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Photochemistry of alkyl halide dimers

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Dimers and other small clusters of CH_3I, C_2H_5I, *i*- and *n*-C_3H_7I, HI, CF_3I, CH_3Br, and C_2H_5Br formed in a supersonic expansion are irradiated at 248 and 193 nm and the halogen molecule product probed *via* laser induced fluorescence spectroscopy. Both dimers and larger clusters of RI (R=H, alkyl) excited at each wavelength yield I_2 in its ground electronic state with very little internal energy. Clusters of CF_3I and those containing alkyl bromides do not give halogen molecule products after excitation at either wavelength. A model for the dynamics in the dimer excited state which explains these results is presented.

INTRODUCTION

The field of cluster photochemistry, though but a decade old, has become well established with several branches of study. Elegant experiments have been carried out on photodissociation[1] and photoinduced ion–molecule reactions[2] in charged cluster beams; neutral cluster studies have included photoinduced processes such as vibrational predissociation of the cluster,[3] charge transfer, resulting in "harpooning" reactions[4] and dissociation of one of the cluster species, leaving a reactive complex.[5] These experiments are of great importance to our understanding of the influence of weak intermolecular forces on chemical reactivity.

The photoinduced cluster reactions which have been studied to date almost exclusively probe the effects of the weak forces binding the cluster together (primarily van der Waals or hydrogen bonds) on the dynamics of processes which also occur in the absence of such forces. These effects are predominantly determined by the restricted number of approach geometries and impact parameters available to the reagents in a cluster, governed by the structure of the cluster itself. Differences in both microscopic (i.e., product energy disposal) and macroscopic (i.e., chemical) branching ratios between clustered and unclustered reagents have been measured.[5]

We have recently reported a qualitatively different type of cluster photochemical reaction, one which *does not* occur using unclustered reagents.[6] Dimers of methyl iodide absorb one photon of 248 nm radiation, and form ground electronic state I_2 with $\sim 2.5\ \text{kJ mol}^{-1}$ of internal energy. We showed that this reaction must involve some form of cooperative effect, since neither the ground state I nor the spin–orbit excited I* atoms may react with methyl iodide to give I_2 under the conditions existing in the dimer. In the following, we report results on a wide variety of other alkyl halide systems using both 248 and 193 nm excitation: ethyl and propyl (both iso- and normal) iodide, HI, CF_3I, methyl and ethyl bromide, and some mixed clusters. We observe an I_2 product from photolysis of all the iodo compounds except CF_3I, but no Br_2 from excitation of the bromides, or IBr from mixed clusters. A "frustrated dissociative attachment" model for the reaction in the excited state of the dimer is developed. It is based on a partial charge transfer from one monomer component to the other in the excited state and is consistent with all the experimental results.

EXPERIMENT

The apparatus and the experimental setup are the same as reported previously.[6] Here we briefly address the conditions under which each measurement is performed. The experiment is a typical two-laser, pump and probe arrangement. The pump laser is an excimer laser operating on either ArF (193 nm) or KrF (248 nm), and the probe laser is a YAG-pumped dye laser using rhodamine 610 dye for detection of I_2 and Br_2 products *via* laser induced fluorescence (LIF) spectra of their B–X transitions. The LIF spectrum of I_2 is measured from 591 to 596 nm and that of Br_2 from 580 to 600 nm. We use LDS 765 dye for detection of the IBr molecule *via* its A–X transition. Typical excimer laser pulse energies used are 5–10 mJ, and the probe pulse energies are in the range 0.5–1 mJ. The relative timing between the two lasers is controlled by a pulse delay generator; all the results presented here are obtained with a 30 ns delay.

Clusters are generated in a supersonic expansion through a 0.2 mm diameter commercial pulsed nozzle. The vapor pressure of liquid samples is controlled using a constant temperature slush bath. Helium is used as a backing gas in these studies. The gas phase samples are used neat with the pressure governed by a regulator. Both HI (Matheson) and methyl bromide (Anachemia) are used directly from their bottles. All other chemicals are from Aldrich Chemical Company, Inc. and are used as obtained.

