

Photoinitiated Reactions in Weakly Bonded Complexes

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This article discusses photoinitiated reactions that occur in cold, weakly bonded binary complexes. Such species are held together by van der Waals or hydrogen bonds (typically 0.1–10 kcal mol⁻¹) that are “intermolecular”, in the sense that the constituents are only mildly perturbed by the bond. Due to the weakness of the bond, such complexes are nonrigid, with large zero-point excursions from equilibrium geometries. There have been many excellent articles and reviews on the structures of such weakly bonded complexes.^{1,2} Thus, we make no attempt to cover this area, despite our reliance on such studies. So far, structures have been determined mainly by rotational spectroscopy (e.g., microwave, molecular beam, and electric resonance techniques), although recent advances in tunable IR laser techniques have led to many valuable results, especially since vibrational transitions can provide fairly direct probes of the intermolecular force field. We will also avoid predissociation where “reaction” involves breaking the weak intermolecular bond following excitation of (i) a high-frequency vibration associated with one of the molecular constituents of the complex^{3,4} or (ii) a rovibrational level within an electronically excited manifold.^{5,6}

The situation under consideration in this article is one in which the weakly bonded complex sets the stage for a reaction that follows electronic excitation of one of the constituents. This can take several forms, but in all cases, specificity is imposed by the character of the complex and the photoinitiation process. The connections to bimolecular and termolecular processes are clear, and the relationship to condensed-phase processes should not be taken lightly. The reactive environments described in this article embody both dynamical and stereochemical aspects of reactivity, hence the label

dynamical stereochemistry.⁷

Research in this area is recent, most publications having appeared since 1983. Thus, we will discuss concepts and examine results and future prospects critically. Simple diagrams will be used in favor of lengthier compendia. In the discussion that follows, we limit ourselves to binary complexes. They are simplest and the relevant physics can be discerned from these examples. However, this is a self-imposed limit spawned by the need for brevity; the remarkable work going on with larger clusters⁸ and high-resolution spectroscopic studies of even tertiary complexes,^{9,10} are a testimony to the vigor of the field. The organization of this article is as follows. A discussion of weakly bonded binary complexes is followed by a description of excited-state reactions, where electronic excitation of one moiety is preserved along a reaction path. The general nature of preserving specificity is then discussed, and reactions are described in which photodissociation of one moiety leads to ground-state products, one of which goes on to react with the other constituent of the complex. We then discuss theory and finally list predictions and guidelines for future work. We apologize to those whose work is slighted by omission; our intentions are without malice.

Weakly Bonded Binary Complexes

The equilibrium geometry of the complex is determined by the anisotropic intermolecular force field between the constituents. However, because the complex is weakly bonded, the average and equilibrium geometries can differ considerably and change from one low-lying state to another. With the low temperatures available when using nozzle expansions to prepare complexes, one can “freeze-out” most internal excitations. Rotations are often equilibrated at a few kelvins, and while vibrational excitation varies from case to case, relaxation is often sufficient to ensure that vibrationally excited molecules constitute a small percentage of the sample. However, zero-point fluctuations are a *fundamental* limit, and when light species are involved, the differences between the equilibrium and average geometries can even be significant for the ground state. For example, in the case of CO₂HF with a linear equilibrium

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- (1) Celli, F. G.; Janda, K. C. *Chem. Rev.* 1986, 86, 507.
- (2) Klemperer, W. *J. Mol. Spectrosc.* 1980, 59, 161.
- (3) Casassa, M. P.; Stephenson, J. C.; King, D. S. *Faraday Discuss. Chem. Soc.* 1986, 82, 1.
- (4) Kolenbrander, K. D.; Lisy, J. M. *J. Chem. Phys.* 1986, 85, 2463.
- (5) Butz, K. W.; Catlett, D. L.; Ewing, G. E.; Kajnovich, D.; Parmenter, C. S. *J. Chem. Phys.* 1986, 90, 3533.
- (6) Haynam, C. A.; Brumbaugh, D. V.; Levy, D. H. *J. Chem. Phys.* 1984, 80, 256.
- (7) Cf. “Dynamical Stereochemistry Issue”, *J. Phys. Chem.* 1987, 91, 5365–5509.
- (8) (a) Smalley, R. E. *Laser Chem.* 1983, 2, 167. (b) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* 1985, 318, 162.
- (9) Fraser, G. T.; Pine, A. S.; Lafferty, W. J.; Miller, R. E. *J. Chem. Phys.* 1987, 87, 1502.
- (10) Prichard, D.; Muenter, J. S.; Howard, B. J. *J. Chem. Phys. Lett.* 1987, 135, 9.

