chemistry.[4] Because of its simplicity and elusiveness it has been a subject of considerable theoretical interest.[5] Much of this interest has centered on its presumed mechanism of reduction, involving symmetry-allowed

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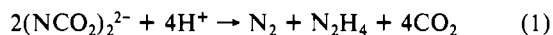(3) Hetterich, W.; Kisch, H. *Chem. Ber.* **1989**, *122*, 621–627.
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concerted dihydrogen transfer.[6-11]

The issue of dihydrogen transfer is, of course, much broader than the chemistry of diazene. In principle, any molecule bearing vicinal hydrogen atoms could behave in this way. However, actual measurements of dihydrogen-transfer rates are exceedingly rare. These appear to be limited to some intramolecular dyotropic rearrangements of hydrocarbons[12,13] and some reactions of diazene in the gas phase.[14] The latter reactions were subject to difficulties attributed to wall effects, and it was inferred that after correction for wall effects the observed reactions had trans to cis isomerization of $N_2H_2$ as the rate-limiting step; moreover, it is not clear that there is a unique solution in the procedure used for extracting rate constants for the steps following the rate-limiting step. Thus, there are virtually no reliable rate constants for intermolecular dihydrogen-transfer reactions.

Thiele prepared potassium azodiformate, $K_2(O_2CN{=}NCO_2)$, and he found that it underwent hydrolysis according to

$$2(NCO_2)_2{}^{2-} + 4H^+ \rightarrow N_2 + N_2H_4 + 4CO_2 \qquad (1)$$

He inferred that diazene was an intermediate in the reaction. This inference has been substantiated in numerous subsequent chemical investigations; the field has been reviewed by Back.[2] Diazene has been observed in the gas phase and in various low-temperature matrices, but in liquid solution it has only been directly observed in liquid ammonia.[15] There have been various reports of its kinetics in solution, but these generally have been limited to the determination of relative rates by measuring product ratios. One notable exception is in the report of its behavior in liquid $NH_3$; it was found to undergo biphasic decay with the second phase showing first-order kinetics and a rate constant of about 0.1 $s^{-1}$ extrapolated to 25 °C.[15] It was suggested that the first-order kinetics reflected the requirement for *trans*-diazene (the stable isomer) to isomerize to the cis configuration prior to disproportionation. Similar behavior was observed in the gas-phase decomposition of $N_2H_2$.[16]

From the brief discussion above it is clear that despite the widespread recognition and use of diazene, it has not been well characterized in solution. The present paper seeks to address this problem through a study of the hydrolysis of azodiformate. Subsequent to Thiele's investigation, King investigated the hydrolysis kinetics in highly alkaline media by manometric determination of $N_2$ evolution.[17] He found that the hydrolysis was first order with respect to $[H^+]$ and $[(NCO_2)_2{}^{2-}]$ and that it showed general acid catalysis. By use of stopped-flow methods we have been able to extend the range of rate constants by several orders of magnitude and to enter the regime in which disproportionation of diazene occurs slowly relative to its generation.

## Experimental Section

**Materials.** Potassium azodiformate, $K_2[(NCO_2)_2]$ was prepared from azodicarbonamide (Aldrich) and aqueous KOH as according to Thiele.[1] The yellow solid was isolated by precipitation from ethanol, washed with methanol and ether, air-dried, and stored in a desiccator. The material appears to be stable indefinitely unless it is exposed to atmospheric moisture.

