Diradicals: Conceptual, Inferential, and Direct Methods for the Study of Chemical Reactions

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It has been known for over a century that the thermal decomposition of polyatomic organic molecules proceeds by the cleavage of covalent bonds. Because of the highly specific preference for the breaking of the weak carbon-carbon bonds in small rings, much attention has focused on the pyrolysis of cyclopropanes and cyclobutanes (*1–6*). The development of this area of chemistry can be seen as a model for the use of new techniques in the recognition and solution of detailed mechanistic problems. As reported on p. 1359 of this issue by Pedersen *et al.* (*7*), the current introduction of femtosecond transition state spectroscopy (*8*) for this purpose signals a welcome new direction for experimental and conceptual methods. Reactive intermediates in the transition state region are directly identified by molecular beam mass spectrometry, and their structural changes are followed with femtosecond time resolution. One now has entered into the third of three rather well-defined (even if temporally overlapping) eras in the study of the mechanisms of unimolecular reactions.

Time	Date	Observations	Methods
	1896-1901	Discovery of Rearrangement 1→2	Classical Structure elucidation
Phase I	1955-present	Tests of energy rerdistribution theories	Low-pressure kinetic measurements
Phase II	1934-1964	Kinetics [*k(T)*] of gas-phase 1→2 reactions	Thermal gas kinetics by chemical and GC analysis
	1958-present	Stereochemistry	Experiment: GC, IR, NMR, OR Theory: Semi-empirical and ab initio quantum calculations
Phase III	1994-	Dynamics & direct observations; *k(E)*	Femtosecond time-resolved mass spectrometry

The first phase was concerned with the exploitation of clean gas-phase chemistry: unimolecular isomerizations, such as the cyclopropane (**1**) to propene (**2**) reaction, as tests of the rival Slater and Rice-Ramsperger-Kassel-Marcus (RRKM) theories of energy redistribution in thermal reactions (*9, 10*). The tests rated the ability of these theories to account for the shape and position of the Lindemann fall-off curve of the rate constant at low pressures. However, the results of the tests were not very sensitive to the model chosen for the structure of the transition state and hence were of limited applicability to the question of mechanism (*1, 9*).

The second phase aimed to explore the consequences of a suggestion by Chambers and Kistiakowsky (*11*) that in the structural isomerization of cyclopropane to propene (**1**→**2**), a plausible pathway could proceed over a fleeting diradical intermediate, the trimethylene species **3**. Early support for this type of intermediate came from the seminal observation by Rabinovitch, Schlag, and Wiberg (*12*) that in the pyrolysis of the isotopically labeled cyclopropane-1,2-d_2, cis-trans isomerization of the starting material competed with the structural isomerization to propene (*13–15*). The corresponding species tetramethylene (**4**) has been invoked in the pyrolysis of stereochemically labeled cyclobutanes, which Walters first showed to undergo stereomutation in competition with cleavage to two ethylenes (*16*).

Numerous experiments, thermochemical calculations, and quantum theoretical computations (*1–5, 14, 15, 17*) have filled in the outlines of this picture of a reactive species with one broken carbon-carbon bond. Exquisitely detailed descriptions of the stereochemical courses of many small-ring pyrolysis reactions have been worked out (*1–5*). Also, for comparison, the diradical intermediates have been generated by independent means, often by the extrusion of small stable molecules such as CO or N_2 by fragmentation of cyclic precursors (*1, 3, 5*). Nevertheless, obscurities remain.

For example, in the case of trimethylene, one must be concerned that despite decades of work, the results of several quantum theoretical calculations (*13*) all indicate little or no barrier to ring closure to cyclopropane, whereas the thermochemical-kinetic approach suggests a definite barrier. Benson (*18*) proposed that the heat of formation of trimethylene could be derived by adding to the heat of formation of propane the dissociation energies of its C1–H and C3–H bonds and subtracting from the result the dissociation energy of the H–H bond of elemental hydrogen. This procedure implicitly assumed that the two C–H bond dissociation energies (BDEs) were the same. The BDEs available at the time of the original work led to the conclusion that diradical **3** lies 9.3 kcal/mol below the energy of the transition state for the stereomutation. The latter value is obtained from the Arrhenius parameters E_a = 65.1 kcal/mol and log A (in seconds) = 16.41 of Schlag and Rabinovitch (SR) (*19*) by adding the activation enthalpy for the reaction in the high-pressure limit, $\Delta H^{\ddagger}$: = $E_a - RT$ = 65.1 kcal/mol – RT, to the heat of formation of cyclopropane.

