A Potential Surface for a Nonlinear Cheletropic Reaction.

The Decarbonylation of Cyclopropanone

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The least-motion linear approach of a carbon monoxide molecule to ethylene, or the reverse fragmentation of a cyclopropanone, is a symmetry forbidden reaction. A nonlinear nonleast-motion approach is favored, with unsymmetrical intermediate bonding. The reaction path is shown by the succession of Figures 4, 7, and 5. At large separations there is available to the reacting molecules a large range of geometries at an energy only slightly higher than that of the optimal configuration.

The thermal decarbonylation of the highly reactive cyclopropanones,[1] eq 1, is an exothermic process which has been observed in some instances.[1a] The reaction is

$$\text{(structure)} \longrightarrow \text{(structure)} + \text{CO} \qquad (1)$$
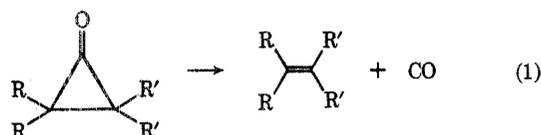
also a prototype nonlinear cheletropic reaction.[2] The significance of the nonlinear designation will become apparent when we draw a level correlation diagram for the least-motion linear decarbonylation or its microscopic reverse, the addition of carbon monoxide to ethylene. Let us locate an ethylene molecule in the xy plane, and consider an approach of carbon monoxide along the z axis, as shown below.
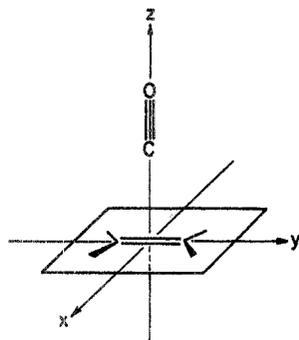
In the correlation diagram (Figure 1) we include the π and π^* levels of the ethylene, the π,π^* and oxygen and carbon lone pairs of carbon monoxide, as well as the corresponding orbitals of cyclopropanone. The approach is of C_{2v} symmetry and the levels are classified accordingly.

It is clear from this correlation diagram that the C_{2v} ground-state reaction is symmetry forbidden.[2] Given the apparent high driving force for fragmentation from the cyclopropanone side it is clear that some way will be

found by the molecule to circumvent the symmetry forbidden least-motion path. Some general arguments for a nonlinear departure have been given;[2] they imply that as the cyclopropanone begins to decompose the CO fragment goes off bending or tilting to one side. To trace the precise nature of this nonlinear departure we have undertaken an exploration of the potential surface by an approximate molecular orbital procedure, the extended Hückel method.[3,4]

Calculations

In our computations we allowed the system six degrees of freedom. Five of these degrees of freedom were varied continuously. These were one distance, D, and four angles θ, ϕ, θ', ϕ' used to describe the location and orientation of a fixed length CO molecule relative to the center of the ethylene (see Figure 2). The sixth degree of freedom was not studied continuously. This was the relaxation of the ethylene moiety from its geometry in free ethylene to its geometry as a fragment of cyclopropanone. We studied in detail only three stages of relaxation. The first geometry, called P, was that of a planar unrelaxed model ethylene with a CC bond length of 1.34 Å. The final relaxed or R geometry was taken from the C_2H_4 fragment of the cyclopropanone structure determined from an analysis of the

(1) (a) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **87**, 2774 (1965); N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969), and references therein; (b) P. Lipp and R. Köster, *Ber.*, **64**, 2823 (1931); D. A. Semenov, E. F. Cox, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 3221 (1956); W. D. DeMore, H. O. Pritchard, and N. Davidson, *ibid.*, **81**, 5874 (1959); A. Kende, Ph.D. Dissertation, Harvard University, 1956; S. E. Schaafsma, H. Steinberg, and T. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, **85**, 1170 (1966); (c) J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 152 (1967); F. D. Greene and N. M. Weinshenker, *ibid.*, **90**, 506 (1968).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers. We have used here the same parameters as those listed in a previous cyclopropanone calculation in ref 4.