Sodium azobenzene-4,4'-disulfonate (ABDS) was prepared from sulfanilic acid (Mallinckrodt) and NaOCl by the method of Clarke.[18]

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**Table I.** Kinetics of Hydrolysis of Azodiformate[a]

| pH | $k_{obs}$, $s^{-1}$ | buffer | pH | $k_{obs}$, $s^{-1}$ | buffer |
|---|---|---|---|---|---|
| 11.73 | $2.26 \times 10^{-4}$ | hydroxide | 6.23 | 58 | 0.1 M MES |
| 9.34 | $7.3 \times 10^{-2}$ | ammonia | 6.21 | 55 | 0.05 M MES |
| 8.02 | 1.16 | Tris | 6.29 | 47 | 0.025 M MES |
| 7.23 | 7.3 | phosphate | 6.39 | 38 | 0.0125 M MES |
| 6.32 | 58 | cacodylate | | | |

[a] 25.0 °C, $\mu$ = 0.05 M (Li, NaClO$_4$), [buffer] = 0.05 M, except [phosphate] = 0.026 M, $[(NCO_2)_2{}^{2-}]_0$ = 0.8 mM.

The product mixture was allowed to stand in a refrigerator overnight, and then the orange powder product was collected, washed with ethanol and ether, and air-dried. The product was purified by gel permeation chromatography on a Sephadex G-15-120 column with water as the eluent; the first three minor bands (red, pale yellow, and brown) were discarded, while the fourth major band (orange) was collected and taken to dryness. It was then recrystallized by dissolution in a minimum volume of water and addition of an equal volume of saturated NaClO$_4$. The UV–vis spectrum of this material in 0.1 M HClO$_4$ has a peak at 438 nm with $\epsilon$ = 954 $M^{-1}$ $cm^{-1}$, which agrees well with Clarke's values. The cyclic voltammogram of a 0.5 mM solution in 0.1 M HClO$_4$ showed a quasi-reversible two-electron wave ($\Delta E_{p/p}$ = 54 mV at 20 mV/s) with $E_{1/2}$ = 132 mV vs Ag/AgCl, which compares well with the literature value.[19]

Water was purified by passage through a Barnstead pretreatment cartridge and subsequent distillation in a Barnstead Fi-streem all-glass still. All other materials, including Tris (tris(hydroxymethyl)aminomethane) and MES (2-morpholinoethanesulfonic acid) were of reagent or AR grade and were used without further purification.

**Methods.** Cyclic voltammograms were obtained with a BAS-100 electrochemical analyzer, Cary 210 and Hewlett-Packard 8452A spectrophotometers were used for UV–vis spectroscopy, and a Hi-Tech SF-51 system was used for stopped-flow measurements as described previously;[20] some of the later data were collected with the OLIS 4300S Zenith-based data acquisition system. pH measurements were performed with a Corning 130 pH meter equipped with a Ross combination electrode (Orion No. 8103) filled with 3 M NaCl.

All reactions that involved ABDS were performed anaerobically because the corresponding hydrazine is O$_2$-sensitive. The solutions were rendered O$_2$-free by bubbling with Ar, and they were transferred with glass syringes and stainless steel needles. When reactions were examined with the Cary 210 instrument, the cuvettes were fitted with stopcock joints, flushed with Ar, and then filled with the reactive solutions. For work on the stopped-flow system, the thermostating water bath surrounding the flow circuit was sparged with Ar, and solutions were transferred though glass lead-in tubes.

Studies of the hydrolysis of azodiformate were initiated by mixing stock solutions of azodiformate in 0.05 M NaOH with appropriate buffer solutions. The reactions were monitored at 400 nm, 25.0 °C, and 0.05 M ionic strength. Fits to exponential decays were excellent and thus demonstrated good pseudo-first-order kinetics. Kinetic studies of the reduction of ABDS were performed similarly, mixing alkaline solutions of $(NCO_2)_2{}^{2-}$ with acidic buffer solutions containing the ABDS, and monitoring at 435 nm.

