J. Am. Chem. Soc. **1998,** *120,* 1641−1642 1641

Evidence for Interception of Nonstatistical Reactive Trajectories for a Singlet Biradical in Supercritical Propane

Mayra B. Reyes and Barry K. Carpenter*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

Received November 3, 1997
Revised Manuscript Received January 9, 1998

From the results of quasiclassical trajectory simulations, we have recently suggested that thermally generated reactive intermediates, such as singlet biradicals, can exhibit bimodal lifetime distributions.[1] The situation is shown schematically in the graph of Figure 1. The short-lived component of such a distribution arises from direct reactive trajectories that do not randomize the internal energy of the "intermediate" prior to product formation.[2] The longer-lived component arises from trajectories that fail to form products on the first pass through the intermediate region of the potential energy surface (PES) and then become trapped in that region for some time, before eventually exiting to products. We have assumed that this latter set would lead to randomization of internal energy prior to product formation and would therefore be adequately described by statistical kinetic models such as transition state theory.[1] The direct trajectories are of potential mechanistic significance because the simulations suggest that they can mimic behavior expected for a concerted reaction—i.e., a process occurring on a part of the PES where there is no local minimum corresponding to an intermediate.[3] In particular, the direct trajectories can lead to product ratios that fail to conform to the symmetry of the PES.[3] It becomes important, therefore, to distinguish when a reaction really is occurring by competitive mechanisms that explore different parts of the PES and when it occurs with coexistence of nonstatistical and statistical dynamic populations of a common "intermediate." This paper describes an experimental technique that we believe may allow such a distinction to be drawn.

The strategy behind the experiment is to try to intercept the putative direct trajectories by collision of the "intermediate" with a chemically unreactive partner. For a direct trajectory, redistribution of internal energy as a result of the collision would correspond to a deflection from the ballistic path to product and might convert it into a trapped, presumably statistical, trajectory. This should result in a change in the product ratio. The situation can be modeled kinetically as shown in the lower left of Figure 1. In this scheme, the PES is assumed to possess an effective symmetry element such that statistical trajectories will lead to the two products, **P** and **Q**, with equal probability. The direct trajectories are assumed to give only one product (in this case **P**), for reasons discussed previously.[3] The phenomenological rate constants, k_P and k_Q, for formation of **P** and **Q** from **A** can be related to the microscopic rate constants of the mechanistic scheme by applying the usual steady-state approximation to the biradical populations **N** and **S**. The result is eq 1. As expected, the ratio of phenomenological rate constants depends on the collision frequency, k_C, on the fraction of trajectories that are nonstatistical, f_N, and on the rate constant, k_N, with which the nonstatistical population proceeds on to its product.

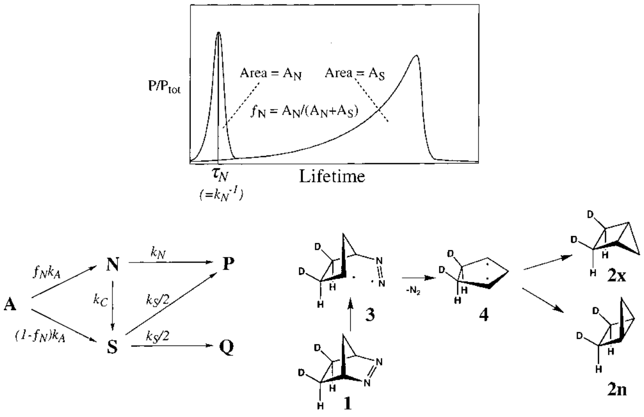

Figure 1.

$$\frac{k_P}{k_Q} = \frac{k_C + (1 + f_N)k_N}{k_C + (1 - f_N)k_N} \tag{1}$$

To intercept the direct trajectories, it is obvious that k_C has to be of a magnitude similar to that of k_N. Our simulations on various biradical species have given values for the average lifetime of the nonstatistical populations ($\tau_N = k_N^{-1}$) of 100−300 fs.[1,3] That means one needs collision frequencies ranging from 10^{12} to 10^{13} s^{-1}. Such high collision frequencies are not easily attained in the gas phase, but are accessible in supercritical fluids.[4] In such a medium, the density, and hence effective collision frequency, can be adjusted over a wide range by changing the pressure.[4,5] As shown by eq 1, the dynamic model leads one to expect that the product ratio should approach unity as the pressure, and hence collision frequency, increases. This expectation stands in contrast to that from the competitive-mechanisms model, as illustrated by consideration of the specific reaction studied in the present work.

