We calculate<sup>20</sup> two electronic absorption bands above 200 nm for 1: for *trans*-1, a weak  $S_0 \rightarrow S_1$  ( $\sigma^2 \rightarrow \sigma^1 p^1$ ) transition at 470 (oscillator strength, f = 0.02), and a much more intense S<sub>0</sub>  $\rightarrow$  $S_2 (\sigma^2 \rightarrow \sigma^1 \sigma_{C-Cl}^{*1})$  transition at 219 nm (f = 0.09). Corresponding cis-1 transitions are calculated at 535 (f = 0.01) and 226 nm (f = 0.07). The calculated transitions and intensities are in good agreement with the observed weak and strong bands of matrix-isolated 1 at 460 and 240 nm, respectively, but only one long wavelength absorption was observed at low temperatures. The observed matrix IR bands of 1 are in reasonable agreement with the calculated<sup>20</sup> bands, but they do not clearly differentiate cis- and trans-1. These spectra will be discussed in detail in a separate publication.

The computed  $\Delta G^*$  for the rearrangement of *trans*-1 to 2 (9.0 kcal/mol) consists of  $\Delta H^*$  and  $\Delta S^*$  at 8.2 kcal/mol and -2.7 eu, respectively. A variable-temperature study of the rearrangment is in progress and will be reported in due course. Note, however, that the intricate "choreography" required for the concerted re-arrangement of 3 to cyclobutene<sup>9a</sup> involves disrotatory motions of the migrating and carbonic carbons in different relative directions before and after the transition state. Should this carry over to the rearrangement of trans-1 to 2, then the free energy (variational) transition state might differ from the calculated (conventional) minimum energy transition state.<sup>23</sup>

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## The 1,2-Hydrogen-Shift Rearrangement in Alkylchlorocarbenes

Joseph A. LaVilla and Joshua L. Goodman\*

Department of Chemistry, University of Rochester Rochester, New York 14627

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The 1,2-hydrogen-shift rearrangement of a singlet alkylcarbene to produce an olefin is a general reaction of current theoretical and experimental interest.<sup>1</sup> Although the rearrangement can be simply regarded as an insertion into an  $\alpha$  C-H bond, the structure and energy of the transition state are still in question. Recent theoretical calculations predict this highly exothermic process to have an extremely low activation energy,  $\leq 5 \text{ kcal/mol.}^2$  For example, the rearrangement of methylcarbene (CH<sub>3</sub>CH) to ethylene is calculated to occur without thermal activation.<sup>2a</sup> However, experimental studies suggest that alkylchlorocarbenes may indeed have an appreciable lifetime in solution.<sup>3-5</sup> In fact,

compd	$\Delta H(1)$ , kcal/mol	$\Delta H(2)$ , kcal/mol	$\tau_2$ , ns
1a	$-27.5(3.0)^d$	-42.1 (3.7)	740 (80)
1b	-61.9 (5.1)	n <sup>e</sup>	≤10
1c	-56.8 (3.4)	n <sup>e</sup>	≤10

<sup>a</sup> In heptane, 295 K, see ref 11-13 for experimental details. <sup>b</sup>Average of at least 5 measurements.  $c_{\tau_1}$  is defined as  $\leq 10$  ns. <sup>d</sup> Values in parentheses are  $\pm 1\sigma$ . <sup>e</sup>Not resolved by PAC.

alkylchlorocarbenes undergo intermolecular cyclopropanation reactions with olefins in competition with the intramolecular hydrogen shift rearrangement.<sup>5</sup>

Unfortunately, no direct experimental kinetic data are currently available concerning the rearrangement of singlet alkylcarbenes. This may be due in part to the anticipated short lifetime of the reactive carbene and the difficulties in its direct spectroscopic detection.<sup>6</sup> In this regard, we wish to report the use of timeresolved photoacoustic calorimetry (PAC) to obtain both kinetic and thermodynamic data on the rearrangement of alkylchlorocarbenes. In particular, both the experimental heat of formation of methylchlorocarbene in solution and the effect of temperature on the rate constant for its 1,2 rearrangement to vinyl chloride are measured. These are among the first direct absolute rate constant measurements for such a process in solution.