## Results

**Hydrolysis of Azodiformate.** Dissolution of the bright yellow salt, $K_2[(NCO_2)_2]$, in alkaline aqueous media (e.g. 0.05 M NaOH) is invariably accompanied by mild effervescence. Presumably hydrolysis, as in reaction 1, is rapid at the dissolving surface, which leads to a diminished yield of $(NCO_2)_2{}^{2-}$ in solution. Once prepared, however, such solutions are quite stable and can be handled for several hours without substantial further decomposition. The UV–vis spectra of these solutions show a broad band with a peak at 400 nm. The molar absorptivity was determined by allowing the solution to hydrolyze at pH 11 (phosphate buffer) in the presence of excess ABDS. Under these conditions the hydrolysis is quite slow, so the steady-state concentration of diazene is low, and the second-order disproportionation of diazene (see below) can be neglected relative to its reaction with the ABDS. Thus by spectrophotometric determination of the consumption of the ABDS, the initial concentration of diazene can be evaluated. Two

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**Table II.** Kinetics of Reduction of Azobenzene-4,4'-disulfonate[a]

| pH | $[(NCO_2)_2{}^{2-}]_0$, mM | $[ABDS]_0$, mM | $t_{1/2}$, s | $\Delta_{ABDS}$, $\mu$M | $10^{-4}k_1$, $M^{-1}$ $s^{-1}$ | $10^{-3}k_2$, $M^{-1}$ $s^{-1}$ | buffer |
|---|---|---|---|---|---|---|---|
| 6.28 | 0.31 | 0.57 | 0.36 | 53 | 1.6 | 1.0 | MES |
| 7.02 | 0.25 | 0.54 | 0.23 | 49 | 2.7 | 1.9 | phosphate |
| 6.22 | 0.25 | 0.54 | 0.25 | 52 | 2.4 | 1.8 | phosphate |
| 4.95 | 0.25 | 0.54 | 0.36 | 49 | 1.8 | 1.2 | phthalate |
| 4.40 | 0.47 | 0.89 | 0.20 | 78 | 2.0 | 1.2 | phosphate |
| 3.62 | 0.23 | 0.89 | 0.27 | 61 | 1.9 | 1.2 | phosphate |
| 3.46 | 0.088 | 0.89 | 0.36 | 40 | 1.9 | 1.3 | phosphate |
| 3.45 | 0.044 | 0.89 | 0.41 | 27 | 2.0 | 1.3 | phosphate |

[a] 25.0 °C, $\mu$ = 0.05 M (Li, NaClO$_4$), [buffer] = 0.05 M, except [phosphate] = 0.026 M. Data are the averages of three replicate runs.

such experiments were performed at 1 mM ABDS, one with 82 and the other with 250 $\mu$M azodiformate. The outcome was $\epsilon$ = 33 $\pm$ 3 $M^{-1}$ cm$^{-1}$ at 400 nm for azodiformate, which is similar to the spectral properties of various alkyldiazenes (RN=NH).[21] From this value of $\epsilon$ it is found that about one-third of the potassium azodiformate disproportionates during dissolution.

The visible absorbance of azodiformate permitted direct spectrophotometric observation of the kinetics of hydrolysis of azodiformate, but because of the low molar absorptivity the data are not of especially high precision. Experiments were performed in various buffers at 0.05 M ionic strength, the results of which are presented in Table I. The result at pH 11.73 is reasonably consistent with that reported by King,[17] considering the slightly different conditions, and it demonstrates that the process he monitored by manometry is the same as that presently monitored by spectrophotometry. A plot of log $k_{obs}$ against $-$pH for these data is linear and has a slope of 0.995. If the possible effects of general acid catalysis are neglected, the data imply the rate law