Azo compound **1** has long been known to give the stereoisomeric biyclopentanes **2x** and **2n** in a ratio that favors the exo isomer by about 3:1 in the gas phase.[6] Correction for interconversion of the products during the reaction allows one to derive the intrinsic ratio (k_P/k_Q), which turns out to be constant at 4.7 ± 0.9:1 over a temperature range of 130−180 °C.[7] One mechanism for explaining the preferential formation of **2x** would be to invoke a concerted C−C bond formation and C−N bond cleavage from the biradical **3**, which is now generally agreed to be the first-formed intermediate.[8] If this concerted reaction occurred with inversion of configuration at the carbon from which N_2 was departing, the result would indeed be to give **2x**.[6] To explain the source of **2n**, one might invoke a competitive process in which C−N bond cleavage occurred prior to C−C bond formation,

---

[1] Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 10329.

[2] (a) Davis, M. J.; Gray, S. K. *J. Chem. Phys.* **1986**, *84*, 5389. (b) Davis, M. J. *J. Chem. Phys.* **1987**, *86*, 3978. (c) Simonson, M.; Bradley, K. S.; Schatz G. C. *Chem. Phys. Lett.* **1995**, *244*, 19. (d) Pais, A. A. C. C.; Voronin, A. I.; Varandas, A. J. C. *J. Phys. Chem.* **1996**, *100*, 7480. (e) Vande Linde, S. R.; Hase, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2349. (f) Hase, W. L. *Science* **1994**, *266*, 998.

[3] (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, *117*, 6336. (b) Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1997**, *119*, 5253.

[4] Randolph, T. W.; O'Brien, J. A.; Ganapathy, S. *J. Phys. Chem.* **1994**, *98*, 4173 and references therein.

[5] For an early experiment in which the influence of a similar phenomenon on the overall magnitude of the phenomenological rate constant was investigated, see: Dutton, M. L.; Bunker, D. L.; Harris, H. H. *J. Phys. Chem.* **1972**, *76*, 2614.

[6] (a) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695. See also: (c) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 7133.

[7] Lyons, B. A.; Pfeifer, J.; Peterson, T. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 2427.

[8] (a) Simpson, C. J. S. M.; Wilson, G. J.; Adam, W. *J. Am. Chem. Soc.* **1991**, *113*, 4728. See also: (b) Adams, J. S.; Burton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 7935. (c) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115.

S0002-7863(97)03774-8 CCC: $15.00

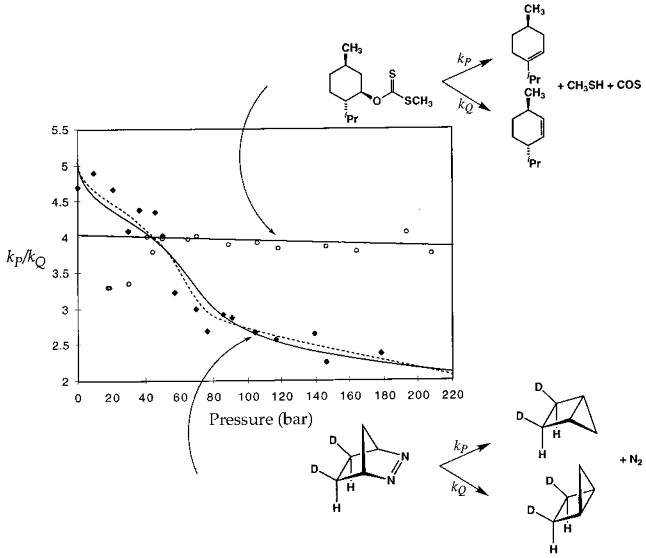

Figure 2. Curves through the azo compound data are from the IBC model (solid line) and the Troe model (dashed line).

affording cyclopentane-1,3-diyl, which could give both stereoisomers of the bicyclopentane.