Irradiation of the alkylchlorodiazirines (1a-c) initially produces alkylchlorocarbenes (2a-c) which subsequently undergo a 1,2hydrogen shift to produce alkenyl chlorides (3a-c).5



PAC allows for the simultaneous determination of the thermodynamic and kinetic properties of photogenerated reactive intermediates.<sup>8-10</sup> Deconvolution of the experimental acoustic waveforms measures the amplitude and time evolution of heat deposition. The details of this method have previously been reported.<sup>8,9</sup> The enthalpic and kinetic data for the photochemical reactions of la-c, as determined by PAC, are given in Table I.<sup>11-13</sup>

Irradiation of 1a in heptane results in two, time-resolved heat depositions. The first,  $\Delta H(1)$ , reflects carbene formation,  $1a \rightarrow$ **2a**, and the second,  $\Delta H(2)$ , the unimolecular rearrangement, **2a**  $\rightarrow$  3a. With use of  $\Delta H(2)$  and the heat of formation of 3a, 8.6 kcal/mol,<sup>16a</sup> the heat of formation of methylchlorocarbene,

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<sup>(11)</sup> The photoacoustic apparatus has been previously described.8 Compounds 1a-c and  $1a-d_3$  are prepared by the Graham procedure<sup>14</sup> by using the appropriate acetonitrile precursor. 2-Hydroxybenzophenone is used as the calibration compound. Excitation is by nitrogen laser (337 nm) and detection employs a  $\sim 0.5$  MHz transducer. Similar results are obtained in toluene or isooctane and are unaffected by sample concentration (0.2–0.8 OD) or argon degassing. The temperature ( $\pm 0.1$  °C) is controlled by Haake 80 bath.

 $\Delta H_f(2\mathbf{a})$ , is 50.7 ± 4.7 kcal/mol.<sup>18</sup> Support for the observed heat deposition  $\Delta H(2)$  corresponding to the H rearrangement is given by (a) product studies,<sup>5,12</sup> (b) the  $\Delta H_f(2\mathbf{a})$  value is in good agreement with that obtained by PAC using the experimental heat of reaction for either the insertion of  $2\mathbf{a}$  into the O-H bond of methanol<sup>8d,19a</sup> or the cycloaddition of  $2\mathbf{a}$  with 2,3-dimethyl-2-butene,<sup>19b</sup> and (c) the overall heat of reaction of  $1\mathbf{a} \rightarrow 3\mathbf{a}$ ,  $\Delta H(1) + \Delta H(2)$ , is similar to that observed for 1b and 1c and in reasonable agreement with thermochemical estimates.<sup>19c,20</sup> Irradiation of either 1b or 1c in heptane results in only one heat deposition,  $\Delta H(1)$ , which reflects both the formation and the rearrangement of the carbene. This suggests the rate constants for rearrangement of  $2\mathbf{b}$  and  $2\mathbf{c}$  are  $\geq 1 \times 10^8 \, \mathrm{s}^{-1}$ .<sup>20b</sup>

The temperature dependence (11.5-61.0 °C) of the rate constant for the rearrangement of **2a** in heptane fits to a single exponential (R = 0.98) and yields Arrhenius parameters  $E_a =$ 4.9 ± 0.5 kcal/mol and log ( $A/s^{-1}$ ) = 9.7 ± 0.3.<sup>11,21,22</sup> The

(13) PAC measures the total volume change of the associated reaction. This includes volume changes from thermal,  $\Delta V_{th}$ , and reaction volume,  $\Delta V_{Tx}$ , changes. The reaction volume contribution has previously been neglected,  $^{8a-4,9,10}$  but it can be significant.<sup>86</sup> We are presently investigating the magnitude of such changes. In both  $1a \rightarrow 2a$  and  $1b - c \rightarrow 3b - c$ , the reaction volume change should be positive which would give an erroneously large value for  $\Delta H(1)$ . However, the reaction volume change for  $2a \rightarrow 3a$  should be small so both  $\Delta H(2)$  and  $\Delta H_f(2)$  should accurately reflect the thermal volume change.

