Energy Distribution in Reaction Products. The Photolysis of Cyclobutanone.

R. J. Campbell[1a] **and E. W. Schlag**[1b]

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Abstract: The distribution of energy among products of a chemical reaction gives information about microscopic rate processes. In a unimolecular reaction from photoexcited states such an energy distribution can be measured indirectly by selecting the initial energy of the system and by observing the energy-dependent, secondary decomposition of products. Although this latter quantity depends on a theoretical relation between rates and energy, this has been well established for a few molecules, such as cyclopropane. In this work we consider the results of the photolysis of monoenergetically excited cyclobutanone undergoing unimolecular decomposition from its first excited state to give internally excited cyclopropane in its electronic ground state and carbon monoxide. The secondary decomposition of the cyclopropane prior to collisional stabilization then gives a measure of its internal energy. A theoretical model for internal energy distribution is considered which assumes statistical equilibration between all the vibrational degrees of freedom available. From such a model one can predict the experimental observed distribution of propylene to cyclopropane as a function of wavelength. It is concluded that the internal energy distribution has not equilibrated among the product species of this reaction, except at the highest energies studied. The nonequilibrium features of the distribution of internal energy among products are so large as to be quite outside the expected errors of this analysis. In phase space language this would mean that, except at high energies, less than the total phase space allowed on the basis of energy conservation is accessible for product species.

There is renewed interest in understanding chemical kinetics on the basis of fundamental microscopic, time-dependent processes involving defined quantum states. The approach can be divided into a theory for the stochastic processes involved as they relate to a macroscopic observable state, and, secondly, into an understanding of the details of the individual processes for a specified microscopic state. Such information must be obtained from experiments involving specially prepared systems, which can be analyzed as to their detailed microscopic state; these include experiments involving fluorescing molecules[2] or molecular-beam experiments.[3] Detailed theoretical treatments have of necessity been carried out only for relatively simple systems for which dynamical calculations are feasible.[4] For more complicated systems, the use of various approximations in the theory, such as a phase space approach[5] becomes a virtual necessity.

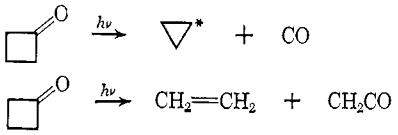
One of the questions relevant to the justifiability of workable approximations is that of the distribution of energy among reactant or product species of a chemical reaction. For example, if all internal degrees of freedom are in an energy equilibrium everywhere on the reaction surface, one could determine the relative concentrations of species simply from phase space considerations. Such simplifications constitute workable theoretical assumptions which, though useful for computational purposes, are still in need of experimental verification.

In particular, if such a constant energy equilibrium exists over the entire reaction surface, one can predict the distribution of energy among the products of a chemical reaction. Some products of bimolecular reactions fluoresce, and hence allow a determination of the detailed energy distribution. Recent results, however, appear to indicate that the distribution of energy among reaction products was not an equilibrium distribution.[2]

A unimolecular decomposition of a large molecule might perhaps be expected to exhibit more nearly a behavior characteristic of an internal equilibrium, as the equilibration of internal energy in reactants appears to be a process which probably precedes the process of unimolecular decomposition,[6] at least for typical experimental conditions. Whether this equilibrium is still preserved in products appears to be unknown, and hence it is unknown whether the microscopic equilibrium is equally valid for products as it apparently is for reactants.

The photolytic decomposition of cyclobutanone is well suited for such a study, since the initial total energy state can be precisely defined by the primary step of absorption of light and since the product states exhibit a well-characterized behavior as a function of energy.

In particular, it has been shown previously that the primary reactions which account for virtually all the products are



where the asterisk denotes vibrational excitation. The

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[1] (a) Abstracted from Ph.D. thesis of R. J. Campbell; (b) Alfred P. Sloan Research Fellow.

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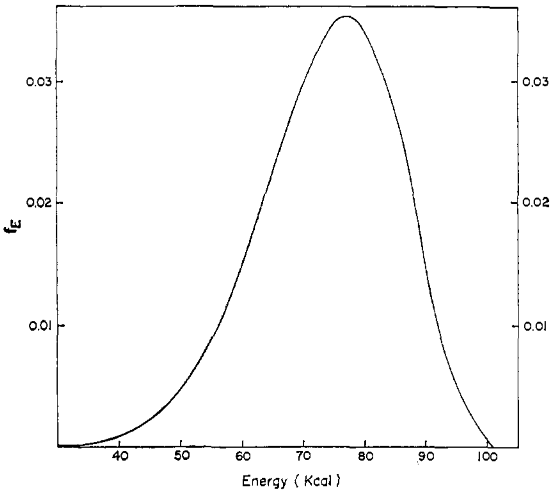
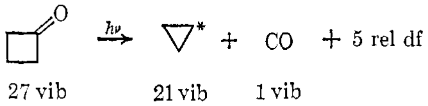