For the vapor pressure dependence study, the liquid sample container is immersed in various constant temperature slush baths. The measurement is made approximately 20 min after the bath reaches its stable temperature to ensure that the liquid sample is at thermal equilibrium.

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[a] Natural Sciences and Engineering Research Council University Research Fellow.

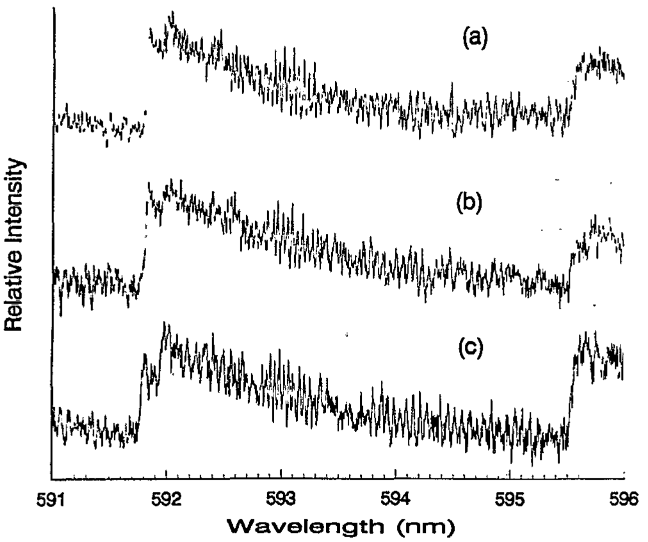

FIG. 1. Laser induced fluorescence spectra of the (10,0), (12,1), (14,2), (16,3) band regions of I_2 measured after excitation of (a) CH_3I dimers at 193 nm; (b) C_2H_5I dimers at 193 nm; (c) C_2H_5I dimers at 248 nm. These spectra are virtually identical to those discussed in Ref. 6.

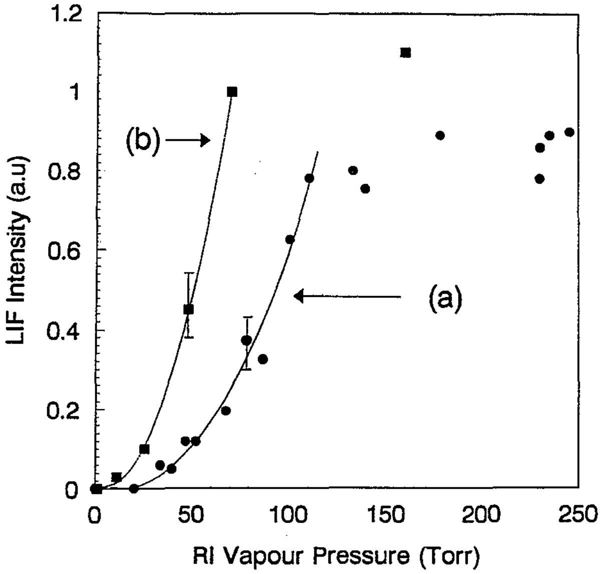

FIG. 2. Dependence of the intensity of the I_2 LIF signal on the partial pressure of (a) CH_3I; (b) C_2H_5I. The total stagnation pressure in each case is ~1300 Torr, using He as the backing gas. The solid lines show quadratic fits to the data.