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(19) (a) Using  $\Delta H_f(CH_3CH(OCH_3CI) = -64.8 \text{ kcal/mol}.^{16} \Delta H_f(CH_3CH) = -48.1 \text{ kcal/mol}.^{16a} \text{ and the heat of reaction, } -65.8 \text{ kcal/mol}. \Delta H_f(2a) = 49.1 \text{ kcal/mol}.$  (b) Using  $\Delta H_f(C_8H_{15}CI) = -7.7 \text{ kcal/mol}.^{17b} \Delta H_f(C_6H_{12}) = -16.4 \text{ kcal/mol}.^{16a} \text{ and the heat of reaction, } -38.6 \text{ kcal/mol}. \Delta H_f(2a) = 47.3 \text{ kcal/mol}.$  (c)  $\Delta H(1) + \Delta H(2) = -62.6 \text{ kcal/mol} \text{ using } \Delta H_f(1a) = 7.1.2 \text{ kcal/mol}.^{17c}$ 

(20) (a) Compounds 1a-c can potentially rearrange to their corresponding diazo compounds. Although this process has not yet been observed in solution for alkylchlorodiazirines, it potentially occurs in the gas phase.<sup>7</sup> This pathway would potentially complicate the PAC thermodynamic results, depending on the quantum efficiency and the rate constant for the decomposition of the diazo compound. However, on the basis of the evidence cited above, it appears unlikely that the PAC intermediate is the diazo compound and not the carbene **2a**, i.e., the PAC kinetic results are unaffected. (b) Quenching experiments suggest that some **3a** may be formed directly from **1a**,  $\leq 10$  ns, possibly via the diazo compound but presumably not via the ground-state carbene. The observed  $\Delta H(2)$  would have to be corrected by dividing by the quantum yield for the reaction which does proceed via the carbene **2a**.<sup>12</sup> Consequently,  $\Delta H_f(2a) = 50.7$  kcal/mol would be a lower limit. Similarly, the large  $\Delta H(1)$  value and the lack of a second heat deposition for both **1b** and **1c** could potentially be explained by the direct formation of **3b** and **3c** from **1b** and **1c**, without the intermediacy of carbenes **2b** and **2c**.

(21) Activation parameters are obtained from a nonlinear least-squares fit of the rate constants (5 determinations, 5 temperatures) to the Arrhenius equation.

(22) For comparison, the Arrhenius parameters for the related 1,2-hydrogen shift in benzylchlorocarbene to chlorostyrene obtained by indirect competition experiments are estimated to be  $E_a = 6.4$  kcal/mol and log  $(A/s^{-1})$ = 12.2.<sup>3a</sup> calculated  $E_a$  for rearrangement of **2b** and **2c** is  $\leq 2.4 \text{ kcal/mol}$ , assuming similar preexponential factors as for **2a** and rate constants for rearrangement of  $\geq 1 \times 10^8 \text{ s}^{-1}$  at 295 K.

The presence of a significant activation energy for rearrangement of 2a (4.9 kcal/mol) relative to methylcarbene (~0 kcal/mol) may result from the stabilization of the carbene 2a by Cl substitution. This is reflected in the lower reaction exothermicity of  $2a \rightarrow 3a$ , -42.1 kcal/mol, compared to that of methylcarbene to ethylene, -76.9 kcal/mol.<sup>2a</sup> Alternatively, stabilization of 2a by the solvent, relative to the gas phase, may contribute, in part, to the observed activation energy.<sup>23</sup> The significantly larger rate constant for the rearrangement of 2b and 2c relative to 2a is consistent with a hydride shift process where the  $\alpha$  C-H bond being broken is highly polarized in the transition state. The incipient positive charge is stabilized by methyl substitution at the migration center on 2b and 2c. A similar rate enhancement is also found for the rearrangement of benzylchlorocarbene to chlorostyrene (5 × 10<sup>7</sup> s<sup>-1</sup> at 298 K), presumably due to aromatic stabilization of the transition state.<sup>24</sup>