Table I
Candidate Systems for PGL Reactions Involving Ground Electronic State Fragments

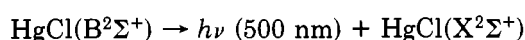
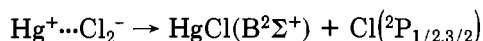
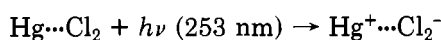
species	equilibrium geometry	comments
CO ₂ HX	linear, ¹¹ slight bend ¹²	geometries determined for X = Cl, F and H → D; ²⁵ PGL reaction: CO ₂ HBr(DBr) ^{21,22}
SCOHX	linear ²⁵	geometries determined for X = F; PGL reaction studied with SCODBr ³¹
N ₂ OHF	linear and bent ²⁶	NNOHF ^{26a} and ONNH ^{26b} isomers have been observed
O ₂ HF	planar ^{27a}	H + O ₂ reaction can be studied under PGL conditions
HCICO	linear ^{27b}	HCO system can be studied under PGL conditions
SO ₂ H ₂ S	cyclic, O...H bonds ²⁸	H + SO ₂ reaction can be studied under PGL conditions
HFHCl	planar ^{29a}	H + FH' → HF + H' can be studied (deuterium substitution)
(N ₂ O) ₂	T-shaped ³⁰	O(¹ D) + N ₂ O → 2NO; product V,R excitation is plentiful ³²
H ₂ HF	FH...H ₂ , T-shaped ^{29b}	H' + H ₂ → H'H + H PGL reaction can be studied (deuterium substitution)
NH ₃ NO	not measured	NH ₃ + hν → NH ₂ + H may allow the ubiquitous NH ₂ + NO reaction to be examined with well-characterized initial conditions

geometry,^{11,12} the average angle between the HF axis and the line connecting the CO₂ and HF centers-of-mass (cm's) is ~20°. Thus, the floppiness of the intermolecular bond leads to a distribution of nuclear coordinates, which serves as the set of initial conditions in the photoinitiated reaction.

Following electronic excitation of one moiety, several forms of reaction may occur in addition to a rich variety of inelastic scattering processes. Implicit in this picture is that excitation initially remains localized rather than spreading throughout the complex, even when there are low-lying excited states for both constituents. In the experiments reported here, initial electronic excitation is dissipated quickly, ensuring that excitation transfer is unimportant.

Reactions of Electronically Excited Species

Electronic excitation of one constituent of the complex can result in direct reaction with the other constituent, thus producing an excited-state reaction with a geometrically constrained entrance channel. An elegant and pioneering series of experiments by Soep and co-workers has exploited this approach in studies of electronically excited atoms reacting with molecules.¹³⁻¹⁷ For example, Hg...Cl₂ complexes were used as precursors in the photoinitiated reaction indicated schematically below.¹³



Clearly, the geometry of the Hg...Cl₂ precursor defines and limits the entrance channels. Throughout the text, we will refer to all such processes (reactions involving ground- or excited-state species, inelastic scattering, etc.) as precursor geometry limited (PGL).

These studies were important because they showed the advantages of using weakly bonded complexes to construct detailed and elegant experiments, such as aligned and oriented reactants and quests for transition

(11) Baiocchi, F. A.; Dixon, T. A.; Joyner, C. H.; Klemperer, W. *J. Chem. Phys.* **1981**, *74*, 6544.

(12) Lovejoy, C. M.; Schuder, M. D.; Nesbitt, D. J. *J. Chem. Phys.* **1987**, *86*, 5337. These authors also discuss the possibility of a nonlinear complex.

(13) Jouvét, C.; Soep, B. *Chem. Phys. Lett.* **1983**, *96*, 426.

(14) Breckenridge, W. H.; Jouvét, C.; Soep, B. *J. Chem. Phys.* **1986**, *84*, 1443.

(15) Duval, M. C.; Benoist D'Azy, O.; Breckenridge, W. H.; Jouvét, C.; Soep, B. *J. Chem. Phys.* **1986**, *85*, 6324.

(16) Zehnacker, A.; Duval, M. C.; Jouvét, C.; Lardeux Dedonder, C.; Solgadi, D.; Soep, B.; Benoist D'Azy, O. *J. Chem. Phys.* **1987**, *86*, 6565.

(17) Jouvét, C.; Boivineau, M.; Duval, M. C.; Soep, B. *J. Phys. Chem.* **1987**, *91*, 5416.

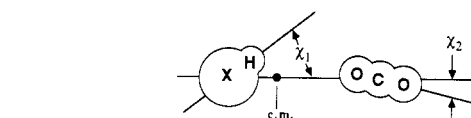


Figure 1. Schematic drawing emphasizing the large angular excursions associated with a weakly bonded complex having a linear equilibrium geometry.

states. The chemistry is that of excited electronic states and is germane to issues of orbital specificity such as those pursued by Zare et al.¹⁸ and Breckenridge et al.,¹⁹ using collisional environments. The work of Soep and co-workers involved many weakly bonded complexes and excited states in which Hg is a participant. Excitation of Hg is facile, and reactions of excited Hg atoms had been studied previously.²⁰ In studies of Hg...Cl₂¹³ and Hg...H₂,¹⁴ action spectra (i.e., varying the frequency of the exciting radiation while monitoring a product) were used to examine excited complexes, and products were detected by fluorescence and laser-induced fluorescence (LIF), respectively. The experimental results show that the excited potential energy surfaces (PES's) can be probed spectroscopically in the region of the ground-state adducts. Complications in interpreting data originated from not knowing equilibrium geometries and the fact that the Hg spin-orbit interaction is strong enough to preclude simple orbital descriptions.

