Communications to the Editor

Dynamics of Organic Reactions

Sir:

Approximate potential energy surfaces have been calculated in recent years for a number of organic reactions by use of semiempirical and *a priori* quantum mechanical techniques. From such a surface, a "reaction path" is usually determined in terms of certain energy criteria (*e.g.*, "minimum energy path"). Conclusions are then drawn concerning the mechanism of the reaction by assuming that it follows the reaction path.[1] In this communication, we demonstrate the feasibility of supplementing this static approach to organic reactions by dynamic results obtained from trajectory calculations on quantum mechanical surfaces.[2] To illustrate the method, we examine the insertion of singlet methylene into a hydrogen molecule. The results reported here demonstrate that the actual behavior of the colliding molecules can be considerably more complex than suggested by an analysis of the reaction path.

Since the techniques used in trajectory calculations of chemical reactions have been described,[3] we outline here only the points of particular interest for the present study. To determine trajectories for complicated systems, efficient methods for evaluating the forces on the atoms and for integrating the equations of motion are needed; the selection of suitable initial conditions and the analysis of the final states, although complicated in some cases, do not introduce significant difficulties. To obtain the forces (*i.e.*, minus the first derivative of the potential surface with respect to appropriately chosen coordinates) one might proceed by computing the potential at a series of points and fitting the results globally or locally with an appropriate analytic expression.[4] An alternative approach, which is expected to be of wider applicability, is employed here; namely, the quantum mechanical expression for the potential surface is used directly for determining the forces along the trajectory. In the SCF-MO formulation for a system with doubly occupied orbitals, the force vector **F** acting on the atoms is[5]

$$-\mathbf{F} = \nabla E = [\nabla\mathbf{H} + {}^{1}/_{4}(\nabla\mathbf{G})\mathbf{P}]^{\dagger}\mathbf{P} - [\nabla\mathbf{S}]^{\dagger}\mathbf{B} + \sum_{A<B}\nabla(Z_A Z_B/R_{AB}) \qquad (1)$$

where **H** is the one-electron Hamiltonian matrix, **G** is the symmetrized electron repulsion supermatrix,[6] **P** is the bond-order charge-density matrix, **S** is the overlap matrix, and **B** is the bond-order charge-density matrix weighted by orbital energies. R_{AB} denotes the distance between atoms A and B with nuclear charges Z_A and Z_B. Use of eq 1 for trajectory calculation requires some simplification to reduce the computing time. We have employed the CNDO model[7] with the Fischer and Kollmar parameters,[8] which yields a satisfactory heat of reaction for $CH_2 + H_2 \rightarrow CH_4$.[9] Given **P**, the time required for obtaining **F** is approximately equal to that needed for determining **P** itself. As to the integration of the equations of motion, we use the adjustable step-size hybrid Gear method,[10] in which two force evaluations are needed per step; the largest step size is 20 au of time (1 au of time = 2.42×10^{-17} sec), about $^{1}/_{12}$th of the isolated H_2 molecule vibrational period. One trajectory of approximately 500 steps takes 3 min on the IBM 360-91; of this time about 80% is used for the energy and force evaluation and the rest for the integration of the equations of motion.

To illustrate the dynamics, we show in Figures 1–3 a set of "snapshots" at intervals of ~200 au of time for three trajectories, whose initial conditions differ only in the choice of impact parameter. In all three trajectories both molecules are initially in the ground vibrational states with zero-point energy (0.034 hartree), in the ground rotational states, and have relative translational energy of 0.0145 hartree. The translational energy, which is significantly higher than the thermal value, was chosen to shorten the calculation time.[11] For the trajectory shown in Figure 1, there is first a repulsive interaction and translation–rotation energy transfer (0–800 au). As shown in Figure 1b, the rotating H_2 molecule remains at $R \simeq 3.0$ au until it picks up enough velocity to move backward and sideways. The relative motion is gradually slowed down by the attraction between the two molecules (1400–3000 au) and finally results in a second encounter (3000–4800 au). Due to the fast rotation of H_2, it hits another repulsive wall and is quickly repelled (5000 au). In the second trajectory (Figure 2), we see that the insertion reaction proceeds smoothly and rapidly. As two molecules approach each other, both CH_2 and H_2 turn counterclockwise so that the empty p orbital of the former points to one of the atoms in the latter. At 600–1000 au, the H_2 molecule rotates clockwise to avoid the repulsion between the lead atom and the lone pair of CH_2, after which a counterclockwise rotation occurs and the H_2 molecule moves into place

