by intramicellar radical–radical reaction. Application of an external field (≤3.2 kG) had no effect on the experiment. The size of SDS micelles can be increased with the addition of NaCl.[16–18] The ketyl lifetime increases to 40 and 70 ns with the addition of 0.4 and 0.6 M NaCl, respectively.

Hyperfine interactions, which are common in other systems, cannot account for the rapid relaxation observed in these experiments, since larger interactions in other systems have not caused similar effects.[4,9] Moreover, $Ph_2C^{\bullet}OH$ has been used in numerous experiments where triplet character has been preserved for hundreds of nanoseconds[4,19] so that the properties of its g tensor cannot account for the relaxation. We interpret our results in terms of rapid relaxation related to the g tensor for $PhS^{\bullet}$.

Relaxation that comes from g-tensor anisotropy is magnetic field dependent but at the fluxes used in these experiments cannot contribute to rapid relaxation.[20] However, both transverse (T_1) and longitudinal (T_2) relaxation times associated with *spin rotational relaxation* are significant. They are defined in eq 3, where τ_0 is the rotational relaxation time and δ_g represents the shift of g-tensor components from the free-electron value,[20] e.g., $\delta g_x = g_x - 2.002\,319$.

$$T_1^{-1} = T_2^{-1} = \frac{(\delta g_x^2 + \delta g_y^2 + \delta g_z^2)}{9\tau_0} \qquad (3)$$

The principal values of the g tensor for $PhS^{\bullet}$ are 2.003, 2.003, and 2.017.[21] While those for $Ph_2C^{\bullet}OH$ are not known, we have used representative values for the structurally related radical $(CH_3)C^{\bullet}(OH)CO_2^-$, viz., 2.0037, 2.0036, and 2.0031, respectively.[21] These values lead to g(isotropic) = 2.003 47, which is close to the value of 2.0030 observed for $Ph_2C^{\bullet}OH$ in fluid solution.[21]

Values of τ_0 depend upon solvent viscosity and radical size and are therefore difficult to define in micelles where viscosities are inhomogeneous and poorly defined. However, $T_1 + T_2$, for $PhS^{\bullet}$, must be less than the radical-pair lifetime (~20 ns). Substitution into eq 3 gives $\tau_0 = 2 \times 10^{-13}$ s, which is in accord with values of 10^{-12} to 10^{-13} s observed for small organic molecules in hydrocarbon solvents.[22] Values of τ_0 in this range lead to T_1($Ph_2C^{\bullet}OH$) in the neighborhood of 1 μs which are consistent with the fact that this radical does not itself induce rapid relaxation in numerous experiments described in the literature.[9] Thus, spin rotational relaxation induced by $PhS^{\bullet}$ accounts for rapid relaxation observed in this work.

Our results by themselves cannot rule out spin–orbit coupling (SOC) as the mechanism for rapid relaxation; however, our preference for an interpretation based on the g tensor should be examined in the context of other studies involving oxygen,[19,23] germanium-centered[24], and benzenesulfonyl[24] radicals. In the last two cases modest magnetic field effects and micellar escape were observed in SDS micelles.[24] This argues against atomic mass as a key parameter.

An implication of this result is that the lower limit for the rate constant, k_c, for encounters between radicals in SDS micelles must be $\sim 5 \times 10^7$ s^{-1}, i.e., the reciprocal of the experimental lifetime of the radical pairs. Thus, in radical pairs where spin rotational relaxation is not rapid and radical-pair lifetimes are ca. 1 μs, the value of f must be $\leq 10^{-2}$; see eq 1.

The dominant effect found in this study is related to the shift of the components of the g tensor from the free-spin value. Thus organic radicals, in which one of the principle values in the g tensor is ca. 2.02, will be capable of reducing triplet-pair lifetimes in micelles to the nanosecond time domain. Radicals such as peroxyl and perthiyl fall into this category.[21]

The present results indicate that organic radicals in which a component of the g tensor differed by unity from the free-spin value would actually be capable of inducing relaxation within the 50-ps lifetime that characterizes a geminate radical pair in the solvent cage. Transient radicals in this category would have broad EPR lines that would be essentially undetectable in homogeneous solution. Examples are alkoxyl and alkanethiyl radicals which, in non-hydrogen-bonding solvents, have extremely anisotropic g tensors due to electron exchange between the degenerate p orbitals.[25] For such "EPR invisible" radicals, all encounters should lead to reaction and f (eq 1) will approach unity.