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

with $k$ = (1.2 $\pm$ 0.2) $\times$ 10$^8$ $M^{-1}$ s$^{-1}$. This result is consistent with the predictions of King, and it extends the applicable pH range of the rate law from King's (pH 13–12) to pH 6.2.[17] As shown in Table 1 for MES buffer, general acid catalysis is only a minor effect.
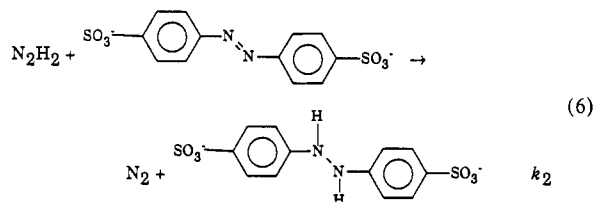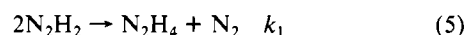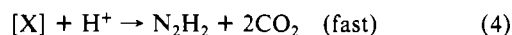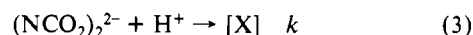
**Reduction of Azobenzene-4,4'-disulfonate.** When the hydrolysis of azodiformate was conducted in the presence of ABDS there was a significant consumption of the ABDS, as judged by the absorbance at 435 nm. A stopped-flow study of this effect in the pH range 3.5–7 showed that the ABDS is consumed on a time scale significantly longer than the time scale of hydrolysis of azodiformate. Furthermore, when the reaction was performed under conditions such that no more than 10% of the ABDS was consumed, the consumption displayed non-pseudo-first-order kinetics, with a rapid early phase and a slower second phase. Plots of log ($A - A_{inf}$) as a function of time were curved at early times, but in the latter half-lives they were linear. The data were analyzed by determining the overall absorbance change, $\Delta A$, and the length of the first half-life, $t_{1/2}$. Since the ABDS is the only component of the solution that absorbs significantly at the observation wavelength, the $\Delta A$ values were converted to $\Delta_{ABDS}$ values (the change in concentration of ABDS) by dividing by $\epsilon l$. These results are displayed in Table II. As can be seen from Table II, the consumption of ABDS is generally much less than the initial amount of azodiformate. Moreover, the values of $t_{1/2}$ and $\Delta_{ABDS}$ were independent of the pH and identity of the buffer. On the other hand, $t_{1/2}$ decreased and $\Delta_{ABDS}$ increased systematically with increasing initial concentration of $(NCO_2)_2{}^{2-}$.

**Discussion**

Our study of the hydrolysis of $(NCO_2)_2{}^{2-}$ has confirmed the prior report of King[17] that the reaction is first order with respect to $[H^+]$ and $[(NCO_2)_2{}^{2-}]$, and it has extended the range of validity of the rate law to the limit of the stopped-flow time scale. Thus, by conducting the reaction at pH 6 or less, it is possible to generate a sample of diazene within a few milliseconds or less.

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The consumption of ABDS when ABDS is present during hydrolysis of $(NCO_2)_2{}^{2-}$ is taken as evidence that the intermediate, $N_2H_2$, reduces ABDS to the corresponding hydrazine. The fact that at low pH only a fraction of the $N_2H_2$ reduces ABDS is qualitative evidence that the dismutation of $N_2H_2$ is competitive with the reduction of ABDS, and the deviations from pseudo-first-order kinetics suggest that the dismutation is a second-order process.

The above ideas are summarized in the following mechanism:

$$(NCO_2)_2{}^{2-} + H^+ \rightarrow [X] \quad k \qquad (3)$$

$$[X] + H^+ \rightarrow N_2H_2 + 2CO_2 \quad (fast) \qquad (4)$$

$$2N_2H_2 \rightarrow N_2H_4 + N_2 \quad k_1 \qquad (5)$$



$$(6)$$

Under the approximation that the first steps, generation of $N_2H_2$ as in reactions 3 and 4, are fast, the subsequent decay of $N_2H_2$ is given by

$$-d[N_2H_2]/dt = (2k_1[N_2H_2] + k_2[ABDS])[N_2H_2] \qquad (7)$$

The validity of this approximation is marginal for the experiment at pH 7.02, where the calculated half-life for $(NCO_2)_2{}^{2-}$ hydrolysis is 60 ms while the observed first half-life for consumption of ABDS is 230 ms. For the other experiments, at pH 6.28 and lower, the approximation is much better, with $t_{1/2} \le 11$ ms for $(NCO_2)_2{}^{2-}$ hydrolysis and $t_{1/2} \ge 200$ ms for ABDS consumption.

