The amplitude spectrum of the new intermediate does not resemble published spectra for OClO or ClOCl, nor does it match a modulation spectrum of ozone obtained by photolyzing NO_2 in oxygen done on this instrument with the same slit widths. An infrared modulation experiment showed no ozone although the ultraviolet and infrared absorption cross sections are comparable. (In the matrix work some ozone was seen.[3b])

The modulation of each species was shown to depend on both oxygen and chlorine concentrations. No modulation can be detected if either reactant is absent. From the Porter and Wright mechanism the effect on the modulation amplitude of halving the oxygen or doubling the chlorine concentrations can be calculated. The experimental results are in satisfactory agreement with these calculations.

A rate constant for the complex reaction

$$\mathrm{Cl} + \mathrm{Cl} + \mathrm{O_2} \longrightarrow$$

can be estimated by combining two literature values. Porter and Wright say this rate is 46 times faster in oxygen than in nitrogen. Combining this with a recent measurement of chlorine atom recombination[6] in argon gives the approximation

$$\mathrm{d[Cl]}/\mathrm{d}t = -2[\mathrm{Cl}]^2[\mathrm{O_2}]k$$

$$k = 5.3 \times 10^{-31}\ \mathrm{cm^6/(molecule^2\ sec)}$$

The phase shift of the fast intermediate (regarded as ClOO) and the value for the light absorbed by chlorine give a rate constant approximately 1.5 times that predicted. However, one would expect nitrogen to be a better gas than argon in catalyzing the recombination of chlorine atoms.

Since the fast intermediate does not match the spectra of known molecules which could be in the system, and since it behaves as ClOO would be expected to, the fast intermediate is assigned as the radical ClOO.

Work is now proceeding to gather kinetic data on this system.

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[6] E. Hutton and M. Wright, *Trans. Faraday Soc.*, 61, 78 (1965).

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Alternate Electrocyclic Pathways. A Quantitative Energy Evaluation

Sir:

We wish to report the rate constants and activation parameters for the gas-phase, unimolecular valence isomerization[1,2] of bicyclo[2.1.0]pent-2-ene to cyclopentadiene: $\log k\,(\mathrm{sec^{-1}}) = (14.2 \pm 0.2) - (26{,}900 \pm 300)/2.303RT$ $(299 \leqslant T(^\circ\mathrm{K}) \leqslant 381)$. The activation energy allows us to make a quantitative evaluation of the energy difference between alternate electrocyclic pathways in cyclobutene isomerizations.

Since the definition and characterization by Woodward and Hoffmann[3] of electrocyclic reactions, a considerable amount of research has been directed toward exploring the validity and extent of applicability of the "Woodward–Hoffmann rules." Thus far, within the limitations of the hypotheses no counterexamples have been observed; the stereochemical products have been only those predicted. It is of considerable importance to evaluate quantitatively the energy difference between allowed and nonallowed processes. The "rules" follow directly from orbital symmetry considerations, and although calculations can be carried out, there is *a priori* no good way of evaluating the added stability of the preferred pathway. The stereochemical results might allow an estimate to be made experimentally. However, since a difference of $\Delta E_a \cong 2 \times 2.303RT$ yields 99% of the favored product, this test is not nearly sensitive enough. Thus, while it is certain that at least 4 kcal/mol separate the possible pathways, the difference may be much greater.

The "rules" do not exclude the possibility of less favored reactions "under very energetic conditions." This might be taken to suggest that the unfavored process will occur only with high activation energies or at high temperatures in situations where the favored process is impossible due to, say, steric constraints.[3] On the basis of such criteria, the disrotatory reaction which we have studied constitutes a counterexample to the "rules" since it has a lower activation energy (and proceeds at a lower temperature)[4] than its allowed, conrotatory, monocyclic analog, cyclobutene → butadiene.[5]

Since there are good reasons to believe that formulation of electrocyclic reactions into allowed and nonallowed processes is valid, it is clear that the hypothesis should be refined to account for the case of bicyclo[2.1.0]pent-2-ene. In doing this, we will, in addition, define a useful quantitative measure of the difference in energy for the alternate pathways.

We propose that the transferable quantity with which the Woodward–Hoffmann rules deal is the *unstrained* bond dissociation energy of the bond between the termini of the π system in the transition state.[6a] Defining strain energy (SE) in a cyclic compound in the usual way,[7] as the difference between the observed and

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[1] Equation 2, $n = 1$.

[2] Reactions were carried out in a 500-cc quartz vessel (situated in an aluminum block oven) which is part of the sampling optical system of a modified Cary 15 spectrometer: D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, 87, 4053 (1965).

[3] R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395 (1965), and succeeding papers. Also, see H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

[4] J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *ibid.*, 88, 846 (1966). The half-life at room temperature reported in this reference (2 hr) is shorter than the "true" unimolecular half-life reported here (40 hr) presumably due to dimerization reactions in solution.

[5] An article by H. M. Frey, B. M. Pope, and R F. Skinner, *Trans. Faraday Soc.*, 63, 1166 (1967), contains a review covering this and similar compounds.

[6] (a) In this proposal we make use of *formal* definitions based on a *model*. Other, similar descriptions will work equally well, and use of the *model* is not meant to imply its existence *per se*. This type of formulation is precisely analogous to the definition of empirical resonance energy. (b) This bond dissociation energy ($\mathrm{UBE}^{\ddagger}$) is the sum of several interactions including σ, π, and delocalized π components. It is the empirically derived quantity most closely related to the calculated Woodward–Hoffmann values. With this definiton, $\mathrm{UBE}^{\mathrm{gs}}$ is the BE of the corresponding saturated system.