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Photoelectron Spectrum of Cyclopropenylidene and Weak Bonds in Cyclopropenyl Radical

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We report the direct determination of the heat of formation for cyclopropenylidene (c-C_3H_2) by photoelectron spectroscopy. An adiabatic ionization potential of 9.15 ± 0.03 eV is measured for the carbene produced in a molecular beam by supersonic jet flash pyrolysis of 3-chlorocyclopropene. Insertion of this ionization potential into a thermochemical cycle yields $\Delta H_f(C_3H_2) = 114 \pm 4$ kcal/mol. In addition, the homolytic C–H bond dissociation energy for cyclopropenyl radical is determined to be 61 ± 6 kcal/mol. *The reduced bond strength in C_3H_3 radical is found to be in quantitative agreement with a proposed general relationship of radical bond strengths to carbene singlet–triplet splittings.*

Time-of-flight (TOF) mass and photoelectron spectrometers and the flash pyrolytic nozzle source are described elsewhere.[2] Laser light at 118.2 nm (10.49 eV) for photoionization was generated by frequency-tripling the Nd^{3+}:YAG third harmonic in a xenon cell.[2] 3-Chlorocyclopropene was synthesized and purified according to the procedure by Breslow.[3] Flash pyrolysis of 3-chlorocyclopropene (1500 °C, 10–50 μs contact time) resulted in clean loss of HCl, as shown in Figure 1. Comparison of the TOF mass spectra with heat off and heat on shows that conversion to C_3H_2 is clean and complete. We find no detectable secondary reactions of the carbene. Similar pyrolyses[4] of chloroform and α-deuterated vinyl chlorides indicate that α-elimination of HCl (DCl) is facilitated only for a singlet ground state carbene like cyclopropenylidene. Isomeric C_3H_2 species, propadienylidene and

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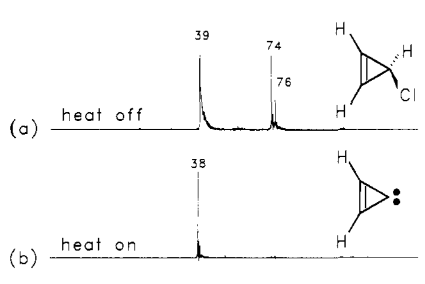


Figure 1. Photoionization mass spectra (10.49 eV) of (a) unpyrolyzed and (b) pyrolyzed 3-chlorocyclopropene, seeded into 2 atm of helium. The tailing peak at $m/e = 39$ in spectrum a is a metastable ion formed by unimolecular dissociation of the parent molecular ion. No mass peak for HCl is observed in spectrum b because the ionization potential is above the 10.49-eV photon energy.

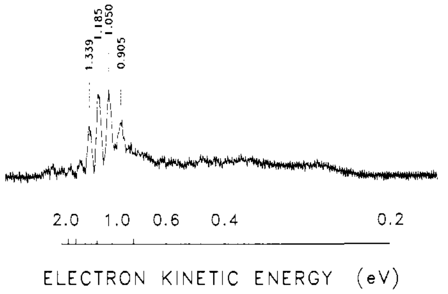


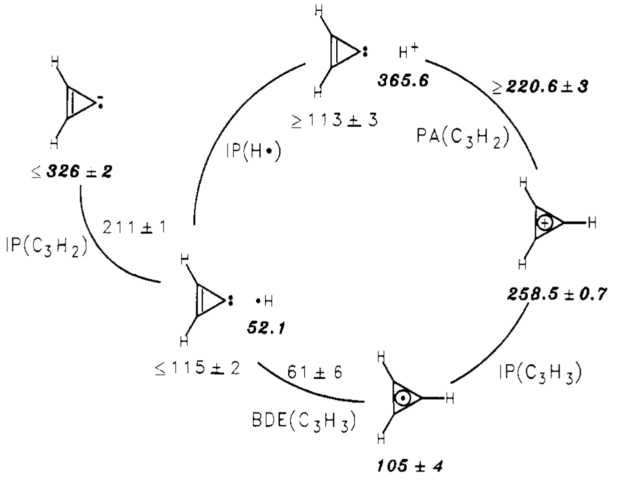
Figure 2. Time-of-flight photoelectron spectrum (10.49 eV) of pyrolytically produced cyclopropenylidene, taken under the same conditions as Figure 1b.

propargylene, are calculated[5] to lie 15 and 22 kcal/mol higher in energy than cyclopropenylidene, so one would not expect rearrangement.