Figure 1. Energy distribution for a total available energy of 101 kcal, assuming a statistical model.

initial photolysis probably originates from the first excited electronic state with negligible activation energy, since the products are quite different from those of the thermal reaction in the ground state. The product cyclopropane shows, however, no electronic, but only internal excitation.[7] The excess vibrational energy of the cyclopropane is large enough to cause its isomerization to propylene unless it is collisionally stabilized. The pressure dependence of the ratio of propylene to cyclopropane (P/Δ) was shown to be due to this effect.[7] This pressure dependence has been studied in many systems which lead to excited cyclopropane. Furthermore, there exists a quite adequate theoretical treatment of this effect which closely agrees with the experimental data over all ranges of internal energy tested, including the thermal isomerization of cyclopropane.[8] Hence this ratio, as a function of pressure and energy, provides a method of determining the energy distribution in the cyclopropane from the known energy dependence of the decomposition of excited cyclopropane and the relevant thermochemical quantities.[7]

For this unimolecular decomposition in an excited electronic state, the initial excitation energy is known, and the final energy of one of the products, cyclopropane, can be determined. Of particular interest is whether this internal distribution of energy in the course of the reaction is what one would predict if complete internal equilibration occurred on the time scale of this reaction. Such equilibration would be predicted by a statistical model.

Statistical Model for Energy Photopartitioning. If a microscopic equilibrium is maintained over the entire surface, one would expect a simple statistical formulation based on the internal degrees of freedom (df) to hold for the energy distribution among products.



For this particular reaction it could be argued that $^{21}/_{27}$ is the fraction of the total available energy that would be carried away as vibrational excitation of the cyclopropane; however, from such a model, in which one only counts the number of degrees of freedom which are effective in removing energy, there is no method of determining the width of the energy spread in the product molecules. Since energy spreads for photolytic fission reactions have been suggested,[9,10] a statistical model should also predict the energy spread in the products as well as the average energy of the products.

If it is assumed that the energy level spacings of product molecules are just given by the overtones and combinations of ground-state species, then an energy equilibrium among products implies that the total state density is determined by simply folding the relevant level schemes into one another. Thus, the fraction of cyclopropane molecules which have an energy E out of a total available energy E_T will be[11]

$$f_E = \frac{D_\nabla(E)D_R(E_T - E)}{\sum\limits_{E_i}^{E_T=0} D_\nabla(E_i)D_R(E_T - E_i)} \tag{1}$$

$D_\nabla(E)$ and $D_R(E_T - E)$ are the energy densities of the cyclopropane and "remainder" species, respectively, where the carbonyl stretching frequency and the remaining five relative degrees of freedom are to be identified with the "remainder." It has been assumed here that all initial excitation energy, except that lost as ΔE_{Rxn}, is available for vibrational excitation.[12] Thus, the total available internal energy is

$$E_T = E(h\nu) + E(\text{thermal}) - \Delta E_{Rxn} \tag{2}$$

where $E(h\nu)$ is the energy of the exciting wavelength, E(thermal) is the initial thermal distribution, and ΔE_{Rxn} is the energy of reaction.

The energy densities of the species involved in this reaction have been calculated using the 27 vibrational frequencies of cyclobutanone, where 21 of them have been roughly identified with the 21 cyclopropane vibrational frequencies and the remaining 6 with the carbon monoxide and the relative motions of the separating fragments. The densities due to all the overtones and combinations were then calculated as a function of the total available energy using the SSHT expansion[13] which gives an *ab initio*, though harmonic oscillator result. For the particular case of 2537-A radiation, the results of (1) are shown in Figure 1.

Quantum Yields. From this energy distribution it is then possible to predict the ratio of propylene to cyclopropane (P/∇) which would be observed for this energy distribution. One is, in fact, interested in the relative quantum yields for propylene *vs.* cyclopropane. It is usually satisfactory to assume that deactivation is an absorbing barrier problem, at least in this case. Furthermore, one assumes that the reaction is a random process, as are collisions, and that by collisions one means an energy-independent frequency determined