Photodissociation to Ground-State Fragments

Another type of reaction occurs when the initially excited species dissociates directly, propelling a "photofragment" toward the other constituent in the complex. This is general, and there are already numerous candidates to choose from designing experiments. A partial list is given in Table I, and the case of CO₂HX is shown schematically in Figure 1 and will be used as an example throughout much of the text, especially for X = Br.^{21,22} The 193-nm photodissociation of HBr is representative of the many cases where photodissociation prepares species with well-defined translational and internal energies. With HBr, it is known that dissociation is quite rapid and that 85 and

(18) Johnson, M. A.; Allison, J.; Zare, R. N. *J. Chem. Phys.* **1986**, *85*, 5723.

(19) Breckenridge, W. H.; Nikolai, W. L.; Oba, D. *J. Phys. Chem.* **1986**, *90*, 5724.

(20) Callear, A. B.; McGurk, J. C. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 97.

(21) Buelow, S.; Radhakrishnan, G.; Catanzarite, J.; Wittig, C. *J. Chem. Phys.* **1985**, *83*, 444.

(22) (a) Radhakrishnan, G.; Buelow, S.; Wittig, C. *J. Chem. Phys.* **1986**, *84*, 727. (b) Buelow, S.; Radhakrishnan, G.; Wittig, C. *J. Chem. Phys.* **1982**, *91*, 5409.

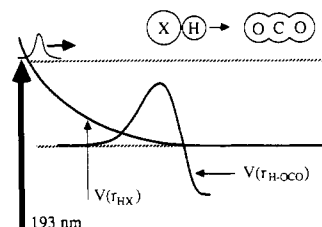


Figure 2. Schematic representation of the serial interaction picture. The asymptotic H-atom speed is almost developed before CO_2 is encountered.

15% of the Br atoms are in the $^2\text{P}_{3/2}$ ground state and $^2\text{P}_{1/2}$ excited state, respectively.^{23,24} The fully developed H-atom speed is $\sim 2 \times 10^6 \text{ cm s}^{-1}$ (200 \AA ps^{-1}), and it takes $<100 \text{ fs}$ to extend the HBr bond by $\sim 1 \text{ \AA}$. Thus, the appropriate picture is one in which 193-nm excitation of HBr causes dissociation to commence immediately on a repulsive potential curve.

With a small reaction cross section, only certain parts of the target molecule are reactive. Products derive from site-specific attack, and at each site there is a *distribution* of approaches that make up a "reactive window". A fundamental limit to the ability of a system to display specificity toward product state distributions is given by the relationship between the reactive window and the distribution of initial conditions. The narrowest possible distribution of initial conditions derives from zero-point fluctuations of the intermolecular modes of the complex, and if this exceeds the width of the reactive window, specificity is unlikely. However, if the distribution of initial conditions is within the reactive window, the approach geometries associated with a particular complex can lead to specific product excitations. Thus, for large cross section reactions that yield a single set of products, nascent distributions may be governed by the characteristics of the PGL complex.

Both mass and bond strength contribute to the distribution of initial conditions. With increasing mass, the nuclei will be more localized for a given bond strength and this will be a large effect when going from hydrogen to heavier elements. For example, diatomic halogens will complex readily and can be photodissociated in the near-ultraviolet. However, unlike the case shown in Figure 1, the range of χ_1 values will be small. Since bond strength affects both the length of the bond and the range of χ_1 values, any effort to minimize the range of χ_1 values by using stronger bonds will introduce concomitant changes in the three-body interactions described below. Weak bonds have the advantage of minimizing three-body interactions and may be quite useful for certain classes of reactions, e.g., if the nature of the PES ensures that only a small range of χ_1 will be reactive. The entries in Table I represent a sampling

(23) Xu, Z.; Koplitz, B.; Baugh, D.; Wittig, C. *J. Chem. Phys. Lett.* **1986**, *127*, 534.

(24) Magnotta, F.; Nesbitt, D. J.; Leone, S. R. *Chem. Phys. Lett.* **1981**, *83*, 21.

(25) Shea, J. A.; Read, W. G.; Campbell, E. J. *J. Chem. Phys.* **1983**, *79*, 614.

(26) (a) Joyner, C. H.; Dixon, T. A.; Baiocchi, F. A.; Klemperer, W. *J. Chem. Phys.* **1981**, *74*, 6550. (b) Lovejoy, C. M.; Nesbitt, D. J. *J. Chem. Phys.* **1987**, *87*, 1450. (c) Kukolich, S. G.; Bumgarner, R. E.; Pauley, D. *J. Chem. Phys. Lett.* **1987**, *141*, 12.

(27) (a) Sapse, A.-M. *J. Chem. Phys.* **1983**, *78*, 5733. (b) Soper, P. D.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1981**, *74*, 2138.

(28) Bumgarner, R. E.; Pauley, D. J.; Kukolich, S. G. *J. Chem. Phys.* **1987**, *87*, 3749.