An alternative explanation for the stereochemistry has arisen from a combination of experiments[7] and molecular dynamics simulations[7,9] on the reaction. In this mechanism, cleavage of the second C−N bond always precedes formation of the C−C bond. Some fraction (f_N) of the population of the resulting cyclopentane-1,3-diyl closes to product **2x** before it has had time to randomize its internal energy. The preference for formation of **2x** over **2n** in such a picture can be ascribed to better dynamic matching[3] between the entrance channel to cyclopentane-1,3-diyl and the exit channel for inversion.[7]

As described above, the dynamic model leads one to expect that k_P/k_Q should decrease with increasing pressure, if the reaction were run in a supercritical fluid. By contrast, one might expect the product ratio to *increase* with increasing pressure from the competitive-mechanisms model. This is because the only influence from change in pressure that one might expect in the latter model would arise from differences in activation volume for the two pathways. It is well-known that activation volumes for uncharged systems are related to numbers of bonds being made and broken in the rate-limiting transition structure.[10,11] By this criterion, the activation volume for the putative concerted pathway should be smaller than that for the stepwise one; thus, the former should be favored at higher pressure, leading to an increase of k_P/k_Q (although it should be noted that the range of pressures explored here is smaller than that used in studies where such effects have been detected[10]). This difference in expected outcomes from the two models is not specific to the reaction studied here. It is generally true that the dynamic model leads to predictions of lower product ratios with increasing pressure whereas the competitive-mechanisms model predicts the opposite (at least for the common situation in which the mechanisms in competition are stepwise and concerted versions of the same transformation).

The experimental results are shown in Figure 2. The lines through the data points correspond to best fits of an isolated-binary collision (IBC) model[12,13] and of a Troe-type model in which the collision frequency in the supercritical propane scales as the inverse of the self-diffusion coefficient.[12,14] It is clear that the ratio of phenomenological rate constants decreases with increasing pressure, as expected for the dynamic model. The data smoothly interpolate between previously determined gas-phase and solution-phase values of k_P/k_Q.[7] Furthermore the best-fit values of the adjustable parameters for the IBC and Troe models seem physically reasonable.[12,15] Of special interest are the fraction (f_N) of reactions occurring via direct, nonstatistical trajectories, which turned out to be 0.67 for both models, and the lifetime ($\tau_N = k_N^{-1}$) of the nonstatistical population which was found to be 130 ± 22 fs by the IBC model and 103 ± 13 fs by the Troe model.[15]

Also shown in Figure 2 are results for a control reaction in which the products really do come from two competitive mechanisms. The competitive pathways for the control are both believed to be concerted reactions,[16] and in accord with that, one sees little dependence of product ratio on pressure in the region where the reactant is miscible with the supercritical fluid (above about 40 bar).[17]

It appears that the study of reactions in supercritical media may be of general value for distinguishing dynamically controlled reactions from those occurring by genuinely different mechanisms. In the cases where the former appears to be the better description, such studies can also afford values for critical parameters that can be compared with simulation results.

Acknowledgment. We thank the National Science Foundation for support of this work (Grant CHE-9528843) for support of this work. In addition, we thank Drs. Thomas Peterson and Kelly Davis for contributing to the design and construction of the supercritical-fluid apparatus.

JA973774X

---

(9) Sorescu, D. C.; Thompson, D. L.; Raff, L. M. *J. Chem. Phys.* **1995**, *102*, 7910.

(10) Klärner, F.-G.; Krawczyk, B.; Ruster, V.; Deiters, U. K. *J. Am. Chem. Soc.* **1994**, *116*, 7646.

(11) For lucid general descriptions of the physical basis for pressure effects on elementary reactions, including some cautionary notes on interpretation of activation volumes, see: (a) Montgomery, J. A., Jr.; Chandler, D.; Berne, B. J. *J. Chem. Phys.* **1979**, *70*, 4056. (b) Troe, J. *J. Phys. Chem.* **1986**, *90*, 357. (c) Hase, W. L. *J. Phys. Chem.* **1986**, *90*, 365.