(4) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).
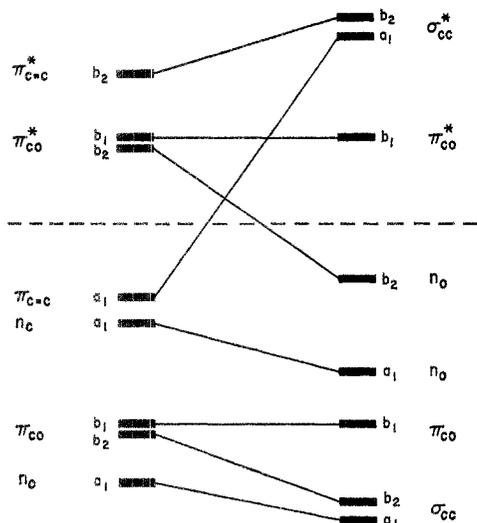
Figure 1. Correlation diagram for the linear addition of CO to ethylene. n_c and n_o at left are carbon monoxide σ levels. The two n_o levels at right are the antisymmetric and symmetric oxygen lone pairs. The exact ordering of bonding and antibonding levels separately is not well defined.
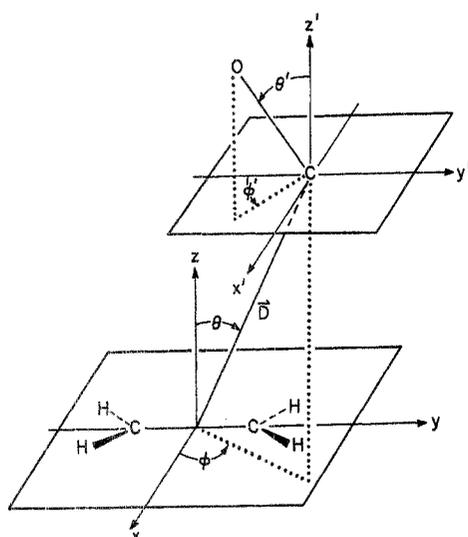
Figure 2. Coordinate system for describing the relative motion of CO and C_2H_4. x',y',z' is a body centered coordinate system with origin at C and axes parallel to x,y,z. Note that the angle ϕ' is measured from the negative y' axis while ϕ is measured from the positive x axis.

microwave spectrum of the molecule.[5] The distinguishing feature of that geometry, aside from its natural puckering of the CH_2 groups from planarity, is the long CC bond of 1.58 Å. The intermediate, or unsymmetrical one carbon planar one carbon relaxed, or PR geometry, was in its bond distances halfway between the planar and relaxed geometries, but had one CH_2 group planar, the other pyramidal as in the totally relaxed structure.

Our computer program was so adapted that for a given D and state of relaxation of the ethylene frag-

ment the values of θ, ϕ, θ', ϕ' were optimized to give the lowest energy. Our only assurance that global minima were located was the achievement of the same set of final angles beginning from very different initial values.

The Reaction Path

Table I lists the global minima found for different values of D. The corresponding energies, relative to separated CO and ethylene, are shown in Figure 3. While the information in Table I is complete, it is not descriptive. We would therefore like to describe in some further detail, with illustrations, the different stages of an approach of carbon monoxide to ethylene.

Table I: Optimum Geometries and Stages of Relaxation as a Function of D

D, Å^a	Relaxa-tion^b	θ, deg	ϕ, deg	θ', deg	ϕ', deg
3.00	P	0	0	86	90
2.75	P	0	0	85	90
2.50	P	0	0	84	90
2.25	P	0	0	82	90
2.20	P	0	0	81	90
2.15	PR	27	80	60	49
2.10	PR	27	81	53	41
2.05	PR	27	90	41	0
2.00	R	31	90	24	0
1.80	R	29	90	16	0
1.60	R	21	90	10	0
1.50	R	0	90	0	0

^{a} D = distance between CO carbon and center of ethylene. See Figure 2. ^{b} See text for definition of states of relaxation.

For $D \geq 2.20$ Å we find a not unexpected preference for a planar ethylene fragment. The optimal geometry in this region is quite invariant. Let us call this approach I; three views[6] of a characteristic geometry in this region, that for $D = 2.20$ Å, are shown in Figure 4.