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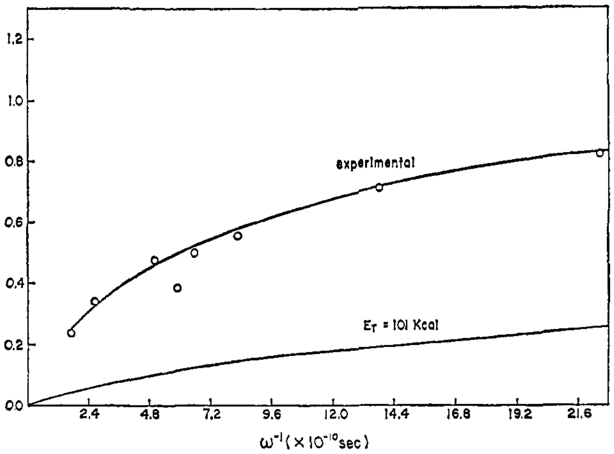

Figure 2. Comparison of experimental results with statistical theory for the 2537-A pressure studies.

from kinetic theory considerations. This latter assumption is open to obvious question, but, within the framework discussed here and within the small arbitrariness in the theoretical formulation of k_E, it is possible to match theory and experimental data,[8] indicating an uncertainty in k_E of less than a factor of 2. Of more serious difficulty is probably the simplifying assumption that all collisions lead to deactivation of excited species. If this is not so, the energy-transfer probabilities must be known, which can then be used in a many-shot expansion to give a quantum yield which includes these multiple scattering effects.[11] The conditions of this experiment were deliberately chosen to minimize these effects, and hence the ratio of

$$\frac{P}{\nabla} = \frac{\sum_{E}^{E_T}\left(\frac{f_E k_E}{\omega + k_E}\right)}{\sum_{E}^{E_T}\left(\frac{f_E \omega}{\omega + k_E}\right)} \tag{3}$$

where f_E and E_T are determined by (1) and (2), respectively, ω is the collision frequency (assumed to be energy independent), and k_E is the microscopic rate constant for isomerization of cyclopropane to propylene at energy E, calculated from RRKM theory. The collision frequency has been calculated from kinetic theory using the Lennard-Jones force constants given in Table I.

Table I. Lennard-Jones Force Constants for Ethylene, Cyclopropane, and Cyclobutanone.

	Ethylene[a]	Cyclopropane[a]	Cyclobutanone[b]
ϵ/k, °K	224.7	248.9	447
σ, A	4.162	4.807	5.07

[a] Taken from R. A. Svehla, NASA Technical Report R132, 1962.
[b] Estimated from L. I. Stiel and G. Thodos, *A.I.Ch.E. J.*, **10**, 266 (1964); *J. Chem. Eng. Data*, **7**, 234 (1962); O. A. Hougen, K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," Part I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1954.

Comparison with Experiment. The analysis of eq 3 can be utilized in two different ways. (1) A Stern–Volmer plot of P/∇ against reciprocal pressure at fixed photolysis wavelength and so, at fixed energy, for reactants, and (2) a plot of $k_a = \omega P/\nabla$ against photolysis wavelength over the entire absorption band and at fixed pressure can be generated. These plots are then, *via* the reasonably well-defined functional dependence of P/∇ on energy, a direct reflection of the internal energy distribution of product species.

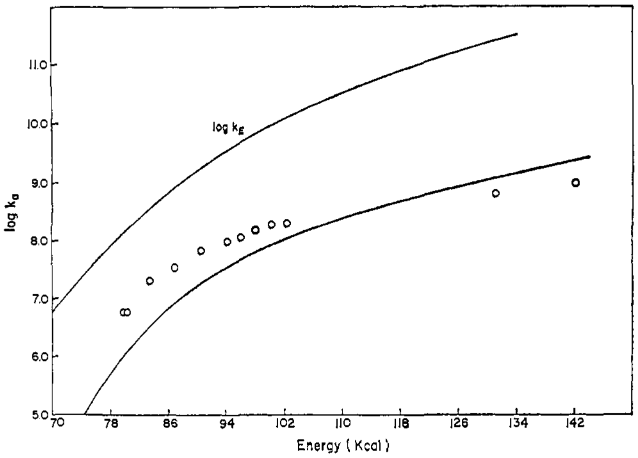

Figure 3. Comparison of statistical theory with experimental points at different photolysis energies (pressure 14.3 torr). The rate constants resulting if all excess energy were to reside in cyclopropane are plotted as log k_E.

Based on a reasonable estimate for the heat of reaction, the total energy available to product species, when photolysis with the 2537-A line of mercury is carried out, is 101 kcal. For this total energy one obtains a distribution of energy from eq 1 which is shown in Figure 1. The corresponding Stern–Volmer plot for this distribution is given in Figure 2. For comparison the experimental ratio of P/∇ *vs.* ω^{-1}, obtained using ethylene as the pressurizing gas over the range 20–500 torr, is also plotted.

