We calculate[20] 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 $S_0 \rightarrow S_2$ ($\sigma^2 \rightarrow \sigma^1 \sigma_{C-Cl}{}^{*1}$) 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[20] 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 rearrangement of **3** to cyclobutene[9a] involves disrotatory motions of the migrating and carbenic 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.[23]

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The 1,2-Hydrogen-Shift Rearrangement in Alkylchlorocarbenes

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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.[1] Although the rearrangement can be simply regarded as an insertion into an α 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, ≤5 kcal/mol.[2] For example, the rearrangement of methylcarbene (CH_3CH) to ethylene is calculated to occur without thermal activation.[2a] However, experimental studies suggest that alkylchlorocarbenes may indeed have an appreciable lifetime in solution.[3-5] In fact, alkylchlorocarbenes undergo intermolecular cyclopropanation reactions with olefins in competition with the intramolecular hydrogen shift rearrangement.[5]

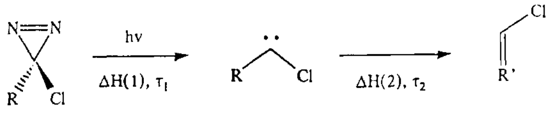
Table I. Enthalpic and Kinetic Parameters Determined by PAC for the Photochemical Reaction of **1** to **3**[a-c]

compd	$\Delta H(1)$, kcal/mol	$\Delta H(2)$, kcal/mol	τ_2, ns
1a	−27.5 (3.0)[d]	−42.1 (3.7)	740 (80)
1b	−61.9 (5.1)	n[e]	≤10
1c	−56.8 (3.4)	n[e]	≤10

[a] In heptane, 295 K, see ref 11–13 for experimental details. [b] Average of at least 5 measurements. [c] τ_1 is defined as ≤10 ns. [d] Values in parentheses are ±1σ. [e] Not resolved by PAC.

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.[6] In this regard, we wish to report the use of time-resolved 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 1,2-hydrogen shift to produce alkenyl chlorides (**3a–c**).[5,7]



1a R = CH_3 2a R = CH_3 3a R' = CH_2
1b R = CH_2CH_3 2b R = CH_2CH_3 3b R' = $CHCH_3$
1c R = $CH(CH_3)_2$ 2c R = $CH(CH_3)_2$ 3c R' = $C(CH_3)_2$

PAC allows for the simultaneous determination of the thermodynamic and kinetic properties of photogenerated reactive intermediates.[8-10] Deconvolution of the experimental acoustic waveforms measures the amplitude and time evolution of heat deposition. The details of this method have previously been reported.[8,9] The enthalpic and kinetic data for the photochemical reactions of **1a–c**, as determined by PAC, are given in Table I.[11-13]

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

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(11) The photoacoustic apparatus has been previously described.[8] Compounds **1a–c** and **1a**-d_3 are prepared by the Graham procedure[14] 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 ~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 (±0.1 °C) is controlled by Haake 80 bath.

ΔH_f(**2a**), is 50.7 ± 4.7 kcal/mol.[18] Support for the observed heat deposition $\Delta H(2)$ corresponding to the H rearrangement is given by (a) product studies,[5,12] (b) the ΔH_f(**2a**) value is in good agreement with that obtained by PAC using the experimental heat of reaction for either the insertion of **2a** into the O–H bond of methanol[8d,19a] or the cycloaddition of **2a** with 2,3-dimethyl-2-butene,[19b] and (c) the overall heat of reaction of **1a** → **3a**, $\Delta H(1) + \Delta H(2)$, is similar to that observed for **1b** and **1c** and in reasonable agreement with thermochemical estimates.[19c,20] 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 **2b** and **2c** are $\geq 1 \times 10^8$ s^{-1}.[20b]

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 $E_a = 4.9 \pm 0.5$ kcal/mol and $\log (A/\mathrm{s}^{-1}) = 9.7 \pm 0.3$.[11,21,22] The calculated E_a for rearrangement of **2b** and **2c** is ≤2.4 kcal/mol, assuming similar preexponential factors as for **2a** and rate constants for rearrangement of $\geq 1 \times 10^8$ 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** → **3a**, −42.1 kcal/mol, compared to that of methylcarbene to ethylene, −76.9 kcal/mol.[2a] Alternatively, stabilization of **2a** by the solvent, relative to the gas phase, may contribute, in part, to the observed activation energy.[23] The significantly larger rate constant for the rearrangement of **2b** and **2c** relative to **2a** is consistent with a hydride shift process where the α 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 (5×10^7 s^{-1} at 298 K), presumably due to aromatic stabilization of the transition state.[24]