RESULTS

CH_3I

This species has been systematically studied in our group.[6] In summary, our results show that the ground electronic state I_2 product is observed from the photolysis of CH_3I and CD_3I dimers at both 193 and 248 nm. The I_2 product is born within the 10 ns time resolution of the experiment. The rovibrational temperature of the I_2 product is estimated[6] to be ~150 K, by comparison with simulated spectra. The internal energy of the I_2 product is insensitive to the photolysis wavelength. Figure 1(a) shows a representative spectrum of I_2 in the 591–596 nm spectral range measured after $(CH_3I)_2$ excitation at 193 nm. The spectrum is taken using room temperature CH_3I ($p_{\mathrm{vap}}=350$ Torr); the total stagnation pressure is about 1300 Torr with He as the carrier gas. It is essentially identical to that obtained using 248 nm excitation, reported previously.[6] Other carrier gases including Kr, Ar, Xe, CO_2, O_2, and N_2 have also been used. For all these seeding gases, the spectra are unchanged as a function of the gas used.[6] We have also varied the nozzle diameter and the total stagnation pressure. We observe no changes in the shape of the spectrum, only a linear increase in the LIF intensity with stagnation pressure in the range of 100–1600 Torr. The excimer laser power dependence shows a clear linear relationship between the intensity of the I_2 LIF signal and the photolysis laser pulse energy, indicating a single photon process.[6] The CH_3I partial pressure dependence depicted in Fig. 2(a) shows that the LIF intensity of the I_2 product is quadratic in the stagnation pressure of methyl iodide vapor, indicating that dimers are most important to I_2 generation, at least for methyl iodide partial pressures below about 100 Torr. A log–log plot of these data is linear with a slope of 2.[6] At higher vapor pressures, the I_2 LIF signal intensity levels off. This type of behavior as a function of pressure has also been reported for other clusters.[7] As we have discussed previously,[6] this pressure dependence does not imply that dimers are the only, or even the predominant species present in the jet. The quadratic relationship between precursor concentration and I_2 product concentration is highly suggestive that, at least at low precursor concentrations, dimers represent a major contributor to the I_2-producing photochemistry.

C_2H_5I

I_2 is observed as a product of the photolysis of ethyl iodide clusters at 193 and 248 nm. Figures 1(b) and 1(c) exhibit the LIF spectra of I_2 formed from 193 and 248 nm photolysis, respectively. The shapes of all of the spectra shown in Fig. 1 and their total intensities are almost identical. For the ethyl iodide sample, only He is used as a seeding gas. To ensure that the ethyl iodide dimer is the important species for I_2 formation, we measure the I_2 LIF signal intensity as a function of the ethyl iodide vapor pressure. The total stagnation pressure is regulated at 1300 Torr and the partial pressure of the sample is varied by changing the slush bath temperature. Figure 2(b) shows the measured result. The clear quadratic relationship in the low pressure region (0–70 Torr) and the behavior at higher pressures ($p_{\mathrm{vap}}>70$ Torr) are the same as those observed in methyl iodide [Fig. 2(a)], indicating that it is ethyl iodide dimers that are important to I_2 generation.

1-iodopropane $CH_3CH_2CH_2I$ and 2-iodopropane $(CH_3)_2CHI$

These two samples are briefly examined. I_2 is observed as a product from the photolysis of clusters of both of these

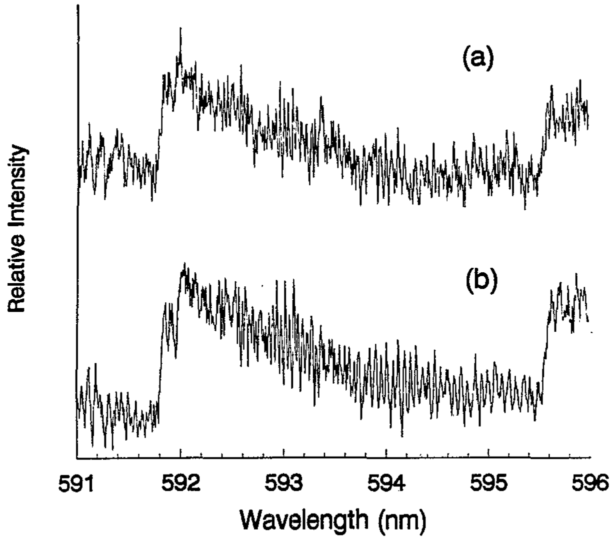

FIG. 3. Same as Fig. 1, but using HI photolysis at 248 nm to produce I_2. Neat HI is used, at a stagnation pressure of (a) 2 atm; (b) 4 atm.