(29) Janda, K. C.; Steed, J. M.; Novick, S. E.; Klemperer, W. *J. Chem. Phys.* **1977**, *67*, 5162.

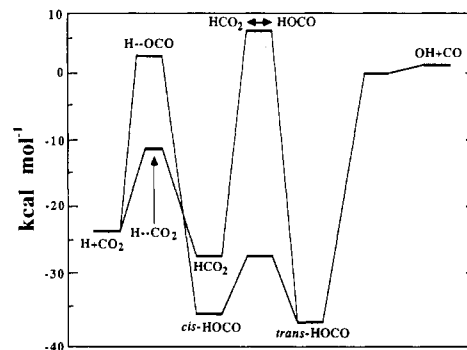


Figure 3. Reaction coordinate diagram for the HOCO system.³⁴

of the available data. Of course, the list is incomplete, since it is possible to bind almost any two atomic/molecular species in a supersonic expansion. The data appearing in Table I were gathered mainly because of interest in the structures of weakly bonded species. Additional needs for structural information, combined with more efficient experimental methods, will result in a rapid expansion of this data base.

In general, as the H atom gains speed, it begins to experience repulsion from the nearby CO_2 . However, if the van der Waals bond is quite long, the H-atom velocity can approach its asymptotic value, approximately $\{(2/m)(h\nu - D_0)\}^{1/2}$, before CO_2 is encountered. This is shown schematically in Figure 2. In this serial interaction picture, the ensuing reaction is similar to a gas-phase bimolecular reaction in which the initial conditions are dictated by the character of the complexes. Because the serial interaction model is only valid with very weakly bonded complexes, the wave function describing the intermolecular coupling will be very spread out in the angular coordinates (χ_1 and χ_2 in Figure 1), and the reaction probability per photolysis event will be low.

Hydrogen moves so rapidly compared to the other nuclei that the system may have trouble following low-energy reaction pathways, such as those shown in Figure 3.^{33,34} This causes entrance channel barriers to be higher than expected and can affect dynamics and reactivity. This can be seen with the series of contour plots shown in Figure 4, from the work of Schatz et al.,³⁴ in which the potential is plotted for different H-atom positions. In Figure 4A, the CO_2 nuclei are held fixed at the equilibrium position and the potential is repulsive for all H-atom positions. With H-atom speeds of $\sim 100 \text{ \AA ps}^{-1}$, modest impact parameters will be favored for reactive collisions, since collisions that involve the region of the classical turning point give the CO_2 nuclei the best opportunity to move, thus trapping the system in the HOCO potential well. Figure 4B shows the effect of bending CO_2 by 30° . Bound regions corresponding to C_{2v} HCO_2 and *cis*-HOCO are apparent, and one can see how important it is for the heavier nuclei to move if reaction is to occur. Figure 4C shows the case where the CO_2 nuclear positions are adjusted to minimize the energy for a given H-O distance and HOO angle. The

(30) Howard, B. J. NATO Advanced Research Workshop, 1986.

(31) Hausler, D.; Rice, J.; Wittig, C. *J. Chem. Phys.* **1987**, *91*, 5413.

(32) (a) Honma, K.; Kajimoto, O. *Chem. Phys. Lett.* **1985**, *117*, 123.

(b) Hausler, D.; Rice, J.; Wittig, C., unpublished.

(33) Polanyi, J. C. *Science (Washington, D.C.)* **1987**, *236*, 680.

(34) Schatz, G. C.; Fitzcharles, M. S.; Harding, L. B. *Faraday Discuss. Chem. Soc.*, in press. Schatz, G. C.; Fitzcharles, M. S. NATO Workshop, 1987.

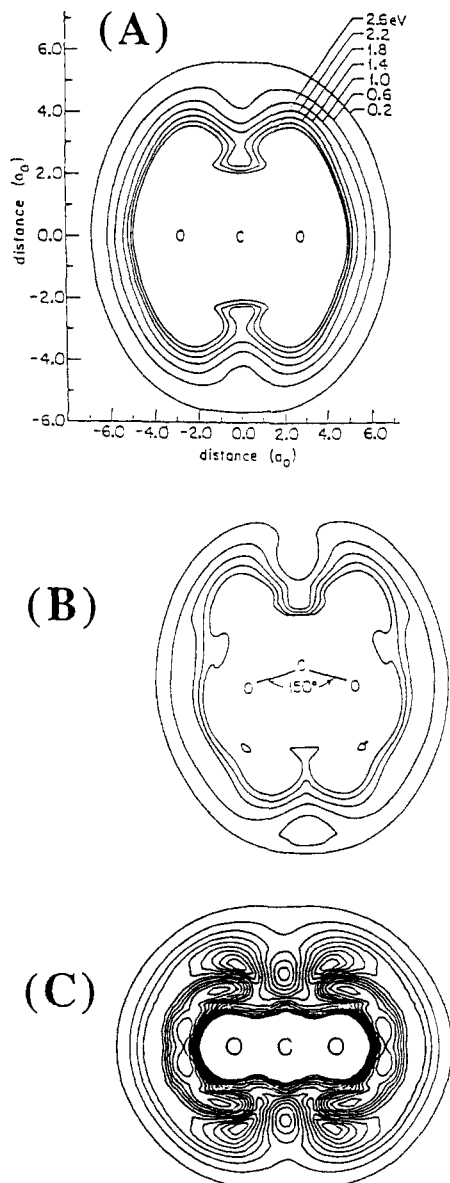


Figure 4. Contour plots of $H + CO_2$ potential energy for CO_2 (A) at its equilibrium geometry, (B) bent by 30° , and (C) configured to minimize energy for a given H-O distance and HOO angle (see text for details).³⁴