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[1] For some examples, see (a) R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, **92**, 1460 (1970); (b) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *ibid.*, **94**, 5639 (1972); (c) J. A. Horsley, Y. Jean, L. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972); (d) M. J. S. Dewar and M. C. Kohn, *ibid.*, **94**, 2704 (1972); (e) A. C. Trindle and D. D. Shillady, *ibid.*, **95**, 703 (1973).

[2] There have been, of course, a number of interesting trajectory studies of organic reactions that have used *empirical* surfaces; see, for example, (a) L. M. Raff, *J. Chem. Phys.*, **44**, 1202 (1966); (b) D. L. Bunker and M. D. Pattengill, *Chem. Phys. Lett.*, **4**, 315 (1969); (c) P. J. Kuntz, E. M. Nemeth, J. C. Polyani, and W. H. Wong, *J. Chem. Phys.*, **52**, 4654 (1970); (d) T. Valencich and D. L. Bunker, *Chem. Phys. Lett.*, **20**, 50 (1973).

[3] M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3259 (1965).

[4] I. G. Csizmadia, J. C. Polanyi, A. C. Roach, and W. H. Wong, *Can. J. Chem.*, **47**, 4097 (1969).

[5] R. Moccia, *Theor. Chim. Acta*, **8**, 8 (1967); A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, **94**, 5612 (1972).

[6] C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

[7] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

[8] H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

[9] J. A. Bell and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **84**, 3417 (1962).

[10] C. W. Gear, *J. SIAM Num. Anal.*, **2B**, 69 (1964); see also the detailed comparison of various methods in P. Brumer, Thesis, Harvard University, 1972.

[11] For the present exploratory study, the initial CH_2–H_2 distance was 5.0 au, inside a small activation barrier (~0.006 hartree) at ~5.5 au for the three trajectories shown in Figures 1–3.