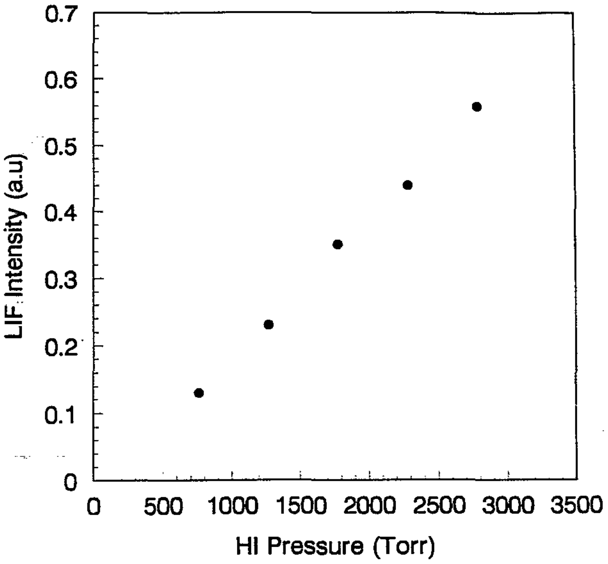

FIG. 4. HI stagnation pressure dependence of the I_2 LIF intensity following 248 nm photolysis of HI clusters. Note the very different pressure dependence and pressure scale than for the alkyl iodides shown in Fig. 2.

species, at each wavelength studied (193 and 248 nm). The LIF spectra of this I_2 product are the same as those given above for methyl and ethyl iodide, though their intensities are somewhat smaller, presumably because of the lower vapor pressure. We use He as a carrier gas and perform measurements with the sample reservoir at room temperature. The vapor pressures of the iodopropanes are 40–80 Torr at this temperature; the total stagnation pressure is regulated to be about 1300 Torr for both samples. Under these conditions, one does not expect significant formation of large clusters. Therefore the mechanism and precursor of I_2 formation is postulated to be the same as that for methyl iodide, i.e., I_2 is formed from photolysis of iodopropane dimers.

HI

Ground electronic state I_2 is also formed from the photolysis of hydrogen iodide clusters at 193 and 248 nm. Figure 3 shows LIF spectra of I_2 formed from 248 nm photolysis. A neat expansion of HI is used in this study; the stagnation pressure is regulated at 2 atm for measuring spectrum (a) and 4 atm for spectrum (b). The LIF signal is very weak below 1 atm stagnation pressure. Since the pressure of HI is quite high in this study, one expects that large clusters are likely to be formed, and could be responsible for the I_2 production. To test this, we measure the I_2 LIF signal intensity as a function of HI pressure. Figure 4 shows the result of such a study. The linear dependence of the I_2 LIF signal on the HI pressure is qualitatively different from the quadratic dependence observed for the alkyl iodides, shown in Fig. 2. These data suggest that photolysis of larger clusters is probably responsible for I_2 formation in this case.

CF_3I

Trifluoromethyl iodide is carefully examined. Despite considerable effort at detection, no I_2 is observed from excitation of CF_3I clusters at either photolysis wavelength, 193 or 248 nm. As in the HI experiments, a neat sample of CF_3I gas is expanded through the pulsed nozzle and the stagnation pressure varied from 100 Torr up to 4 atm. The rest of the experimental conditions are exactly the same as for CH_3I. CF_3I mixed with He gas is also tried, again with no I_2 observed. Assuming similar clustering for CF_3I and CH_3I, we estimate that photolysis of CF_3I clusters is 50–100 times less effective at producing I_2 than photolysis of CH_3I dimers.

CF_3CH_2I

The photolysis of 1, 1, 1-trifluoroethyl iodide at 248 nm does yield I_2 as a product. These experiments use the room temperature sample and He as the carrier gas, at a total stagnation pressure of 1500 Torr. The I_2 spectrum obtained is identical to those measured using methyl iodide, but about one-half as intense.

CH_3Br and CH_3CH_2Br

No Br_2 is observed from this group of samples at either of the excimer laser wavelengths used. Given our experimental signal-to-noise ratio, and measurements of the LIF intensity of expansions of I_2 (Ref. 6) and Br_2, we estimate that photolysis of clusters of RBr yields at most about one-tenth the amount of Br_2 as photolysis of the corresponding $(RI)_2$ yields I_2. Neat CH_3Br is used for this study and the stagnation pressure is varied between 100 and 1300 Torr. CH_3CH_2Br is a liquid with about the same vapor pressure as CH_3I;[8] for this sample we use the same experimental conditions as in the CH_3I studies. The dye

TABLE I. Energetics of the process $(RX)_2 \xrightarrow{h\nu} X_2+2R$.