C atom therefore assumes many values above and below a line through the oxygen nuclei. However, this cannot be shown in the figure, so the reader must view Figure 4C carefully.

The *serial interaction* situation described above is an idealized limit and will not be applicable to most experimental situations. Again, using CO_2HX as an example and *assuming* that the pairwise H-X and H-OCO interactions can be taken from their isolated-molecule counterparts, one can obtain qualitative insight by examining these curves. Figure 5 shows this schematically, by using a slice taken from the HOCO contour map shown in Figure 4C; as discussed above, the barrier seen by the approaching H atom will probably be higher because the other nuclei cannot keep up with the light H atom. The most important aspect of Figure 5 is that for realistic bond lengths and potential surfaces, the H atom does not become completely free of the X species before it encounters CO_2 . Thus, there is simultaneous pairwise H-X and H-OCO repulsion,

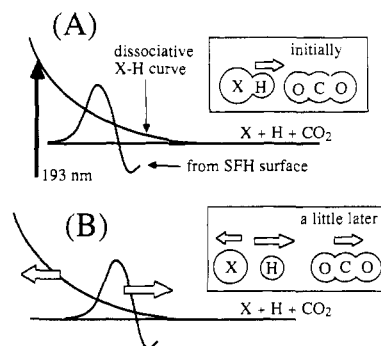


Figure 5. Schematic representation of the three-body interaction in which simultaneous H-X and H-OCO repulsions lead to significant $E(cm)$.

which has the effect of allowing repulsive forces to be effectively transmitted to the heavier objects. This does not happen with *serial interactions* (e.g., the light H atom would convert only about 3.4% of the kinetic energy available in the HBr cm system into relative translation of Br and HOCO in the CO_2HBr cm system). Thus, the typical *close encounters* environment has a built-in sterically constrained three-body effect.

Since cm kinetic energy increases as a consequence of the three-body interaction, less energy is available for product internal excitation. $HOCO^\ddagger$ decomposition into OH and CO depends on E^\ddagger , the energy in excess of D_0 , and E^\ddagger will determine both the unimolecular rate constant and nascent OH and CO product distributions. In this example, reaction is via a long-lived intermediate, so there will be little or no memory of entrance channel specificity. Thus, rate constants and nascent product distributions will serve as indicators of the distribution of E^\ddagger , and therefore the efficacy of the three-body interaction.

Another point concerning initial conditions is that by tuning the photodissociation frequency, the energy of the system can be varied continuously. This has led to important experimental results in homogeneous gas-phase environments and should prove equally useful in PGL experiments.

Experimental Results: CO_2HBr , CO_2DBr , and $SCODBr$

The first report of a PGL reaction in which photodissociation prepared the system on a PES connecting ground-state reagents and products was by Buelow et al. using CO_2HBr .^{21,22} Subsequent experiments with CO_2DBr ^{22b} and $SCODBr$,³¹ in which nascent OD was detected, gave no surprises. The most general result for the CO_2HBr and CO_2DBr systems was OH and OD rotational distributions which were slightly colder than those obtained under bulk conditions (i.e., single-collision at the same E^\ddagger). Results are shown in Figure 6 for the CO_2/HBr system, where data are presented for both PGL and bulk environments. The results are clear, and even vibrations, Λ doublets, and spin-orbit populations were in accord with a unimolecular reaction on a ground PES.

The fact that OH rotational distributions obtained under bulk conditions are not in quantitative agreement with those calculated with statistical methods^{35,36} does

(35) Pechukas, P.; Light, J. C. *J. Chem. Phys.* 1965, 42, 3281.

(36) Levine, R. D.; Kinsey, J. L. *Atom-Molecule Collision Theory*; Plenum: New York, 1979; p 693.