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 π-bond formation mechanism.[1,4a] 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_H/k_D, of ≤1.3 at 22 °C.[25] This value is similar to those measured by product competition studies for other singlet carbenes ($k_H/k_D \cong 1.1$–1.5)[2,4] and probably reflects the predicted reactant-like, nonlinear transition state for the hydride migration.[1,2]

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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(12) (a) The experimental enthalpic fitting parameter, α_n, is the fraction of incident photon energy released in a given heat deposition. The corresponding heat of reaction is $\Delta H(1) = (1 - \alpha_1)E_{h\nu}/\Phi$ or $\Delta H(2) = \alpha_2 E_{h\nu}/\Phi$, where Φ is the reaction quantum yield and $E_{h\nu}$ is the incident laser energy. (b) The values in Table I assume a quantum yield of 1 for each process, i.e., **1a–c** → **2a–c** and **2a–c** → **3a–c**. The quantum yield for the disappearance of **1a** in hexane is 1.00 ± 0.08 as determined by phenylglyoxylic acid actinometry[15] and UV–vis spectroscopy (ϵ_{337}(**1a**) = 48.6). This value is similar to gas-phase measurements, 0.95.[7a] A medium-pressure Hg lamp with bandpass filters to isolate the appropriate wavelengths is used. By ^{1}H NMR, the only product observed (>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 is supported by previous studies,[5] ^{1}H NMR studies which show only alkenyl chloride products (**3b–c**), and the overall reaction thermodynamics.

(13) PAC measures the total volume change of the associated reaction. This includes volume changes from thermal, ΔV_{th}, and reaction volume, ΔV_{rx}, changes. The reaction volume contribution has previously been neglected,[8a–d,9,10] but it can be significant.[8e] We are presently investigating the magnitude of such changes. In both **1a** → **2a** and **1b–c** → **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** → **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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(18) The PAC ΔH_f(**2a**) value includes the differential heat of solvation between **2a** and **3a**. Although the heat of solvation of **3a** is probably small, the stabilization of **2a** by solvent may be quite significant. Consequently, the ΔH_f(**2a**) value may be lower than that obtained in the gas phase.

(19) (a) Using $\Delta H_f(CH_3CH(OCH_3)Cl) = -64.8$ kcal/mol,[16b] $\Delta H_f(CH_3OH) = -48.1$ kcal/mol,[16a] and the heat of reaction, −65.8 kcal/mol, ΔH_f(**2a**) = 49.1 kcal/mol. (b) Using $\Delta H_f(C_8H_{15}Cl) = -7.7$ kcal/mol,[17b] $\Delta H_f(C_6H_{12}) = -16.4$ kcal/mol,[16a] and the heat of reaction, −38.6 kcal/mol, ΔH_f(**2a**) = 47.3 kcal/mol. (c) $\Delta H(1) + \Delta H(2) = -62.6$ kcal/mol using ΔH_f(**1a**) = 71.2 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.[7] 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**, ≤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**.[12] Consequently, ΔH_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**. In this regard, the PAC experiment would yield no information about the lifetime 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 $\log (A/\mathrm{s}^{-1}) = 12.2$.[3a]

(23) The rearrangement of **2a** is not observed by PAC in the more polar solvent CH_3CN at 22 °C, suggesting the lifetime of **2a**, ≥2 μs, is significantly longer than that in heptane. Irradiation of **1a** in CH_3CN produces only one heat deposition, ≤10 ns. The $\Delta H(1)$ value, −40.5 kcal/mol, indicates significant stabilization by the solvent, ~13 kcal/mol relative to heptane, presumably by formation of the acetonitrile ylide.

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(25) The rate constants for rearrangement of **2a** and **2a**–d_3 are equal within the error limits of the photoacoustic experiment. We are examining the temperature dependence on the rate constant for rearrangement of **2a**–d_3.

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

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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,[1] the fixation of dinitrogen by divalent

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