RX	λ (nm)	ΔH_0 (kJ/mol)
CH_3I	248	−161
	193	−298
C_2H_5I	248	−181
	193	−318
CF_3I	248	−202
	193	−340
CH_3Br	248	− 88
	193	−226
C_2H_5Br	248	−106
	193	−244
HI	248	− 37
	193	−175

laser is scanned from 580 to 590 nm which covers the B–X (8,0), (9,0), (10,1), (11,1),... bands of Br_2.[9]

CH_3I-CH_3Br

For this study, CH_3Br is used as the carrier gas, bubbling through the CH_3I liquid reservoir. The probe laser is scanned from 770 to 780 nm, which covers the A–X (5,0), (7,1), (9,2), (10,2),... vibration bands of IBr.[9] No IBr is observed, despite varying several experimental parameters. Many different reservoir temperatures are used and stagnation pressures from 400 up to 1300 Torr are used. Under these conditions, we anticipate that cluster formation is highly probable.

DISCUSSION

The salient experimental results may be summarized as follows: I_2 is formed in its ground electronic state with very little internal excitation upon 248 or 193 nm excitation of dimers of RI, where R=alkyl radical. It is also formed upon excitation of clusters of HI, although the cluster size responsible is less well established in this case. Whenever I_2 is formed, from any cluster size, or following excitation at the wavelength of either electronic state (valence, at 248 nm, or Rydberg, at 193 nm) of the corresponding monomers, the I_2 internal energy distribution remains similar. No I_2 is observed when clusters of CF_3I are photoexcited at either 193 or 248 nm, nor is Br_2 a product of RBr cluster excitation at 248 or 193 nm wavelengths.

The formation of X_2+2R (or R_2) after photolysis of $(RX)_2$ at either wavelength used here (248 and 193 nm) is energetically favorable for all the molecules studied here. Table I shows the relevant energetics. There is no strictly energetic reason why some of the RX dimers produce X_2 and others do not. The monomer absorption cross sections are very similar for CH_3I and CF_3I;[10] likewise, those of RI at 248 nm and RBr at 193 nm are close in magnitude.[11] The dimer binding energies are not expected to be vastly different among the various species studied here. However, there must be some qualitative difference between CF_3I and CH_3I, and between RI and RBr, to give rise to the observed different reactivities.

We have discussed previously[6] the evidence behind our conclusion that I_2 is formed from methyl iodide dimers *via* some cooperative photoinduced process, rather than as the product of the reaction of an I(I*) atom left behind in the photolysis of one dimer unit with the remaining (intact) methyl iodide. Ground state I atoms do not have enough energy to abstract I from CH_3I and, at least in the absence of clusters, spin–orbit excited I* is quenched entirely *via* E–V transfer in collisions with CH_3I.[12] We explained the latter result by considering the correlation diagram for I-atom abstraction from RI by I*: I_2 cannot be formed in its ground electronic state.[6]

Of course, in a cluster, the spin–orbit correlation diagram applicable to isolated species might not maintain any significance, and since the reaction with I* is energetically allowed, the dimer might act merely as a symmetry-breaking perturber. However, the analogous reaction with HI is not energetically feasible at the collision energies available to the clustered reagents. We observe I_2 with the same internal energy distribution from photolysis of HI clusters as from methyl iodide dimers. If a common mechanism holds in the two cases (as it surely must for a one-photon process) then it seems unlikely that a removal of symmetry restrictions is alone responsible for I_2 formation. In addition, it is difficult to reconcile this mechanism with the absence of the dihalogen product in the brominated molecules and in CF_3I.

An attractive explanation is suggested by the identical nature of the dimer partners. The "exciton" theory of dimer excited states has been well documented.[13,14] In a system of two identical noninteracting molecules, A and B, the ground state wave function is simply $\psi_g=\psi_A\psi_B$. The excited state wave functions consist of the (degenerate) symmetric and antisymmetric combinations of the two $\psi_i^*\psi_j$'s:

$$E'=1/\sqrt{2}(\psi_A^*\psi_B+\psi_A\psi_B^*),$$

$$E''=1/\sqrt{2}(\psi_A^*\psi_B-\psi_A\psi_B^*),$$

where ψ^* denotes the monomer excited state. An interaction potential between the two molecules lifts the degeneracy of the E' and E'' states, giving rise to an energy splitting which may be estimated using perturbation theory. Symmetry considerations demand that for dimer structures in which the transition dipole moments of the A and B monomers are aligned parallel or collinearly, only one of these two states may be excited from the ground state.