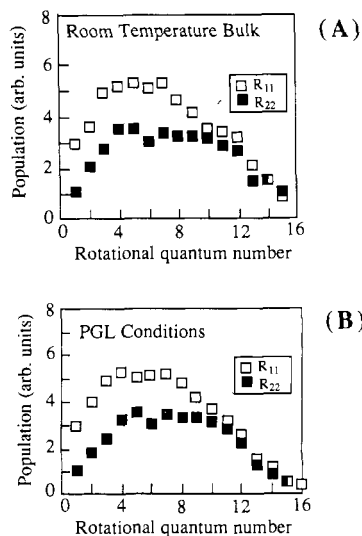


Figure 6. Rotational distributions obtained with (A) room temperature $\text{CO}_2 + \text{HBr}$ bulk samples and (B) CO_2HBr PGL complexes.

not imply dynamical bias. Slightly lower than statistical rotational excitation can be explained by consideration of the unimolecular reaction of HOCO^\ddagger , with explicit account taken of the evolution of vibrations to product angular momenta.^{37,38} In the case of OH, there is little torque since exit channel forces are directed toward the O atom, which is very near the OH cm. Thus this leads to a natural kinematic bias. However, the data cannot be reconciled by entrance channel specificity being carried over to product excitations. This would be contrary to all of our experiences with unimolecular reactions; the HOCO^\ddagger lifetime is too long to accommodate such bias, even considering the natural separation that occurs between H-atom stretch and other molecular vibrations.³⁹ Thus, we believe that the bulk results are statistical in the usual sense that decomposing HOCO^\ddagger carries no information about the entrance channel other than energy and angular momentum.

The differences between the OH rotational distributions obtained with PGL and bulk environments are in qualitative accord with the *close encounters* picture described above. By increasing $E(\text{cm})$ $E^\ddagger(\text{HOCO})$ is lowered, and this results in less OH rotational excitation, even though HOCO^\ddagger behaves statistically. Preliminary estimates using trajectories support this mechanism qualitatively.⁴⁰ Results involving nascent OD distributions deriving from SCODBr^{31} are also consistent with this model, but uncertainty in the heat of formation of CS precludes a quantitative statement.

Rate measurements for such systems can be important. For example, with $E^\ddagger(\text{HOCO}) \sim 12000 \text{ cm}^{-1}$, theoretical estimates place $\tau_{\text{uni}} < 1 \text{ ps}$.³⁴ However, Zewail and co-workers repeated the work of Wittig and co-workers using picosecond lasers, and measured a unimolecular lifetime of $\sim 5 \text{ ps}$.^{41a} They speculated that such a long lifetime may be contrary to RRKM theory.^{41b} However, since the close encounters model predicts that there will be a distribution of $E^\ddagger(\text{HOCO})$

(37) Quack, M.; Troe, J. *Bunsenges. Phys. Chem.* **1975**, *79*, 170.

(38) Quack, M.; Troe, J. *Int. Rev. Phys. Chem.* **1981**, *1*, 97.

(39) Hose, G.; Taylor, H. S. *Chem. Phys.* **1984**, *84*, 375.

(40) Schatz, G. C., private communication.

(41) (a) Scherer, N. F.; Khundkar, L. R.; Bernstein, R. B.; Zewail, A. H. *J. Chem. Phys.* **1987**, *87*, 1451. (b) *Los Angeles Times*, Dec 3, 1987, Section 1, p 3.

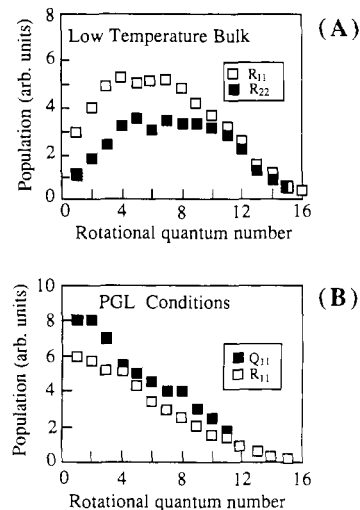


Figure 7. Rotational distributions obtained with (A) low-temperature $\text{CO}_2 + \text{H}_2\text{S}$ bulk samples and (B) $\text{CO}_2\text{H}_2\text{S}$ PGL complexes.

below 12000 cm^{-1} , the observation of a 5-ps lifetime is in qualitative agreement with this model. Whether agreement is quantitative awaits further experiments.

H + CO_2 Reactions from Different Approaches

It is desirable to probe different entrance channel geometries and approaches, and this can be done by (i) exciting intermolecular vibrational modes, thus shifting probability density, and (ii) using different PGL complexes, which offer qualitatively different entrance channel geometries. Approach i may be viable if optical methods can be used to prepare a vibrationally excited intermediate. Approach ii is conceptually straightforward but requires cooperation on the part of nature; i.e., an appropriate set of complexes must be available. Alternatives are to use tertiary and higher complexes to provide a means of systematically changing geometries or to adsorb the gases on an inert surface and photoinitiate the reactions at the surface. This has been demonstrated by Polanyi and co-workers,⁴² who photodissociated H_2S , HBr , and CH_3Br adsorbed on a LiF surface, thus promoting geometrically constrained H-atom reactions.