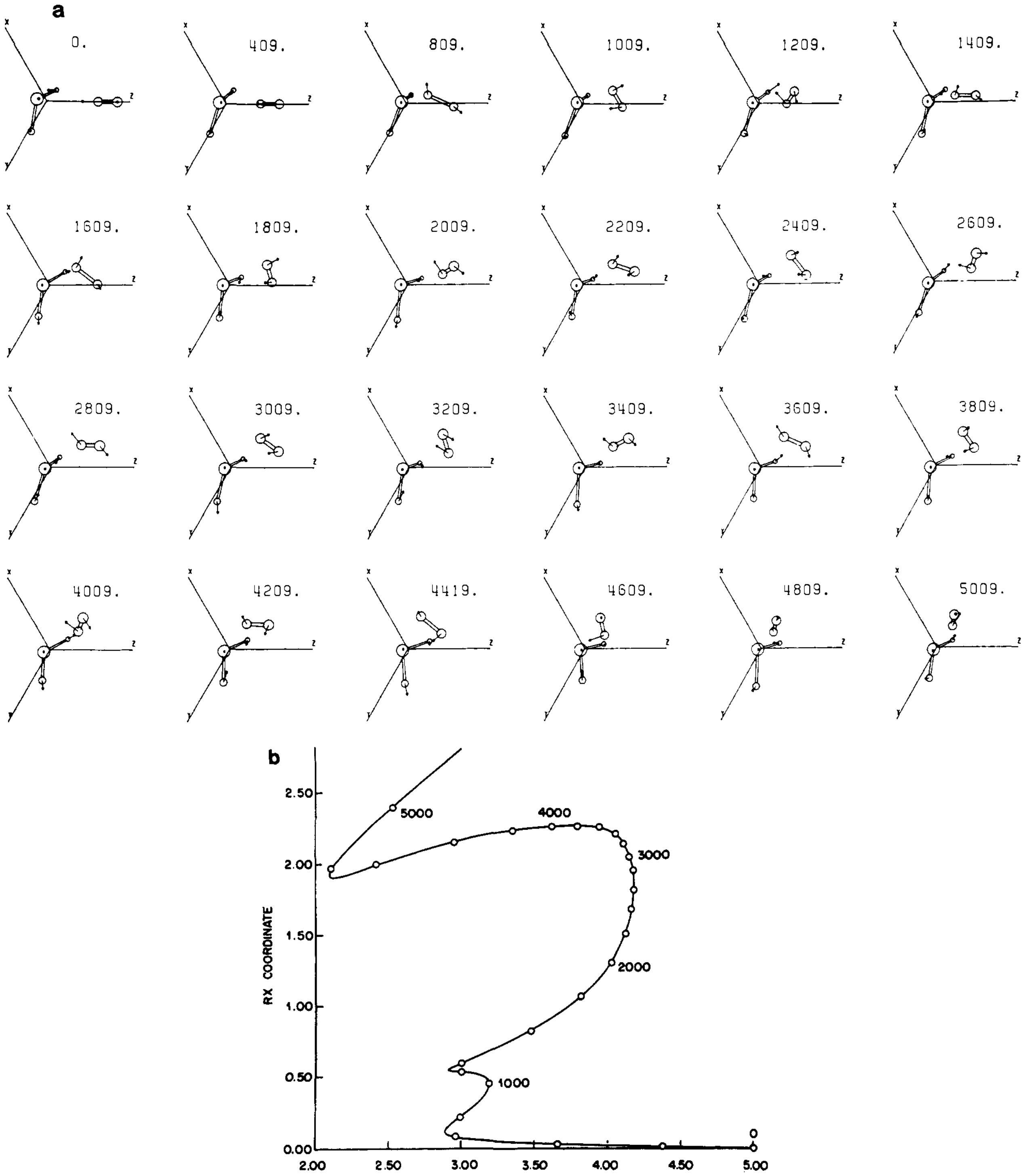

Figure 1. (a) Projected snapshots looking down the 111 axis of $CH_2 + H_2$ collision; origin at center of mass of the system. The CH_2 molecule is initially in the xy plane placed symmetrically with respect to the xz plane; the H_2 molecule is in the xz plane with the vector **R** from the center of mass of CH_2 to that of H_2 equal to (0, 0, 5 au). The arrows show the direction of the velocity of the atom at the time of the snapshot and correspond in length to the distance the atom would move in 200 au if no force acted on it. (b) Trajectory of **R**; the plot gives the components X and Z at times (circles) corresponding to the snapshots in Figure 1a; $Y \cong 0.0$ au at all times.

primarily by displacement of the lead atom. From 1400 to 3600 au, the system corresponds to a CH_4 molecule rotating counterclockwise with stretching and wagging motions highly excited. Since a deactivating collision with another species is not included in this trajectory study, the final snapshots (3600–4400 au) show the departure of H_2 in the forward direction. For the trajectory in Figure 3, the negative impact parameter approach results in a repulsive interaction which leads to reorientation of the CH_2 molecule (up to 600 au) such that the empty p orbital is in line with the nearest H atom of H_2. Closer approach results in lone-pair repulsion and counterclockwise rotation of H_2 by ~120° during 400 au (700–1100 au). At 1100 au, with the other H atom now closest, the H_2 molecule is acted on by a reverse torque, which results in a clockwise