The low preexponential factor for the rearrangement of **2a** suggests a highly ordered transition state which supports a highly coupled or "concerted" hydride shift and  $\pi$ -bond formation mechanism.<sup>1,4a</sup> Alternatively, quantum mechanical tunneling could be responsible for the observed A factor. However, kinetic analysis of the rate constant for rearrangement of **2a** and **2a**- $d_3^{11}$  gives an intermolecular kinetic isotope effect,  $k_{\rm H}/k_{\rm D}$ , of  $\leq 1.3$  at 22 °C.<sup>25</sup> This value is similar to those measured by product competition studies for other singlet carbenes ( $k_{\rm H}/k_{\rm D} \approx 1.1$ -1.5)<sup>2,4</sup> and probably reflects the predicted reactant-like, nonlinear transition state for the hydride migration.<sup>1,2</sup>

The application of PAC to the 1,2-hydrogen-shift rearrangement of alkylchlorocarbenes demonstrates its utility in the study of "invisible" or nonspectroscopic reactive intermediates in solution. However, PAC provides no structural information about the reactive intermediates so care must be exercised in relating a given heat deposition to a specific chemical reaction. Further experiments will examine the effect of carbenic substitution and solvent on the kinetics and energetics of the 1,2-hydrogen-shift rearrangement of alkylhalocarbenes.

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## Divalent Vanadium and Dinitrogen Fixation: The Preparation and X-ray Structure of $(\mu-N_2)\{[(o-Me_2NCH_2)C_6H_4]_2V(Py)\}_2(THF)_2$

Jilles J. H. Edema, Auke Meetsma, and Sandro Gambarotta\*

Laboratorium voor Anorganische Chemie Rijksuniversiteit Groningen, Nijenborgh 16 9747 AG Groningen, The Netherlands

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Since the initial discovery by Shilov that a  $V(OH)_2/Mg(OH)_2$ system acts as a 1-electron reductant for the transformation of dinitrogen to  $N_2H_4$  and  $NH_3$ ,<sup>1</sup> the fixation of dinitrogen by divalent

<sup>(12) (</sup>a) The experimental enthalpic fitting parameter,  $\alpha_n$ , is the fraction of incident photon energy released in a given heat deposition. The corresponding heat of reaction is  $\Delta H(1) = (1 - \alpha_1)E_{hv}/\Phi$  or  $\Delta H(2) = \alpha_2 E_{hv}/\Phi$ , where  $\Phi$  is the reaction quantum yield and  $E_{hv}$  is the incident laser energy. (b) The values in Table I assume a quantum yield of 1 for each process, i.e.,  $\mathbf{la-c} \rightarrow \mathbf{2a-c}$  and  $\mathbf{2a-c} \rightarrow \mathbf{3a-c}$ . The quantum yield for the disappearance of 1a in hexane is 1.00  $\pm$  0.08 as determined by phenylglyoxylic acid actinometry<sup>15</sup> and UV-vis spectroscopy ( $\epsilon_{337}(\mathbf{1a}) = 48.6$ ). This value is similar to gas-phase measurements,  $0.95.^{*a}$ . A medium-pressure Hg lamp with bandpass filters to isolate the appropriate wavelengths is used. By <sup>1</sup>H NMR, the only product observed ( $\geq 90\%$  yield) after photolysis of 1a in toluene- $d_8$  is 3a. A quantum yield of 1 is assumed for both 1b and 1c. This supported by previous studies, <sup>5</sup> <sup>1</sup>H NMR studies which show only alkenyl chloride products (3b-c), and the overall reaction thermodynamics.

<sup>(23)</sup> The rearrangement of **2a** is not observed by PAC in the more polar solvent CH<sub>3</sub>CN at 22 °C, suggesting the lifetime of **2a**,  $\geq 2 \mu s$ , is significantly longer than that in heptane. Irradiation of **1a** in CH<sub>3</sub>CN produces only one heat deposition,  $\leq 10$  ns. The  $\Delta H(1)$  value, -40.5 kcal/mol, indicates significant stabilization by the solvent,  $\sim 13$  kcal/mol relative to heptane, presumably by formation of the acetonitrile ylide.