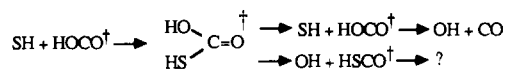
Experiments by Rice et al. with $\text{CO}_2\text{H}_2\text{S}$ complexes revealed an OH distribution that was quite different from that obtained with CO_2HBr as shown in Figure 7.⁴³ Note that the results shown in Figure 7A were obtained with expansion-cooled samples in which there was little or no complex formation. These distributions differed very little from those obtained with room temperature bulk samples, indicating that initial CO_2 angular momentum hardly affects product excitations. Although there has been no measurement of the $\text{CO}_2\text{H}_2\text{S}$ geometry, circumstantial evidence supports several different possibilities for a nonlinear $\text{CO}\cdots\text{HS}$ equilibrium angle. This is distinct from CO_2HX , where linear equilibrium geometries are the rule. Kukolich and co-workers have shown that $\text{SO}_2\text{H}_2\text{S}$ is cyclic, with two $\text{O}\cdots\text{H}$ hydrogen bonds,²⁸ and $\text{CO}_2\text{H}_2\text{S}$ may be similar. This would promote a broadside H-atom attack, and Figure 4 shows that a larger entrance channel barrier

(42) Bourdon, E. B. D.; Das, P.; Harrison, I.; Polanyi, J. C.; Segner, J.; Stanners, C. D.; Williams, R. J.; Young, P. A. *Faraday Discuss. Chem. Soc.* **1986**, *82*, 343.

(43) Rice, J.; Hoffmann, G.; Wittig, C. *J. Chem. Phys.*, in press.

is encountered for such approaches. This will result in even lower $E^\ddagger(\text{HOCO})$ than for end-on approaches at the same total energy. The PGL distribution shown in Figure 7 cannot be reconciled with a single value of $E^\ddagger(\text{HOCO})$, and different E^\ddagger can accrue from the different H-atom speeds from H_2S photodissociation acting in concert with the three-body mechanism. We note that partitioning of energy between $E^\ddagger(\text{HOCO})$ and $E(\text{cm})$ depends strongly on the height and shape of the entrance channel barrier.

Although three-body repulsive interactions are undoubtedly present in complexes such as CO_2HBr and $\text{CO}_2\text{H}_2\text{S}$, we dare not assign the distribution shown in Figure 7 solely to this effect. For example, can the SH photofragment be captured momentarily by the HOCO^\ddagger complex:



Theory

Theory will play an important role because (i) without computations, there is so much flexibility that qualitatively distinct mechanisms can be used to explain the same data, (ii) it is reasonable to demand *quantitative* agreement between theory and much of the data, and (iii) while PGL environments may introduce novelty into reaction mechanisms, a host of reliable computational techniques can be applied without delay.

Theory can be divided roughly into electronic structure and dynamics. With weakly bonded complexes, ab initio calculations can provide guidance for the entire system, including both ground and excited potentials localized on the species being photodissociated. Dynamics calculations at the level of classical trajectories can be instructive, and wavepacket analyses can be carried out when the number of dimensions can be kept low.⁴⁴ It may also be possible to segregate systems into parts that can be treated classically and quantum mechanically. Although each system will have its own personality, several specific aspects are listed here: (1) The PGL environment is a microcosm that nurtures many elementary processes whose counterparts in more conventional media are presently subjects of active research (cage effects,⁴⁵ phonon production,⁴⁶ three-body collisions,⁴⁷ aligned and oriented reactants, etc.). Since experimental studies of PGL reactions produce species-resolved, state-resolved, and single-collision data, theories can be tested more carefully than in less microscopically well-defined media. (2) The entrance channels are unique and a careful study of the different many-body interactions will be revealing. The *close encounters* effect discussed above is but a single mechanistic picture that elucidates some of the important physics that follows photodissociation. The dynamics calculations needed to describe such effects depend strongly on estimates of the interactions between species. (3) In reactions that proceed via long-lived intermediates, rates and product state distributions are insensitive to entrance channel properties. Thus, the dynamics problem can be separated into the entrance channel, which may be amenable to simplify-

ing assumptions, and a unimolecular decay problem, which can be treated with statistical methods with no loss of accuracy. Here, collisions between reaction products and the nearby photofragment (e.g., $\text{Br}\cdots\text{HOCO}^\ddagger \rightarrow \text{Br}\cdots\text{OH}\cdots\text{CO} \rightarrow \text{BrOH}^\ddagger\cdots\text{CO} \rightarrow \text{Br} + \text{OH} + \text{CO}$) may be unimportant provided the unimolecular lifetime is sufficiently long. For example, with CO_2HI complexes, HOCO^\ddagger lifetimes of 5 ps are observed, and even with very modest I-HOCO speeds (e.g., $\sim 4 \times 10^4 \text{ cm s}^{-1}$), the I atom and HOCO^\ddagger will move 20 Å during a lifetime. Thus, secondary collisions can be avoided for such systems.

Calculations relevant to the experiments described above were carried out by Schatz, Fitzcharles, and Harding (SFH).³⁴ They calculated the HOCO surface ab initio, checking stationary points against experimental values wherever possible. They then ran trajectories, essentially mimicking the experimental H + CO_2 bulk system. Both reactive and inelastic channels were examined, and comparisons to experimental results were very reasonable. The SFH surface was then combined with an HBr excited-state repulsive curve, by using the assumption of pairwise additive interactions to obtain a PES for the photoinitiated CO_2HBr reaction. Trajectories were again used to examine the dynamics. Although preliminary, several points are noteworthy: (i) HBr photodissociation commences as if there were no nearby CO_2 , (ii) CO_2 makes its presence felt after about 1 eV of the HBr repulsion has decayed and the three-body effect sets in, (iii) after HOCO^\ddagger is formed, this species decomposes statistically, and (iv) relaxation of OH by Br-OH collisions is unimportant. These results show how experiment and theory can work together to further our understanding of such complex environments. This is more than a cliché; we are certain that challenges passed between experiment and theory will bring excitement and progress.