In the case of RI dimers, *both* the E' and E'' states must contain some character of the dissociative valence state of the monomer. This is known to dissociate directly, in less than 0.5 ps,[15] into R+I(I*). Thus, if such a state is excited, one can imagine a concerted process breaking both R–I bonds, and perhaps forming I_2 in the process if the two iodine atoms are close enough. This could well be the case, if the dimer geometry calculated by Zeigler and coworkers[16] is correct. This calculation predicts an iodine–

iodine separation of about 3 Å, with the methyl groups directed away from one another. The I···I distance in the dimer is thus only about 10% greater than in the ground state of the I_2 molecule.[9] This structure is rationalized[16] on the basis of the large polarizability of iodine atoms outweighing the dipole–dipole interaction; since the methyl iodide dipole moment is not too great this seems not too unreasonable. The crystal[17] exhibits a somewhat similar structure, with I–I interactions appearing to be important.

Though this model could explain the alkyl iodide data nicely, there are some problems with it. The exciton photochemistry model fails to explain the selective nature of X_2 production. It does not predict that I_2 is not observed from CF_3I cluster photolysis, or that Br_2 is not a product of RBr cluster photolysis. To rationalize these observations using the exciton model requires hypothesizing either different excited state electronic structures, or very different dimer geometries for the X_2 producing vs non-X_2-producing species. Since excitation is into the same valence state continuum of each compound, it seems unlikely that dimer formation would cause qualitative differences among these states. It could be that the different dimers have quite different geometries. However, none of the dimer geometries have been experimentally measured, making this a rather *ad hoc* explanation.

In addition, since the monomer states accessed at 248 and 193 nm are of very different character (valence and Rydberg, respectively), one might expect different types of dimer–exciton photochemistry in the two cases, in particular, different patterns of energy disposal into the I_2 product. Quite different patterns of fragment energy disposal are seen in the monomer photodissociation.[18,19] As shown in Fig. 1, however, this is not the case for I_2 formation from RI dimers. As a final point against this model, the methyl iodide dimer absorption spectra are not at all suggestive of the importance of exciton states.[20]

Here we present an alternative model which does adequately explain all the experimental data. It also relies on the proximity of the I atoms in the RI dimers, but does not have to postulate a large difference in geometry between the I_2-producing and the RBr and CF_3I dimers in order to predict the nonreactivity of the latter systems. This model, which we call the "frustrated dissociative attachment" model, is based on a partial charge transfer in the excited state of the dimer, from one partner to the other. This may induce partial anion character in the other partner, if its electron attachment cross section is favorable. This in turn can give rise to a simultaneous lengthening of *both* R–X bonds; under favorable conditions a "concerted" reaction may occur, producing X_2+2R.

Consider the molecular orbitals involved in the excitation of the monomer. An electron is excited from a nonbonding *p* orbital centered on the halogen atom, into an R–X sigma antibonding orbital. This type of orbital possesses significant halogen p_z character (5*p* for I, 4*p* for Br). Therefore, if the dimer geometry places the two halogen atoms in proximity, with the alkyl groups directed away from each other, the unoccupied R–X sigma antibonding orbitals of the ground state dimer will be physically overlapped to some extent. This is shown schematically in Fig. 5(a).