(12) The density and viscosity of propane were obtained from the NIST12 database (NIST12 version 3.0, Fluid Mixtures Data Center, Thermophysics Division, National Institute of Standards and Technology, Gaithersburg, MD). In the IBC model, the density was used to compute the collision frequency from the equation $k_c = [1/(\rho^{-1/3} - \sigma_{12})][(8k_B\mathrm{T})/(\pi M)]^{1/2}$, where ρ is the number density, σ_{12} is the collision diameter for propane and cyclopentane-1,3-diyl, k_B is Boltzmann's constant, and M is the reduced mass. The best fit value of σ_{12} turned out to be 4.9 Å. In the Troe model, the viscosity of propane was used to compute the self-diffusion coefficient by Troe's interpolation (ref 14) between the gas−kinetic and Stokes−Einstein limits: $D_0 = (3/8)[(\sqrt{RT/2\pi M})/(N_A\sigma_{11}^2\Omega^{(1,1)*}](1/\rho)$; $D_\infty = (k_B\mathrm{T})/(3\pi\sigma_{11}\eta)$; $(k_B\mathrm{T})/(\eta D) \approx (k_B\mathrm{T}/\eta D)_\infty\{1 - \exp[-(k_B\mathrm{T}/\eta D)_0/(k_B\mathrm{T}/\eta D)_\infty]\}$. In these equations, N_A is Avogadro's number, σ_{11} is the self-collision diameter for propane, $\Omega^{(1,1)*}$ is a reduced collision integral (*Molecular Theory of Gases and Liquids*; Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., Eds.; Wiley: New York, 1954), and η is the viscosity. The collision frequency was then computed from $k_c = (k_c^0 D)/D_0$, where k_c^0 is the gas−kinetic collision frequency at low pressure (we used 10^{-5} bar). The best-fit value of σ_{11} was 5.9 Å.

(13) Schultz, K. E.; Russell, D. J.; Harris, C. B. *J. Chem. Phys.* **1992**, *97*, 5431.

(14) (a) Otto, B.; Schroeder, J.; Troe, J. *J. Chem. Phys.* **1984**, *81*, 202. (b) Hippler, H.; Schubert, V.; Troe, J. *J. Chem. Phys.* **1984**, *81*, 3931. (c) Maneke, G.; Schroeder, J.; Troe, J.; Voss, F. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 896.

(15) The values for τ_N are based on two additional assumptions. The first is that clustering of propane molecules around the solute should be relatively unimportant here because we are more than 40 K above the critical temperature for propane (369.85 K). The second assumption is that the collision efficiency for redistribution of internal energy in the cyclopentane-1,3-diyl is unity. Collision efficiencies for vibrational energy *transfer* between molecules are generally not unity (see Troe, J. *J. Phys. Chem.* **1983**, *87*, 1800), but one may surmise that efficiencies of collision-promoted *redistribution* of vibrational energy might be higher. Overestimation of the latter type of collision efficiency would lead to an underestimation of the lifetime of the nonstatistical population of the biradical.

(16) Nace, H. R. *Org. Reactions* **1962**, *12*, 57.

(17) The azo compound **1** is known to be homogeneously mixed with the propane under all conditions because it is in the vapor phase, as shown by the following data. We have determined the vapor pressure for **1** as a function of temperature. It is given by log P (Torr) = −1796.6/T + 7.746. Assuming ideal-gas behavior, this equation suggests that up to 1.8 mmol of azo compound **1** could be completely vaporized in our 19 mL cell at 140 °C. In practice, we never used more than 0.3 mmol. By contrast, the less volatile xanthate used in the control experiment need not be completely vaporized and therefore could be expected to come out of solution at low propane pressures. We assume that this is what is occurring below 40 bar in our experiments. Supporting this assumption is the observation that the product ratio obtained for a sample of the xanthate in a sealed capillary matched that observed below 40 bar in propane.