The TOF photoelectron spectrum of cyclopropenylidene, calibrated before and after the run using the NO photoelectron spectrum, is shown in Figure 2. Subtraction of the photoelectron kinetic energy for the first sharp peak (1.34 eV) from the photon energy (10.49 eV) gives the adiabatic ionization potential of 9.15 ± 0.03 eV. The mean spacing of 0.145 eV for the four sharp peaks corresponds to excitation of a totally symmetric mode in cyclopropenylidene radical cation with a frequency of $\approx 1170\ \text{cm}^{-1}$. Ab initio calculations[6] at the CISD/6-31G* level for both cyclopropenylidene neutral and monocation (both structures are global minima[5-7] on their respective potential hypersurfaces) predict an increased C=C and decreased C—C bond length upon ionization. Such a geometry change should induce a vibrational progression in the photoelectron spectrum. The observed vibrational frequency agrees well with the calculated 1217-cm^{-1} value for the mode[8] corresponding to the predicted distortion and provides additional support for our structural assignment. The assignment of the 1.34-eV peak to the adiabatic ionization potential rather than a hot band is supported by control experiments in which variation of expansion conditions can suppress or enhance several smaller, faster peaks.

In Scheme I, $\Delta H_f(C_3H_2) \leq 115 \pm 2$ kcal/mol from our ionization potential and a recently determined upper limit[9] on $\Delta H_f(C_3H_2^{\bullet+})$. We also find that $\Delta H_f(C_3H_2) \geq 113 \pm 3$ kcal/mol according to an ion cyclotron resonance (ICR) proton transfer study.[10] Therefore, by bracketting, $\Delta H_f(C_3H_2) = 114 \pm 4$ kcal/mol. With use of $\Delta H_f(C_3H_3)$[11] and $\Delta H_f(C_3H_3^+)$[12] from the literature, we complete the thermochemical cycle to derive a C–H bond dissociation energy (BDE) for cyclopropenyl radical of 61 ± 6 kcal/mol. We find that this BDE is reduced vis-à-vis a nominal sp-hybridized C–H bond strength[13] of 131 kcal/mol by the 65–70 kcal/mol singlet–triplet splitting[7] in cyclopropenylidene, to within experimental error. *We interpret this numerical agreement to be experimental confirmation of a valence-bond picture*[14] *of radical bond strengths in which homolytic bond dissociation energies in the radical are reduced by the valence promotion energies of the resulting fragments* (*relative to their respective ground states*). For radicals, like C_3H_3, that cleave to produce a *singlet* carbene, like C_3H_2, the valence promotion energy of the carbene fragment is approximated by the singlet–triplet splitting. For cyclopropenylidene, the near-exact identification of the valence state[15] with the lowest eigenstate having an open-shell configuration arises from constraint of bond-angle changes at the carbenic carbon by the small ring, from absence of polar substituents, and from the extremely large singlet–triplet splitting. For the more general case of acyclic, π-donor substituted radicals, we predict that bond-strength reductions will scale with singlet–triplet splittings, although exact numerical agreement may not be as good.

Scheme I. Thermochemical Cycle for the Heat of Formation and Proton Affinity (PA) of Cyclopropenylidene and the Bond Dissociation Energy (BDE) of Cyclopropenyl Radical[a]



[a] Numerical quantities are all indicated in kcal/mol units. Literature heats of formation are indicated by italic numbers; quantities determined in this work are indicated by roman type.

We have measured the adiabatic ionization potential of cyclopropenylidene and used it to complete experimental verification of a general model for substituent effects on radical bond strengths. Further spectroscopic studies on C_3H_2 are underway to confirm the structural assignment.

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