Under the approximation that the concentration of ABDS is constant, eq 7 can be integrated to give

$$[N_2H_2] = \frac{k_2[ABDS]}{\left(\dfrac{k_2[ABDS]}{[N_2H_2]_0} + 2k_1\right)\exp(k_2[ABDS]t) - 2k_1} \qquad (8)$$

where the subscript 0 indicates the initial concentration. This is an acceptable approximation, because in our kinetic experiments never more than 10% of the ABDS was consumed. Making no approximations, the consumption of ABDS is simply

$$-d[ABDS]/dt = k_2[N_2H_2][ABDS] \qquad (9)$$

Although all the $N_2H_2$ is consumed, only a small fraction of the ABDS is consumed and so the concentration of ABDS on the right-hand side of eq 9 can be approximated as a constant. With this approximation, substitution of eq 8 into eq 9 yields

$$\frac{-d[ABDS]}{dt} = \frac{(k_2[ABDS])^2}{\left(\dfrac{k_2[ABDS]}{[N_2H_2]_0} + 2k_1\right)\exp(k_2[ABDS]t) - 2k_1} \qquad (10)$$

In principle, the individual kinetic traces could have been fitted

by eq 10. However, we have used a different procedure to extract the rate constants from the data. Because the dominant variable in the right-hand side of eq 10 is $t$, it is reasonable to make the approximation that [ABDS] is a constant in the right-hand side. With this approximation, eq 10 can be integrated to give

$$[ABDS]_0 - [ABDS]_t = \frac{k_2[ABDS]}{2k_1} \ln \left\{ \left( 1 + \frac{2k_1[N_2H_2]_0}{k_2[ABDS]} \right) - \frac{2k_1[N_2H_2]_0}{k_2[ABDS] \exp(k_2[ABDS]t)} \right\} \quad (11)$$

and evaluated at infinite time to give

$$\Delta_{ABDS} = [ABDS]_0 - [ABDS]_{inf} = \frac{R[ABDS]}{2} \ln \left( 1 + \frac{2[N_2H_2]_0}{R[ABDS]} \right) \quad (12)$$

where $R$ is the ratio $k_2/k_1$. Thus, $R$ was determined from the overall consumption of ABDS simply by solving eq 12 numerically (Newton–Raphson or bisection method). For this purpose the value of [ABDS] used was the average of the initial and final concentrations.

Equation 11 can also be evaluated at $[ABDS]_t = [ABDS]_0 - \Delta_{ABDS}/2$ to obtain an expression in terms of the first half-life, $t_{1/2}$:

$$k_2 = \frac{1}{[ABDS]t_{1/2}} \times \ln \left\{ \frac{2[N_2H_2]_0}{R[ABDS]\left( 1 + \frac{2[N_2H_2]_0}{R[ABDS]} - \exp\left( \frac{\Delta_{ABDS}}{R[ABDS]} \right) \right)} \right\} \quad (13)$$

Thus $k_2$ can be obtained from $t_{1/2}$, $R$, and other experimental data. Then, from the values of $R$ and $k_2$, values of $k_1$ can also be obtained. These results are presented in Table II. Somewhat more scatter than normal is shown in these data, but it must be remembered that two rate constants are being extracted from each run. Overall, there seems to be no systematic dependence of the rate constants on the experimental conditions, except, perhaps, for the data at high pH where hydrolysis of $(NCO_2)_2{}^{2-}$ is slowest. In summary, it is believed that the above mechanism is an adequate description of the reaction, and that the best values of the rate constants are $k = (1.2 \pm 0.2) \times 10^8$ $M^{-1}$ $s^{-1}$, $k_1 = 2.0 \times 10^4$ $M^{-1}$ $s^{-1}$, and $k_2 = 1.4 \times 10^3$ $M^{-1}$ $s^{-1}$ at 25 °C and 0.05 M ionic strength. The uncertainty in $k_1$ and $k_2$ is difficult to specify, but probably it is less than a factor of 2.

