Photoinduced Electron Transfer in a Prototypical Mulliken Donor–Acceptor Complex: C2H4···Br2

Lisa George, Laura Wittmann, Aimable Kalume, and Scott A. Reid*

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

ABSTRACT We report a new dual nozzle late mixing scheme for the trapping and interrogation of prereactive donor–acceptor complexes that is used initially to examine photoinduced electron transfer in the prototypical Mulliken donor–acceptor (halogen-bonded) π-complex, C2H4···Br2. Excitation into the intense charge-transfer band of the complex leads exclusively to the anti conformer of the single reaction product, 1,2-dibromoethane, in agreement with the Mulliken theory of electron transfer.

SECTION Dynamics, Clusters, Excited States

The electron-transfer archetype for chemical reactivity underlies important processes in diverse areas ranging from biochemistry to solar cell development to nanomaterials and molecular electronics, and donor–acceptor organizations are widely exploited in all of these areas. As originally suggested by Mulliken, electron transfer in these assemblies involves initial formation of a donor–acceptor complex (D···A), which exhibits an intense charge-transfer transition, representing the transfer of a single electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied MO (LUMO) of the acceptor. It is widely accepted that photoexcitation of the complex generates the ion radical pair (D*···A*), which can react reversibly to products or regenerate the complex via back electron transfer, and these processes have, for selected donor–acceptor pairs, been followed in solution using ultrafast spectroscopy.

The prototypical Mulliken D···A complexes are also model systems for exploring halogen bonding and involve donors such as ethylene (C2H4) with acceptors such as the dihalogen Br2, which is the textbook example of electrophilic bromination of an olefin. Isolation and subsequent charge-transfer excitation of the complex is an appealing route to probe the reaction mechanism; however, this has proven difficult. Thus, the complex has been detected and structurally characterized in a supersonic expansion using microwave spectroscopy and, following an initial report of the IR spectrum in a low-temperature mixture of ethylene and bromine, was trapped in an inert (Ar) matrix at 10 K using a continuous co-condensation approach. Excitation into the intense charge-transfer band (λmax = 237 nm) is in excellent agreement with theoretical predictions, and we find that excitation at λ > 300 nm does not access this band but rather transitions localized on the Br2 chromophore (Figure 1). The dominance of the radical mechanism in this case is then understood; as illustrated in Scheme 1a, cleavage of the Br–Br bond leads to bromine atom attack on the double bond, forming the bromoethyl radical, which, following our recent report, has a classical ground-state structure. Cis or trans addition of the second bromine atom to the radical center, occurring with equal preference, then leads to the anti or gauche conformers of 1,2-dibromoethane. In contrast, charge-transfer excitation should initiate electron transfer, Scheme 1b, leading through a bridged bromonium ion intermediate to the anti conformer of the reaction product. This Letter describes the development of a new method for isolation of the complex in high yield and reports initial studies of the charge-transfer photochemistry of this textbook Mulliken complex.

Our experiments utilized a dual pulsed nozzle late mixing scheme in combination with matrix isolation, Figure 2a. Apart from the late mixing source, which is similar in design to sources reported for molecular beam studies, the apparatus used in these experiments has been described in detail in earlier publications. The source utilized two solenoid pulsed valves, which produced 1 ms duration pulses at a variable repetition rate and variable delay, controlled by a pulse/delay generator (SRS DG535). Three different experiments were conducted in an attempt to isolate the C2H4···Br2 complex, and the results are illustrated in Figure 2b, which displays a region of the infrared (IR) spectrum near the ethylene monomer ν12 band (CH2 scissor). The spectral region shown is convenient for monitoring...
complex formation since the complex shows two absorptions in this region that are infrared-inactive in free ethylene.

In our initial experiments, trace (i), the timing of the C₂H₄/Ar and Br₂/Ar pulses was adjusted for maximum overlap, so that both gas pulses were simultaneously present in the mixing channel. This resulted in the complete thermal reaction of the ethylene monomer, as evidenced by the loss of the corresponding bands in the IR spectrum, and the appearance of two broad bands in the IR that we tentatively ascribe to formation of polymeric products. In this case, a thermal reaction occurs in the mixing channel prior to expansion and subsequent deposition.

In a second set of experiments, we delayed the C₂H₄/Ar and Br₂/Ar pulses by 1/2 of the inverse repetition rate of the experiment (167 ms), so that a “sandwich” matrix comprised of alternating layers of C₂H₄ and Br₂ in Ar was deposited. Following annealing of the matrix to 33 K and recooling to 5 K, the C₂H₄···Br₂ complex was formed, but in very small yield (trace (ii) in Figure 2b). Presumably, the diffusion length of the C₂H₄ monomer is insufficient to afford transport to a Br₂ matrix site. From the integrated IR intensities and calculated (MP2/aug-cc-pVTZ) IR spectrum of C₂H₄ and the C₂H₄···Br₂ complex, we estimate that the ratio of monomer to complex in this case is >50:1.

In the final set of experiments, we slightly delayed (by 1 ms) the Br₂/Ar pulse in order to limit mixing in the gas phase but ensure that the pulses arrived at the cold window in rapid succession. As shown in Figure 2b (trace iii), this resulted in a much larger yield of the desired complex, even without annealing. The observed spectrum of the complex is in good agreement with theory and previous work. Due to the very small shift in the ν₁₂ band of the monomer upon complex formation (Figure 2), we used the stronger ethylene

![Figure 1. UV/visible spectrum of the C₂H₄···Br₂ complex. The calculated (TDCAM-B3LYP/aug-cc-pVQZ) spectrum is shown as the stick spectrum.](image)

![Scheme 1. Radical (a) and Charge-Transfer (b) Mechanisms for Reaction of the C₂H₄···Br₂ Complex](image)

![Figure 2. (a) Schematic of the matrix isolation apparatus with a dual nozzle late mixing source. (b) Infrared spectra for three different experiments, as described in the text. The calculated (unscaled MP2/aug-cc-pVTZ) spectra of C₂H₄ and the C₂H₄···Br₂ complex are shown.](image)
In conclusion, we have developed a new scheme for the trapping and interrogation of prereactive donor–acceptor complexes that was used to examine photoinduced electron transfer in the prototypical Mulliken donor–acceptor (halogen bonded) π-complex, \( \text{C}_2\text{H}_4 \cdot \cdot \cdot \text{Br}_2 \). Excitation into the intense charge-transfer band of the complex leads exclusively to the anti conformer of the reaction product, in agreement with both Mulliken theory and the product distribution of the thermal reaction.\(^{19}\)

This work opens new opportunities for direct observation of ultrafast electron transfer in this benchmark system, and we plan to use this approach to study other model halogen-bonded systems.

**AUTHOR INFORMATION**

**Corresponding Author:**

*To whom correspondence should be addressed. E-mail: scott.reid@mu.edu.*

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