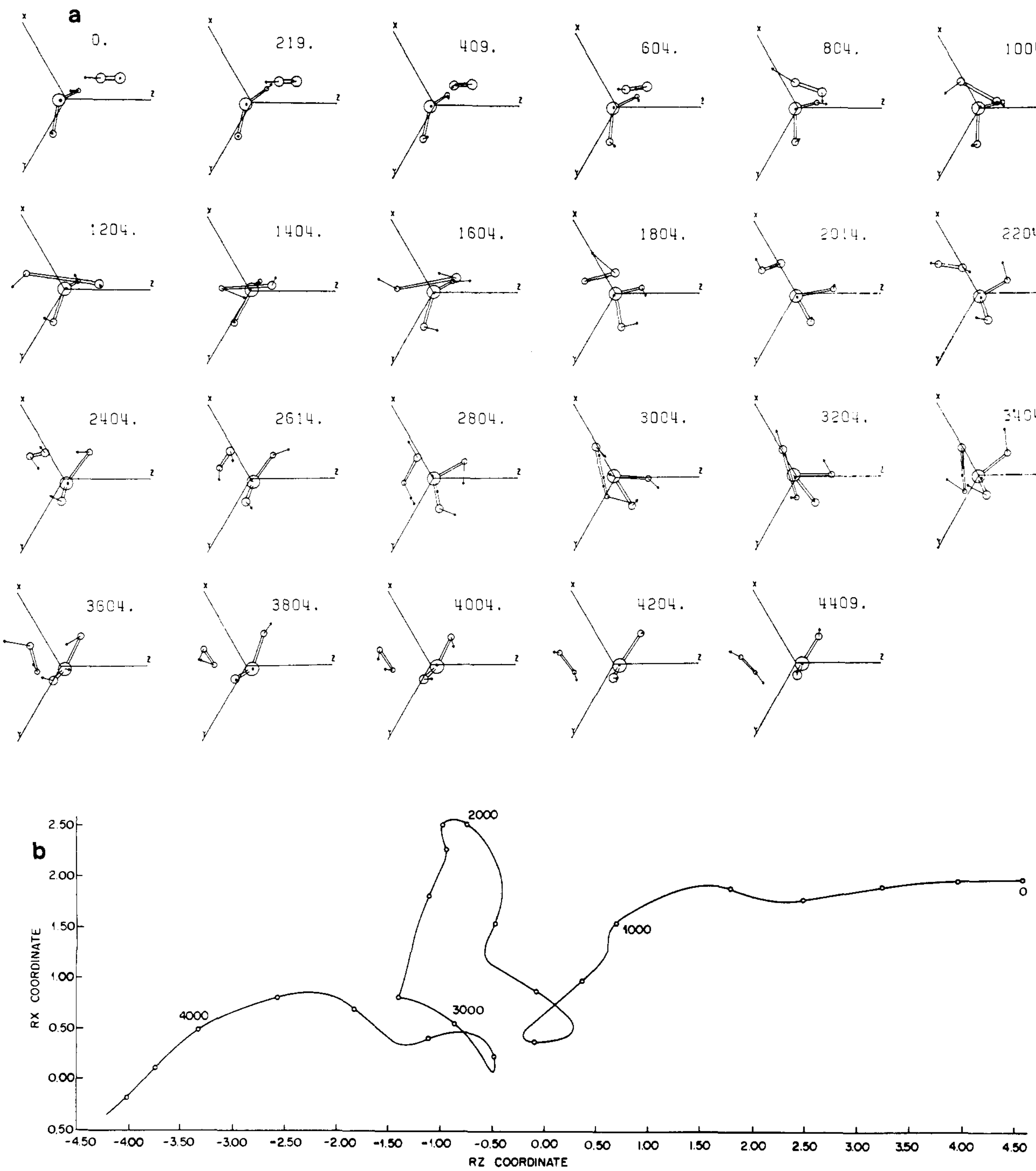

Figure 2. Same as Figure 1, except initial **R** equal to (2 au, 0, 4.58 au).

rotation that continues until 1400 au. The H_2 interatomic distance then rapidly increases (*via* motion of both atoms) and a CH_4-like geometry results (1400–2000 au). From 2000 au onward, the motion corresponds to that of vibrationally excited CH_4 with clockwise rotation; deactivation would lead to formation of stable CH_4.

In the "least-motion" (C_{2v}) geometry, collisions with relative translational energy significantly below the calculated barrier (0.021 hartree) are repulsive, while those with relative translational energy well above the barrier height result in direct reaction.