While the preferred orientation is the one illustrated, it should be noted that the energy does not deteriorate significantly if the CO is swung in a circle with the carbon fixed and the oxygen fixed at the same z value (see 1 below). Thus the loss in energy as a result of swinging 90° away from the optimal orientation is 0.12 eV at $D = 2.50$ Å, 0.29 eV at $D = 2.25$ Å. This is to be contrasted with the deterioration on swinging to the least-motion approach, CO along the z axis. This entails an energy loss of 0.99 and 2.22 eV, respectively. Aside from the specific preference for geometry I, this region can thus be characterized by the avoidance of the

(5) J. M. Pochan, J. E. Baldwin, and F. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968); **91**, 1896 (1969).

(6) These are views, not projections, of the molecule from a vantage point 8 Å removed from the origin, along each of the three coordinate axes. These illustrations were produced by the program OR TEP, C. K. Johnson, ORNL 3794.
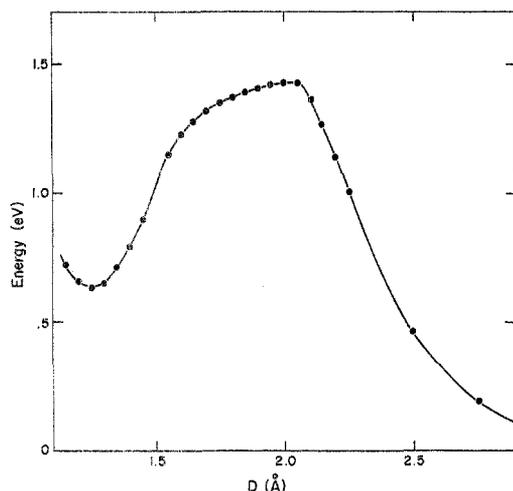
Figure 3. Energy along the reaction coordinate D. The energy zero is for separated CO and C_2H_4.
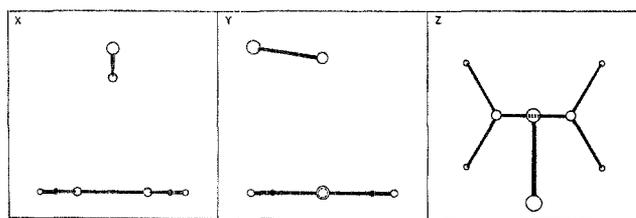
Figure 4. Three views, from vantage points along the positive x, y, and z axes, of an optimal approach geometry at $D = 2.2$ Å. See ref 6.

least-motion approach and a general preference for placing the carbon monoxide molecule in a plane approximately parallel to the plane of the ethylene.

1
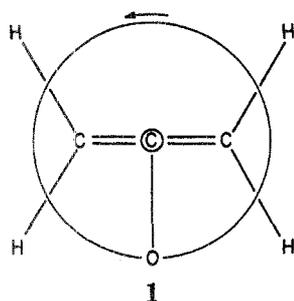
The preference for location of the carbon atom of CO above the ethylene center is probably a consequence of the primary stabilizing interaction in this region, that is between the relatively low-lying π^* orbital of carbon monoxide and the π orbital of the ethylene. The CO π^* is concentrated on the carbon atom. Note the interesting relation between geometry I and the transition state postulated by us for the concerted addition of ketenes to olefins.[2]

It might have been thought that approach I could smoothly move over to cyclopropanone by swinging CO up in the xz plane (*i.e.*, changing θ' gradually from $\sim 80°$ to $0°$). This motion, however, is still a for-

bidden one. Notice that the xz plane remains a symmetry plane throughout such an approach. The resulting correlation diagram remains in its main features identical with that shown in Figure 1. The reduction in symmetry from C_{2v} to C_s correlates a_1 and b_1 to a', and b_2 to a''. There is still a level crossing. The CO molecule must abandon the crucial xz plane if it is to bypass a forbidden reaction.

Our discussion will be made easier if we momentarily skip the transition point around $D = 2.10$ Å and consider the approach region III for $D \leq 2.00$ Å. In this region we essentially are close to cyclopropanone. Full relaxation of the ethylene fragment is accordingly preferred. Three views of a typical optimized geometry, $D = 2.00$ Å, in this region are shown in Figure 5. Geometry III is highly asymmetric, this being also reflected by the charge distribution shown below in **2**.