Both plots in Figure 2 exhibit curvature due to the broad distribution of energy (Figure 1), but clearly the experiments show that cyclopropane contains far more internal energy than predicted on the basis of microscopic equilibrium among product species.

A further test of the statistical theory can be made by evaluating eq 3 for various wavelengths, at fixed total pressure. The total energy is then specified by eq 1, and the ratio P/∇ predicted by eq 3. Experimental data are available over the entire n → π^* absorption band[14] of cyclobutanone, 2500–3200 A, at a pressure of 14.3 torr. A comparison between the two is presented in Figure 3. Again it is clear that the excited cyclopropane contains energy far in excess of the statistical model, though this difference disappears at higher energies (shorter photolysis wavelengths). The upper curve represents the predicted ratio of P/∇ if one assumed that the total energy appeared entirely as excitation energy of cyclopropane, clearly an upper limit to any theoretical model. The first series of points span the entire envelope of the first, n → π^* absorption band. The two high-energy points belong to the next absorption band at 2000 and 1850 A. The photolyses at these wavelengths are plotted on the same curve, since unimolecular reaction of the cyclobutanone is probably preceded by an intersystems crossing to the first excited singlet state.[15]

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Discussion

The results shown in Figures 2 and 3 clearly indicate that the experimentally observed ratio of P/∇ is much higher than that predicted from statistical theory, except at very high energies. The discrepancy is so large that it is quite outside the expected uncertainties in k_E, ω, or ΔE_{Rxn}, particularly in view of the known fit of k_E and ω against other experimental data. The qualitative conclusion drawn from these results appears unavoidable: the statistical theory of energy fractionation based on phase space arguments is inadequate for predicting the experimental results, and hence the microscopic equilibration of internal energy in this reaction does not extend to products.

All the parameters that were used in the calculation were varied in an attempt to obtain better agreement between the statistical model and the experimental results; however, only an extremely large error in the estimate of the various quantities could account for the large discrepancy between theory and experiment. In particular, one of the critical thermochemical values was the heat of reaction, estimated to be $\sim$16 kcal. An error of 12 kcal would give fair agreement at the lower energies in Figures 2 and 3; however, it would give very poor agreement at the higher energies. Likewise, a factor of 3–4 in the calculation of the microscopic rate constants, a factor quite outside the reasonable variation, would not be enough to obtain agreement at the lower energies. It also should be noted that the general form of the energy distribution does not depend critically on the exact identification of cyclobutanone frequencies with the product species. No variation of these frequencies could possibly account for the very large discrepancy at the lower energies in Figure 2 and 3.

The very high energy results, obtained from photolyses at 2000 and 1850 A, provide good direct experimental evidence for a wide energy spread at least similar to that predicted by the statistical theory. The experimental k_a values obtained correspond to P/∇ ratios of 2.5 and 3.8, for 2000- and 1850-A photolyses, respectively, which indicate that a considerable fraction of the cyclopropane has not isomerized to propylene in spite of the very high excitation energy (143–155 kcal). If the cyclopropane were formed with a narrow energy spread around $^{21}/_{27}$ of E_T (102–111 kcal), the ratio of P/∇ at the pressure studied would have been 50–100. The statistical theory predicts a ratio of 3.5–7.0. This low value of P/∇ is due to the large fraction of cyclopropane molecules which are formed at such low energies that stabilization completely dominates over isomerization. The critical energy for isomerization is $\sim$63 kcal, but even those molecules which are formed with as much as 75–80 kcal tend to be trapped as cyclopropane *via* collision before isomerization can occur. Such an agreement at high energies between the experimental values for P/∇ so near the value calculated on the basis of a statistical model is evidence of the broad energy distribution among product molecules, as one might expect.

The severe disagreement between a statistical theory and experiment at lower energies raises serious doubt about the validity of using statistical arguments for predicting the energy distribution of products, at least for this photolytic decomposition. Hence, at least in this unimolecular reaction, the distribution of energy among product species has gross nonequilibrium features, indicating that the internal energy of all product species is not equilibrated among all degrees of freedom. Hence, even though reactants may be in internal equilibrium before chemical reaction, such an equilibrium does not exist among the various product species of the reaction, except in the limit of high energies.

Such a limiting approach to internal equilibrium in the high-energy region is perhaps not surprising. It may indicate that the system partitions its energy according to dynamic considerations for the particular potential surface. At higher energies, however, one would expect the reaction to traverse the critical surface more quickly, a process which leads to a better coupling between the internal modes and hence a more nearly statistical behavior.[16] Clearly more work is needed on other reactions to understand more fully the reasons for this nonequilibrium partitioning of energy among the products of a unimolecular reaction involving polyatomic molecules.

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