[7] G. J. Janz, "Thermodynamic Properties of Organic Compounds," revised ed, Academic Press Inc., New York, N. Y., 1967, p 107.

calculated heat of formation, we may also define the bond dissociation energy (BE) of any of the ring bonds as the difference between the BE of a similar bond in an open-chain compound[8] (*unstrained* bond energy, UBE) and the same SE.[7,9] Thus, the C–C BE in cyclopentane (76) is equal to the C–C BE in *n*-pentane (82) minus the SE in cyclopentane (6). Bearing in mind that the enthalpy change for a reaction is equal to the sum of BE's of the bonds broken in the reactants minus the sum of the BE's of bonds formed in the products, and applying this along with the usual transition-state formulation of the activation energy of a unimolecular reaction, we have

$$\begin{aligned} E_a - RT = \Delta H_f^{\ddagger} - \Delta H_f^{gs} &= BE^{gs} - BE^{\ddagger} \\ &= UBE^{gs} - SE^{gs} - UBE^{\ddagger} + SE^{\ddagger} \end{aligned} \tag{1}$$

What the Woodward–Hoffmann rules describe are the UBE‡'s for conrotatory and disrotatory processes;[6b] what determines the *stereochemical course* of the reaction are the relative BE‡'s; what determines the *rate* of the reaction is BE^{gs} − BE‡. Thus, compounds with unusually strained ground states will react unusually rapidly only if the corresponding transition states are relatively strain free, and reactions involving unusually strained transition states will be slow only if the ground states are relatively less strained. In view of this analysis, it is clear that bicyclo[2.1.0]pent-2-ene reacts rapidly because the transition state is significantly less strained than the ground state. Naturally, the transition state for the conrotatory process is extremely strained.

If the SE for transition states and ground states can be estimated, UBE^{gs} − UBE‡ can be determined. Then, UBE‡ can be evaluated for allowed and nonallowed processes. As a first approximation, in considering reactions of the cyclobutene → butadiene type we assume that the transition state has SE of the product diene. The SE's can be estimated from known thermochemical data.[7,9] For the series of nonallowed transformations[10,11] (eq 2), UBE^{gs} − UBE‡ = $E_a - RT + SE^{gs} - SE^{\ddagger}$. The results are tabulated in Table I. The spread in values of UBE‡ is undoubtedly due to slight underestimation of SE‡ for $n = 1$. Thus, a value of UBE$^{\ddagger}_{\text{nonallowed}}$ ≅ 5 ± 3 kcal/mol is probably correct. That this formulation is reasonable is shown by the fact that it fits compounds varying by *ca.* 20 kcal/mol in E_a with a single model. Our confidence is increased significantly by inclusion of bicyclopentene which displays unique behavior.

(2)

Table I. Energies (kcal/mol) for Disrotatory Reactions[a]

n[b]	$\Delta H^{\ddagger}$	UBE^{gs}	SE^{gs}	SE‡	UBE‡
1	26[c]	78[f]	57	6	1
3	44[d]	78	36	7	5
4	42[e]	78	36	8	8

[a] Thermochemical data taken from ref 7, 8, and 9. [b] Equation 2. [c] Present work. [d] Reference 10. [e] Reference 11. [f] BE for diisopropyl.

A similar treatment of the allowed reaction of cyclobutene gives UBE$^{\ddagger}_{\text{allowed}}$ ≅ 20 kcal/mol.[12] This number may be somewhat low since it assumes no strain in the transition state. Nevertheless, this analysis clearly shows that the difference in energy with which the Woodward–Hoffmann rules deal is ≅15 kcal/mol. Consequently, it is clear why compounds with essentially no added strain for either pathway react only by the allowed process.[13] The observed stereochemistry is, indeed, an inadequate measure of the added stabilization. Another value of our formulation lies in its predictive power. By making use of appropriate thermochemical data it is possible to determine the stereochemical outcome of a given reaction and to estimate its rate. This is likely to be of importance, for example, in the larger bicyclic systems where the allowed processes are no longer sterically prohibited.

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(8) Bond strengths: S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

(9) Strain energies: S. W. Benson, *et al.*, *Chem. Rev.*, in press.

(10) G. R. Branton, H. M. Frey, D. G. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, 62, 659 (1966).

(11) G. R. Branton, H. M. Frey, and R. F. Skinner, *ibid.*, 62, 1546 (1966).

(12) $E_a - RT = 32$, UBE^{gs} = 82, SE^{gs} = 30, SE‡ = 0 (kcal/mol).

(13) The nonallowed path (eq 2) is not necessarily concerted. Since only one product is possible, the energy difference calculated here may be that between an allowed-concerted and a nonallowed-stepwise process.

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Biosynthesis of *Conium* Alkaloids Using Carbon-14 Dioxide. Interrelation of γ-Coniceine, Coniine, and N-Methylconiine

Sir:

Poisonous hemlock (*Conium maculatum*) contains a number of structurally similar propylpiperidine bases: γ-coniceine (I), coniine (IIa), N-methylconiine (IIb), conhydrine (III), and pseudoconhydrine (IV). Cromwell and Roberts,[1] Fairbairn and Suwal,[2] and Leete and Adityachaudhury[3] have presented evidence supporting a central role for γ-coniceine in the biosynthesis of this group of alkaloids. We now present kinetic evidence derived from short-term exposures of young plants to $^{14}CO_2$ which clearly establishes the primacy of γ-coniceine in the nonoxygenated series. In addition estimates of the amount of ^{14}C incorporation into the alkaloids in relation to the total $^{14}CO_2$ fixation have been obtained.

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(1) B. T. Cromwell and M. F. Roberts, *Phytochemistry*, 3, 369 (1964).

(2) Y. W. Fairbairn and P. N. Suwal, *ibid.*, 1, 38 (1961).

(3) E. Leete and N. Adityachaudhury, *ibid.*, 6, 219 (1967).