Of particular importance in the above analysis is the observation that a 10-fold variation in $[(NCO_2)_2{}^{2-}]_0$ led to no significant effect on the values of $k_1$ and $k_2$. This supports the contention that the dismutation of $N_2H_2$ is a second-order process in aqueous solution. This is important because it has been reported previously that the dismutation is a *first-order* process in liquid ammonia.[15] Since the dismutation is second-order in aqueous solution, it is necessary to maintain a low concentration of $N_2H_2$ when $(NCO_2)_2{}^{2-}$ is used as a reducing agent in synthesis in order to obtain good yields. Thus, the hydrolysis of $(NCO_2)_2{}^{2-}$ should be conducted in mildly alkaline media so as to maintain a low steady-state concentration of $N_2H_2$.

It is widely believed that hydrogenation by $N_2H_2$ occurs through concerted transfer of two hydrogen atoms from *cis*-$N_2H_2$ to the

coreactant, with the transition state being cyclic. The basis of this belief is in the stereospecificity of reduction of olefins by diazene. The present results do not conflict with this concerted dihydrogen-transfer mechanism, but there are some aspects of the mechanism that require some comment. These have to do with the relative energies of the trans and cis isomers of $N_2H_2$, the barrier to interconversion between them, and the potential energy barrier in the concerted dihydrogen-transfer step.

There is no experimental value for the energy difference between *trans*- and *cis*-$N_2H_2$. According to ab initio calculations, the cis isomer is higher in energy that the trans isomer by 28.0 kJ/mol.[22] If it is presumed that *trans*-diazene is generated in the hydrolysis of $(NCO_2)_2{}^{2-}$, then isomerization to the cis isomer must precede dihydrogen transfer. On the basis of ab initio calculations it has been estimated that the barrier to intramolecular trans–cis isomerization is 263 kJ/mol.[22] Clearly, such a barrier cannot be surmounted with the rapid reactions that we have observed. There are two resolutions to this dilemma: one is that the species generated by hydrolysis of $(NCO_2)_2{}^{2-}$ is actually *cis*-$N_2H_2$. The other is that in solution the isomerization reaction goes by a mechanism different from that calculated for the gas phase. A value of 3.8 D has been calculated (at the ab initio 4-31G level) for the dipole moment of *cis*-$N_2H_2$.[23] Such a large dipole moment might lead to enough solvent stabilization to make *cis*-$N_2H_2$ the predominant species in solution. It should also be noted that aqueous solution provides an optimal medium for solvent-catalyzed trans–cis isomerization, so that, even if the predominant solution species were *trans*-$N_2H_2$, the cis isomer would be present in rapid equilibrium. Thus, although it is not presently known which isomer of $N_2H_2$ is present in aqueous solution, the proposed mechanism of concerted dihydrogen transfer is not invalidated by theoretical calculations regarding interconversions between the two isomers.

The other problematic aspect of the concerted dihydrogen-transfer mechanism is the reported value of 100 kJ/mol for the potential energy barrier to dihydrogen transfer from *cis*-$N_2H_2$ to $N_2H_2$.[10] This barrier was obtained from an ab initio calculation at the HF/4-31G level. Since such a reaction should have a considerably negative value for its activation entropy, the predicted rate constant is vastly less than our observed value. A possible solution to this conundrum is that the calculated barrier[10] may be highly overestimated due to neglect of electron correlation. Calculations presently under way support this idea.[24]

The magnitude of $k_2$ (reaction with ABDS) also deserves some comment. It is approximately a factor of 14 less than $k_1$. It is not yet clear whether the difference in rate reflects steric or electronic effects, but the difference does provide ample scope for selectivity in the reactions of diazene.

Finally, the considerable stability of diazene in aqueous solution raises the possibility that other types of reactivity could be observed, as has been suggested for its participation in electron-transfer reactions.[25]

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