Predictions and Guidelines

Even for simple systems such as CO_2HX , a number of important measurements have yet to be carried out. For example: (1) The energy can be varied by changing X and/or tuning the photodissociation frequency. Deuterium substitution will be revealing in the region where the reaction cross section falls toward zero. (2) Nascent $\text{CO}(X^1\Sigma^+)$ can be detected with high sensitivity using VUV LIF. This species lies on the spectator side of the reaction, and is not directly subject to 3-body effects. (3) Kinetic energy measurements will further quantify the three-body effects. (4) Inelastic channels such as $\text{Br} + \text{H} + \text{CO}_2$ can be studied with a tunable IR diode laser to probe CO_2 .

With other systems, a variety of important problems can be studied.

(1) How well can branching ratios be controlled? When the potential energy decreases monotonically past the entrance channel barrier for a specific attack geometry (i.e., there is no bound intermediate), product species specificity is straightforward. However, when complicated intermediates are involved, the picture is not so clear. Rearrangements such as hydrogen migration can erase even entrance channel site specificity. To test this, PGL complexes can be prepared in which the initial attack site favors the less thermodynamically favored products, and both high- and low-energy product channels can be detected spectroscopically. For

(44) Davis, M. J.; Heller, E. J. *J. Chem. Phys.* 1984, 80, 5036.

(45) Hynes, J. T. *Springer Ser. Chem. Phys.* 1986, 46, 288.

(46) Gerber, R. B.; Amirav, A. *J. Phys. Chem.* 1986, 90, 4483.

(47) Forst, W.; Barker, J. R. *J. Chem. Phys.* 1985, 83, 124.

example, SCOHX is biased toward CS + OOH, whereas CO + SH is much lower in energy; thus a measurement of [OH]/[SH] would be very valuable. Similarly, N₂OHF complexes have been observed by using molecular beam electric resonance,^{26a} a tunable IR laser,^{26b} and Fourier transform microwave spectroscopy.^{26c} Both NNOHF and ONNHF isomers have been identified, although the latter is considerably more stable than the former. We have observed NH(X³Σ⁻) from both bulk (H + N₂O) and PGL (N₂O/HBr) environments, and this may prove to be a quite interesting system, since (i) NH + NO lies ~100 kcal mol⁻¹ above N₂ + OH, (ii) NH and OH can both be detected by LIF in the 300–340-nm region, making a measurement of [NH]/[OH] straightforward, (iii) NO(X²Π) can be detected with very high sensitivity by two-photon photoionization, and (iv) theory is both interesting (H + N₂O does not correlate to NH(X³Σ⁻) + NO(X²Π) in C_s symmetry, since the products must correlate on a surface of α'' symmetry) and within reach of ab initio and trajectory methods. Lastly, the HNNO intermediate is so weakly bound that the reaction may display direct character.

(2) Large cross section processes allow a detailed examination of entrance channel specificity carried over to product degrees of freedom, since the reactive window is larger than the distribution of initial conditions.

(3) It will be possible to form binary complexes consisting of a molecule and radical, where the radical is in a shallow well outside the usual activation barrier. These can be very interesting and useful precursors. For example, photodissociation of the molecule can lead to a radical–radical reaction starting from near a transition state, such as in the cases H₃N...NO + hν → H

+ H₂N...NO; RNO₂...H + hν → R + ONO...H. Alternately, oxygen atoms can be attached to a simple molecule such as HCl. However, what is an appropriate description of such a species? Does it ever look like OH...Cl? HOCl? Can excitation of an HCl vibration promote reaction?

(4) PGL reactions of electronically excited species, such as the studies pioneered by Soep and co-workers,^{13–17} will continue to provide important results for excited-state reactions; this is very fertile ground.

(5) A series of experiments by Polyanyi and co-workers uses a surface as a chemically inert substrate that holds reactive species in place.⁴² This relaxes the need to find a suitable precursor, albeit at the expense of added complexity. A surface can adsorb almost any molecule and some geometrical control can be achieved by adjusting the coverage. Photoinitiation then promotes reactions much like those discussed here.

(6) The gaseous counterparts to (5) would involve tertiary and conceivably higher complexes. We note that Smalley and co-workers have studied reactions on large clusters whose properties are sometimes closer to those of the corresponding bulk media than their binary and tertiary counterparts.^{8a} Recently, Miller and co-workers⁹ and Howard and co-workers¹⁰ detected (CO₂)₃ and (C₂H₂)₃, respectively, using IR laser spectroscopy, suggesting that photoinitiated experiments with such complexes may be someday possible.

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