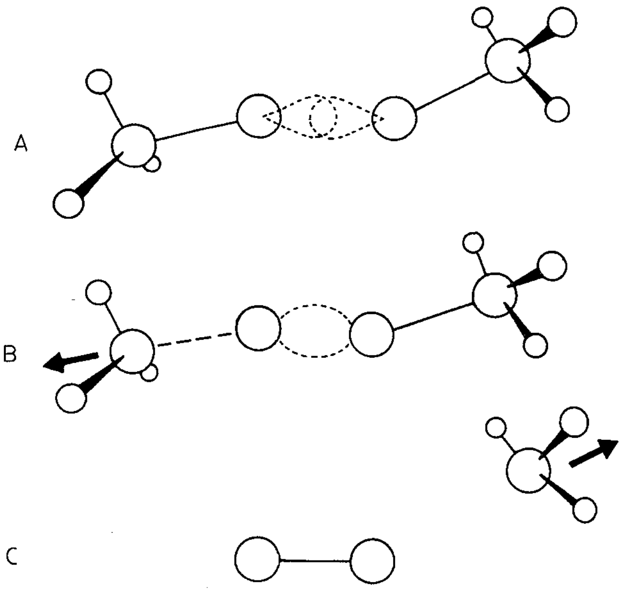

FIG. 5. Diagram showing the "frustrated dissociative attachment" model for dimer photochemistry. (a) shows how the dimer geometry (Ref. 16) allows physical overlap of the σ^* antibonding orbitals. In (b) the dimer excited state consists of a mixture of purely dissociative and partially anionic monomer states. In (c), the I_2 is born "cold," due to the original proximity of the I atoms in the dimer.

Now consider what happens when the (weakly interacting) dimer $(RX)_2$ absorbs a photon resonant with the dissociative valence state of the constituent monomers. (Since the Rydberg states are predissociated by this valence state on a subpicosecond time scale,[16] initial excitation of the Rydberg level will very rapidly populate the valence level.) An electron is promoted into the sigma antibonding orbital of monomer unit 1 which, because of its halogen *p*-orbital character and the dimer geometry, increases the electron density between the two halogen atoms. Due to the overlap between the antibonding orbitals of the two monomer units, monomer unit 2 acquires some additional electron density in its R–X σ antibonding orbital as well. This process is conceptually similar to the "back-bonding" which occurs in transition metal complexes.

From the perspective of monomer unit 2, this increase in electron density corresponds to the partial capture of a zero kinetic energy electron; if fully captured this would result in RX^- anion formation. Thus we may write the excited state wave function as

$$\psi_{\pm}=1/\sqrt{2}(\psi_A^{*}\psi_B^{@}\pm\psi_A^{@}\psi_B^{*}),$$

where now the wave functions $\psi_i^{@}$ are no longer strictly ground state neutral wave functions, but possess some anionic character as well.

The alkyl halide anions are all energetically unstable with respect to a radical and a halide ion: $RX+e^-\rightarrow R+X^-$.[21] If the dimer excited state wave function has some character of *both* the dissociative valence state of the monomer *and* the dissociative anion of the monomer, it is easy to visualize a concerted process in which both R–X bonds start to break at once. This is illustrated in Fig. 5(b). Since this type of excitation presupposes the halogen atoms to be close enough to enjoy significant overlap of their R–X antibonding orbitals (one of which is occupied), it follows that there is an incipient bond already formed between the two halogens. As the two R–X bonds elongate, the two X atoms will be drawn together, eventually forming X_2+2R [Fig. 5(c)]. The X_2 might be expected to be fairly "cold" in its internal degrees of freedom, since it is formed through the relaxation of the X–X bond from its length in the RX dimer (3.0 Å calculated for methyl iodide)[16] to its final value (2.666 Å in I_2)[9] when both R–X bonds have broken. Experimentally, we do observe a very modest amount of energy deposited into I_2 vibrations and rotations,[6] consistent with this picture.

This model thus predicts that the propensity to undergo photochemical X_2 formation is related to the amount of overlap of the two R–X antibonding orbitals (governed by the dimer geometry), and the cross section for low energy electron capture by neutral RX. This quantity, the dissociative attachment (DA) cross section, has been measured as a function of electron kinetic energy for a wide variety of alkyl halides.[22] There are two results of importance to the present work. The first is that the DA cross section for low energy electrons is at least ten times larger for alkyl iodides than for the corresponding bromides. This is a consequence of the much more favorable Franck–Condon overlap between the neutral and anionic ground states for the iodides—the two surfaces intersect at or near the zero point of the neutral.[23] Thus the transition from the neutral to the anionic surface is reasonably facile for "cold" neutral molecules interacting with zero-kinetic-energy electrons. On the other hand, in the bromides the intersection occurs at higher energies, corresponding to 25–30 kJ mol^{-1} of vibration in the neutral molecule, thus decreasing its Franck–Condon overlap with the anion.