2   3
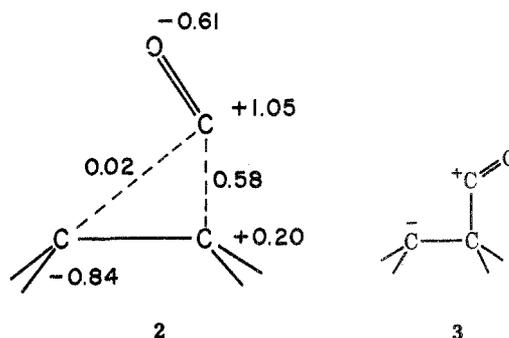
In the case of another nonlinear cheletropic reaction, the addition of singlet methylene to ethylene, we found considerable symmetry in the charge distribution along the reaction path.[4,7] The polarity that is being exhibited in the cyclopropanone case may be an indication that in polar solvents a real zwitterionic intermediate, written as **3**, could be stabilized.[8]

The final collapse from III to cyclopropanone is accomplished by a smooth motion of CO to the symmetrical position. This is illustrated by a series of superimposed snapshots in Figure 6.

We now return to region II, the transition region. Our original searches maintained the same intermedi-
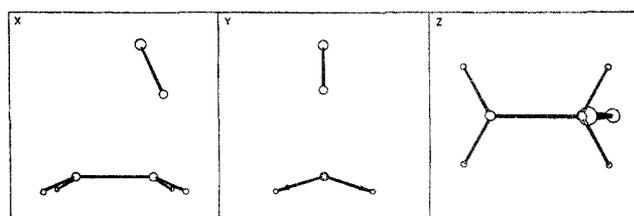
Figure 5. Three views, from vantage points along the positive x, y, and z axes, of an optimal approach geometry at $D = 2.0$ Å. See ref 6.

(7) R. Hoffmann and P. S. Skell, to be published.

(8) See A. S. Kende, *Chem. Ind. (London)*, 1053 (1956); J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).
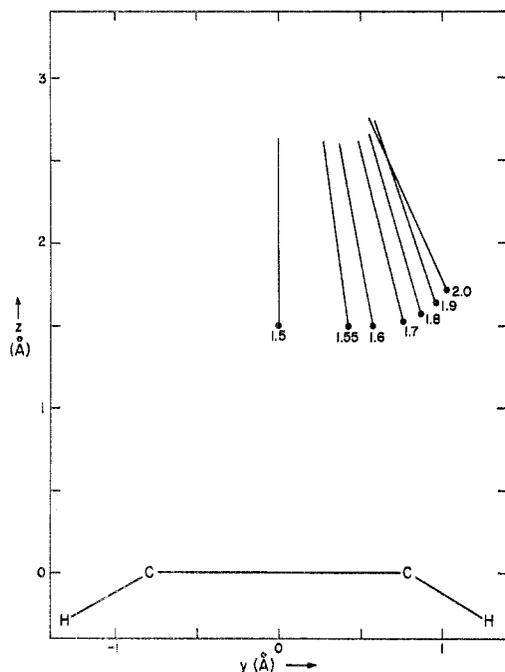
Figure 6. Superimposed snapshots of the terminating approach. A projection on the yz plane is shown. The numbers below the successive CO projections are the values of D.

Figure 7. Three views, from vantage points along the positive x, y, and z axes, of an optimal approach geometry at $D = 2.1$ Å. See ref 6.

Figure 8. Superimposed snapshots of the optimum approach for large D when the CO is constrained to remain in the yz plane. A projection on the yz plane is shown. The ethylene moiety is kept planar.

ate stage of relaxation at both carbon atoms. The very unsymmetrical optimum geometry at the edge of region III, $D = 2.00$ Å, was an indication to us that in region II, the molecule might prefer unsymmetrical relaxation at the two ethylene carbons. This led to the construction of the PR geometry. The PR unsymmetrical geometry is the preferred state of relaxation for $2.00 < D < 2.20$ Å. This appears to be a short interval, but in terms of the other angles very many changes take place in this region. A typical geometry, that at $D = 2.10$ Å is shown in three views in Figure 7. Both from the comparison of Figure 7 with Figures 5 and 4 and from direct examination of the angles in Table I it is clear that geometry II is in every geometrical parameter intermediate between I and III. We have essentially caught a snapshot of a typical molecule as it traverses the region between valleys I and III.