More recent BDE determinations on simple alkane models were interpreted to favor higher C–H bond strengths, which led to the suggestion that the energy of the diradical in the Benson additivity model therefore should be raised by about 5 kcal/mol (*20*). This still left the trimethylene diradical below the transition state by 4.3 kcal/mol. It was then proposed (*20*) that this gap could be eliminated if one replaced the earlier SR Arrhenius parameters (*19*) with new values, log A (in seconds) = 14.13 and E_a = 61.3 kcal/mol, derived (in an unspecified way) from results in a paper by Waage and Rabinovitch (WR) (*21*). However, the proposed (*20*) Arrhenius parameters do not correlate the experimental data, as is clear from the rate constants calculated from them, which are smaller than the reported ones (*19*) by factors of 11 to 15 over the available temperature range. In fact, Waage and Rabinovitch (*21*) were concerned with a different subject and made no reference to revision of the SR high-pressure data. To announce the disap-

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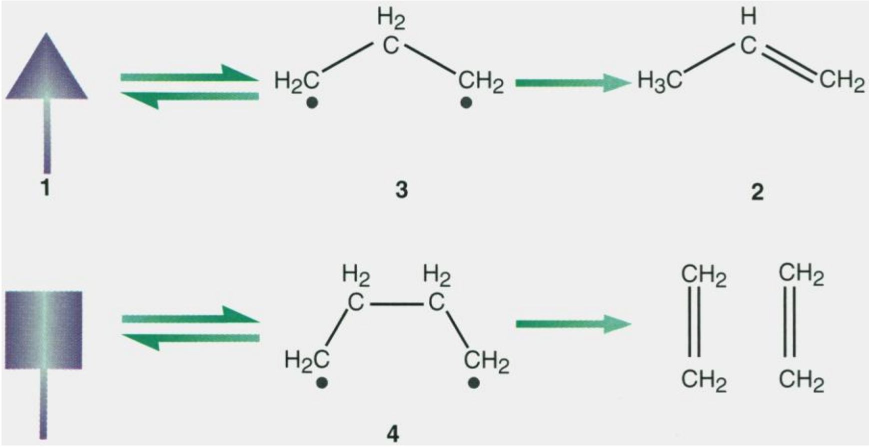

pearance of the "Benson barrier" on the basis of the suggested line of reasoning (*20*) therefore seems unwarranted.

One might imagine that the remaining discrepancy could be associated with the assumption of equal C–H bond strengths in the two steps of the gedanken reaction propane → propyl + H → trimethylene + 2H. Thus, if the second C–H bond were stronger than the first by about 4 to 5 kcal/mol, the heat of formation of trimethylene and that of the stereomutation transition state would become about equal. Borden and coworkers (*15*) have investigated this computationally at the GVB-PP(1)/6-31G* level of quantum mechanical theory. They conclude that there is such an effect, but it amounts to only 1.6 kcal/mol. Whether this value is method-dependent remains to be seen. Similar uncertainty has surrounded the question of an energy barrier to the recyclization of tetramethylene (*1*, *3*, *5*).

These difficulties expose again (*1*, *2*) two major problems inherent in attempts to use thermochemical-kinetic approaches to derive information about reaction energy surfaces. The first is the requirement for extreme accuracy in thermochemical and kinetic measurements. It is conceivable that future technical advances might satisfy this, but the form that such improvement might take is not yet apparent. The second is that the entire rationale of the bond-additivity thermochemical-kinetic approach is based on modeling the heat of formation of a reactive intermediate with data derived from stable compounds that do not embody the characteristic diradical structure.

Other problematic issues include the absence of direct information on the rates of internal rotation, which permit loss of stereochemistry in diradical intermediates (*1*, *5*, *7*); the question of the diradical's spin multiplicity; and potentially important issues associated with dynamical effects (*22*).

Thus, although substantial understanding has been gained by both the stereochemical experiments and theoretical calculations, major problems remain for which the previous methods seem to be unsuited. This circumstance assures an enthusiastic reception for the current approach (*7*) of femtosecond transition state spectroscopy to diradical chemistry.

In the earlier thermal kinetic experiments carried out under pyrolysis conditions, the basic information necessarily was limited to overall conversion of reactants to products. Rate constants $k(T)$ were determined as functions of temperature, which meant that they measured an average over all of the accessible energy states. The femtosecond techniques now measure rate constants $k(E)$ as functions of energy rather than temperature and permit direct examination of the temporal dynamics of the intermediates. One of the especially significant results of the femtosecond work is the recognition from the analysis of the relation of lifetime versus energy that the energy surface for tetramethylene contains a definite multidimensional basin, whereas that for trimethylene does not. These findings will interest quantum theorists who are concerned with the shape of the reaction potential surface in the vicinity of the transition state. They also provide experimental determinations of actual lifetimes of the transients as standards of comparison for the lifetimes derived theoretically by dynamical trajectory calculations (*22*). Proposed explanations for experimental stereochemical results ultimately must be made compatible with these lifetimes.

The conditions of the new experiments assure that one is dealing with the singlet states of the diradicals. The triplets could give stable products only by a violation of spin-conservation and would be essentially inert on this time scale. Also, because internal rotations are slow on this time scale, one can prepare well-defined and aligned initial rotational states by means of a polarized initial energy pulse (*8*). Interrogation with a polarized probe pulse would permit the direct measurement of the long-sought internal rotational rates of the diradicals.

Further applications of femtosecond methods to problems of unimolecular reaction mechanisms seem imminent, and it is safe to predict that these studies will bring to light mechanistic questions that could not be asked before. Moreover, it seems likely that one can directly observe diradical intermediates in bimolecular reactions. The design and construction of these and other related experiments promise to engage chemical physicists, theoreticians, and organic chemists in a fruitful collaborative enterprise.

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