This provides a clear picture for the nonreactivity of the alkyl bromides studied here. Even for similar dimer geometries and therefore similar physical overlap of the antibonding orbitals in the two cases, the bromides are predicted to be less reactive than the iodides. The amount of anion character in the dimer excited state wave function will be smaller for them, since the electron capture cross section for zero-kinetic-energy electrons is much smaller for the bromides. Thus the probability for concerted breaking of *both* R–X bonds is smaller for RBr than for RI, and Br_2 is not readily formed.

The second important result from electron capture studies concerns the effect of fluorination on alkyl halide dissociative attachment. In general, perfluorinated hydrocarbons (and alkyl halides) have higher DA cross sections than the corresponding hydrogenated molecules.[22] For instance, that of CF_3Cl is about an order of magnitude greater than that of CH_3Cl. However, another aspect of the perfluorinated compounds R^FX is that their anions, though dissociative, are metastable with respect to fragmentation into R^F and X^-. A consequence of this is an increase in their lifetimes towards dissociation—up to tens or hundreds of microseconds.[22] The hydrogenated compounds, by contrast, are *directly* dissociative. These types of anions typically have lifetimes in the subpicosecond range.[23] Table II displays the relevant energetics for CH_3I, CH_3Br, and CF_3I, their anions and fragments.

TABLE II. Energetics of $RX+e^-$ processes.

	RX		
Process	CH_3I	CH_3Br	CF_3I
$RX\rightarrow R+X$	+223 kJ/mol	+293 kJ/mol	+215 kJ/mol
$X+e^-\rightarrow X^-$	−295	−325	−295
$RX+e^-\rightarrow R+X^-$	−72	−32	−80
$RX+e^-\rightarrow RX^-$	−19	$(\sim -10)^a$	−143

^{a}Estimated.

Dynamically, the long lifetimes for the perfluoro compounds mean that following electron capture the anions are born with energy distributions far from the optimum for fragmentation. Consequently, many (millions, apparently) of vibrational periods are required until the exit channel for fragmentation to R^F+X^- is found. Since this exit channel must involve a lengthening of the R^F–X bond, and this is the motion required by our model for the concerted breaking of both C–X bonds, we would predict that the fact that it is not accessed immediately has the consequence of diminishing the amount of X_2 product formed in the dimer photolysis. This is what is observed in CF_3I. Our observation of I_2 product from the photolysis of CF_3CH_2I samples suggests that the anion of this molecule undergoes very rapid DA. This is not too surprising, since because the iodine atom is bonded to the hydrogenated end of the molecule we might well expect similar behavior to the fully hydrogenated species.

Thus all of our results are consistent with a "frustrated dissociative attachment" model for alkyl halide dimer photochemistry. In this model an electron excited into the R–X antibonding orbital of one of the partners in the dimer may induce partial anion character in the other partner, if the electron attachment cross section is favorable. If the anion is directly dissociative, this can give rise to a simultaneous lengthening of *both* R–X bonds at the same time as the excited electron creates an incipient bond between the two halogens. Under favorable conditions then, a "concerted" reaction may occur:

$$(RX)_2\rightarrow X_2+2R,$$

as is observed in the alkyl iodide dimers and HI clusters. This process is not expected to deposit a lot of energy into the X_2 internal degrees of freedom if the dimer geometry places the two halogens near the X_2 equilibrium bond length. This is exactly the geometry the calculated methyl iodide dimer structure predicts; experimentally, we observe very little energy disposal into vibration and rotation of I_2. Finally, also in agreement with experiment, the model suggests that there should not be a difference in the dynamics between monomer Rydberg state excitation at 193 nm and valence state excitation at 248 nm. This is because the Rydberg state is predissociated by the valence state in $\leqslant 1$ ps; the R–I antibonding orbital is then populated as before. The excess energy (1.4 eV) should appear in the alkyl fragments.

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