Because the single-determinant molecular orbital potential energy surface does not include $CH_3 + H$ as an alternative path, redissociation into $CH_2 + H_2$ is the only possibility. Use of a more general potential and comparison of the various product contributions at thermal and higher energies, as well as a detailed study of the complex dynamics,[12] would clearly be of interest. Also, the importance of rotational motion in this reaction suggests that it would be worthwhile to examine trajectories in which the molecules initially have rotational energy; this is in progress.

From the sample trajectories, and other trajectories that we cannot detail here, it appears that the dynamic results for the singlet methylene insertion confirm the

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[12] See, for example, the KCl + NaBr study by P. Brumer and M. Karplus, *Discuss. Faraday Soc.*, in press.

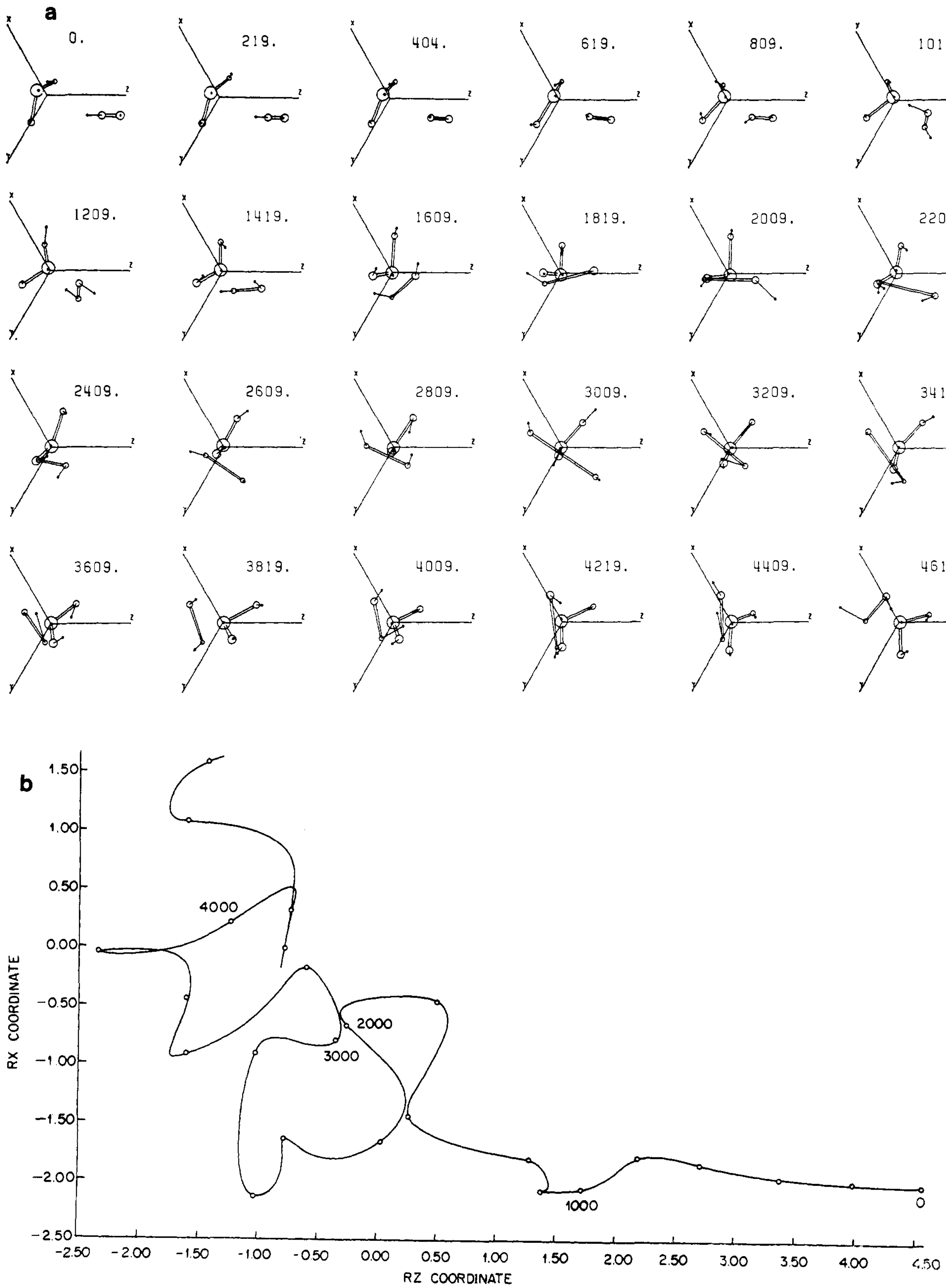

Figure 3. Same as Figure 1, except initial **R** equal to (−2 au, 0, 4.58 au).