Dynamics

We can now summarize our conclusions on the reaction path for the addition of carbon monoxide to ethylene. For large D, region I, a symmetrical placement of the CO molecule in the xz plane is favored (Figure 4). No relaxation of the ethylene occurs for $D \geq 2.2$ Å. In the region $2.0 < D < 2.2$ Å several changes take place. The carbon monoxide swings to an unsymmetrical position in the yz plane (Figure 7) while the ethylene relaxes the geometry of the nearer carbon. This is region II. Having avoided in this manner the level crossing at the symmetrical position, the carbon monoxide proceeds in region III to fully form the second CC bond.

This is accomplished by a motion toward the symmetrical product structure accompanied by relaxation at the further ethylene carbon.

In the context of modern collision theory the number of molecules traversing precisely this reaction path will be very small. The gross features of the potential surface far in, namely the unsymmetrical approach in region III, will no doubt have consequences on typical molecular trajectories in the cyclopropanone fragmentation. That is, decomposing cyclopropanone molecules will clearly want to avoid the forbidden linear departure and will explore instead unsymmetrical modes in the yz plane. This should have measurable consequences in the isotope effects on the reaction rate entropy of activation for the reaction.

The consequence of the reaction path viewed from the ethylene plus carbon monoxide side is much less certain. It was already pointed out above that in region I the energy does not vary greatly with rotation in a

plane parallel to the xy plane (1). Still another indication of the softness of the potential in this region was obtained from the following numerical experiment. We decided to compute the energy along a trajectory which merged smoothly with a region III geometry. This was accomplished by constraining CO to lie in the yz plane but allowing it the full two degrees of freedom of motion in that plane. The resultant constrained reaction path, Figure 8, indeed merges smoothly with approach III. In the region $2.1 \leq D$ the energy along this path is at most 0.1 eV above the global minimum approach of Figure 4. Clearly, molecules with an approach geometry resembling that of Figure 8 will be nearly as likely to react as those in the optimal geometry of Figure 4. Though we would extrapolate that there is a wide range of reactive impact geometries for this reaction (provided the forbidden approach is avoided), the actual ways in which dynamic effects will manifest themselves must await many-dimensional trajectory calculations.

Given the unsymmetrical reaction path geometries

near $D = 2.0$ Å the question arises whether in fact the reaction would be stereospecific. That is, would the stereochemical relationship, cis or trans, of labels in a hypothetical, appropriately labeled cyclopropanone, be retained in the product ethylene. To probe this question we calculated the energy required to twist the far end of the ethylene fragment by 90°. This torsional barrier is understandably large in region I, smaller in region II. It reaches its lowest magnitude near $D = 1.9$ Å, and then rises again as the product cyclopropanone geometry is approached. The lowest value for this torsional barrier is approximately 7 kcal/mol. Though this number is not very reliable we believe the reaction will be stereospecific retaining this particular criterion of a process which though highly unsymmetrical should still be termed concerted.

A Virial Treatment for the Adsorption of Gases on Liquids

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For the adsorption of gases on liquids a virial treatment of the relationship between spreading pressure and gas (bulk) pressure is developed. Analysis of gas–liquid adsorption data in terms of these intensive variables leads to a direct determination of s_0, the distance at which the net interaction between gas and surface is zero, in contrast to the case of gas–solid systems where one obtains the product As_0. Adsorption data for xenon on liquid mercury are analyzed.

I. Introduction

During the past few years a great deal of work has been devoted to the theoretical analysis of high-temperature gas–solid interactions. Due to the paucity of accurate data on gas–liquid interactions, a virial treatment appropriate for the adsorption of gases on liquids has not been formulated. Cassel and Neugebauer made spreading pressure measurements for argon, krypton, and xenon on liquid mercury.[2] The analysis of such data by a virial treatment should provide a valuable supplement and contrast to the gas–solid data.

Theoretical analysis of experimental measurements for the interaction of rare gases with the nearly homogeneous graphitized carbon black P33 is used as a com-

parative system, since precise measurements were made in the same reduced temperature range. However, this comparison of gas–solid and gas–liquid interaction parameters must be made judiciously since the present analysis assumes the liquid surface is planar, even in the presence of adsorbate molecules. As usual, we assume the adsorbent is unperturbed by the adsorption process.

The study of gas adsorption at the liquid–vapor interface offers certain unique advantages in comparison to the study of the gas–solid interface. Advantages in-

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(2) H. M. Cassel and K. Neugebauer, *J. Phys. Chem.*, **40**, 523 (1936).