importance of certain interactions suggested by earlier studies.[13-15] A "minimum energy path" is followed approximately for appropriate initial conditions (Figure 2). However, insertion can take place over a very wide

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(13) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964); W. B. DeMore and S. W. Benson, *ibid.*, **2**, 219 (1964).

(14) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6188 (1971).

(15) H. Kollmar, *Tetrahedron*, **28**, 5893 (1972).

range of initial conditions, for some of which (Figure 3) the dynamics are considerably more complicated than suggested by a reaction path calculation.

The results reported in this paper represent only the first step in dynamic investigations of organic reactions by trajectory techniques on quantum mechanical potential surfaces. It is clear, nevertheless, that such investigations are now feasible and that they can lead to conclusions that are not evident from an analysis of the reaction path. Moreover, they can serve as an efficient way of isolating the portions of the potential surface of importance for the reaction *prior* to an examination by static methods. In future calculations, it would be helpful to utilize more reliable potential surfaces than the one employed here. One way of doing so, without a great increase in computing time, could be to employ a simple semiempirical functional form, such as that of the CNDO type, with parameters specifically chosen to fit accurate *a priori* calculations for the system of interest.

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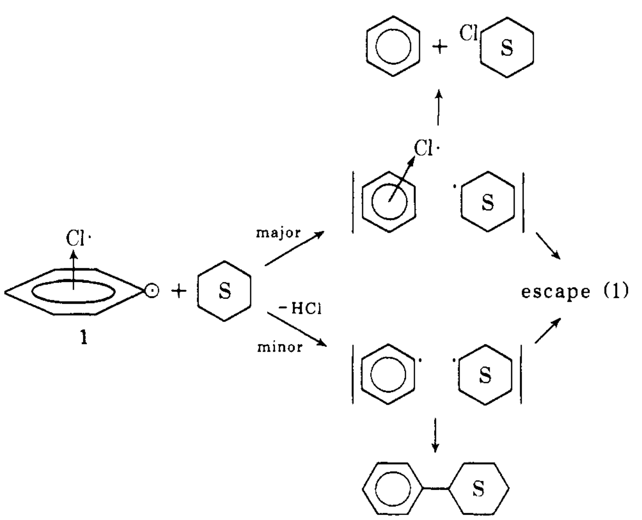
π-Chlorobenzene

Sir:

We wish to present evidence that irradiation (2537 Å) of chlorobenzene[1] in solution yields the high-energy isomer **1**, which we call π-chlorobenzene, and to comment on the nature and reactivity of this novel biradical.

An early clue to its existence was the finding that chlorocyclohexane (~53%) accompanies benzene (~90%) and HCl (~35%) as the major photolysis products of chlorobenzene in dilute (0.025 *M*) cyclohexane solution. Formation of chlorocyclohexane by combination of free cyclohexyl radicals and chlorine atoms is out of the question,[2] for a chlorine atom cannot survive more than a few collisions in the solvent cyclohexane before abstracting hydrogen.[3] One might propose that the phenyl radical of a geminate phenyl radical–chlorine atom pair attacks the solvent, producing a cyclohexyl radical–chlorine pair which collapses to chlorocyclohexane. This possibility is clearly ruled out by the fact that *phenyl radicals attack cyclohexane at least 10,000 times slower than do chlorine atoms.*[4]

Due to π complexation, however, chlorine atoms in benzene solvent show selectivities so enhanced[3,5] that they resemble phenyl radical selectivities[6] (*e.g.*, for tertiary *vs.* primary hydrogens). Moreover, the observed chlorine selectivities undershoot the true values for complexed atoms by an unknown amount since the observed quantities represent a weighted average of complexed and free chlorine atom selectivities.[7] The product composition from photolysis of chlorobenzene in cyclohexane is thus understandable in terms of eq 1. Indeed, the very small amount of phenylcyclohexane formed (~1%) argues for considerably greater reactivity at the carbon radical center of **1** than at chlorine.



Solvent exerts a dramatic influence over the efficiency of chlorobenzene photolysis at 2537 Å: *the quantum yield for destruction* (Φ_D) *is 0.38 in cyclohexane, but only 0.012 in the inert Freon 113.*[8] This contrast is readily explained in terms of the π intermediate, which

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[1] Earlier studies of chlorobenzene photolysis include the following: (a) T. Ichimura and Y. Mori, *J. Chem. Phys.*, **58**, 288 (1973); (b) G. E. Robinson and J. M. Vernon, *J. Chem. Soc. C*, 3363 (1971); (c) J. Wojtczak and W. Augustyniak, *Poznan. Tow. Przyj. Nauk, Pr. Kom. Mat.-Przyr.. Pr. Chem.*, **12**, 61 (1971) (*Chem. Abstr.*, **75**, 43054*m* (1971)); J. Wojtczak and M. Elbanowski, *ibid.*, **12**, 87 (1971) (*Chem. Abstr.*, **74**, 43037*h* (1971)); (d) I. Loeff, H. Lutz, and L. Lindquist, *Isr. J. Chem.*, **8**, 141 (1970) (*Chem. Abstr.*, **73**, 93476*e* (1970)); (e) J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Lett.*, 1267 (1969); (f) G. E. Robinson and J. M. Vernon, *J. Chem. Soc. D*, 977 (1969); (g) J. A. Barltrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc. C*, 1142 (1967); (*h*) B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, **62**, 1793 (1966); (i) A. Basinski and E. Latowska, *Rocz. Chem.*, **40**, 1747 (1966); (j) G. Porter and B. Ward, *Proc. Roy. Soc., Ser. A*, **287**, 457 (1965); (k) V. G. Vinogradova, B. N. Shelimov, N. V. Fok, and V. V. Voerdoskii, *Dokl. Akad. Nauk SSSR*, **154**, 188 (1964) (*Chem. Abstr.*, **60**, 14045*f* (1964)); (l) Y. S. Kim and Y. J. Park, *Ta Han Hua Hsueh Hui-Chih*, **6**, 148 (1962) (*Chem. Abstr.*, **60**, 2476*b* (1964)). See also J. A. Barltrop and D. Bradbury, *J. Amer. Chem. Soc.*, **95**, 5085 (1973).

[2] Furthermore, chlorocyclohexane is still formed in abundance when a radical scavenger such as O_2 is present. The possibility that this product results from HCl addition to cyclohexene is eliminated by the finding that triethylamine fails to prevent its formation.

[3] G. A. Russell, A. Ito, and D. G. Hendry, *J. Amer. Chem. Soc.*, **85**, 2976 (1963).

[4] Compare ref 3 with G. A. Russell and R. F. Bridger, *J. Amer. Chem. Soc.*, **85**, 3765 (1963).

[5] (a) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987, 4997 (1958); C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959); (b) E. S. Huyser, *Advan. Free-Radical Chem.*, **1**, 77 (1965); (c) R. E. Buhler and M. Ebert, *Nature (London)*, **214**, 1220 (1967); R. E. Bühler, *Helv. Chim. Acta*, **51**, 1558 (1968).

[6] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

[7] Russell fit his data successfully (but not uniquely) using the assumption that complexed chlorine is *completely* selective, *i.e.*, incapable of attacking primary hydrogen. The existence of both 1:1 and 2:1 (at least) complexes of aromatic rings with chlorine atoms considerably complicates analysis of the problem.

[8] Since very low Φ_D values are also obtained with small amounts of cyclohexane present, one can be certain that the value in pure Freon 113 is not low because of reconstitution of chlorobenzene from radicals turned loose into the medium.