Photochemical Generation of a Primary Vinyl Cation from (*E*)-Bromostyrene: Mechanisms of Formation and Reaction

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Received September 27, 2002

The photochemistry of (*E*)-bromostyrene was investigated to determine the nature of the product-forming intermediates and to clarify the mechanism of formation of vinylic cations and vinylic radicals. Both a cation- and a radical-derived product are formed, and the ionic origin of the former product is demonstrated by significant scrambling of the label, starting from specifically deuterated (*E*)-bromostyrene. MO calculations show that the isolated incipient primary vinyl cation is not a metastable species, but that specific interaction with a counterion in combination with a polar environment makes it metastable. The effects of variation of the wavelength of irradiation, solvent polarity, temperature, and isotopic substitution all agree with a mechanism of direct heterolytic C−Br bond cleavage producing an ion pair followed by formation of a radical pair via electron transfer. The vinylic cation is proposed to stem directly from the indirectly populated lowest excited singlet state of bromostyrene with an energy of activation of 6.7 kcal/mol. Branching between proton loss and electron transfer in the resulting ion pair determines the ratio of cation- to radical-derived product. The *E*/*Z*-isomerization occurs in a separate process and does not involve C−Br bond cleavage.

Introduction

The photochemistry of vinylic halides in solution has been studied for more than two decades.[1] A major impetus has been the fact that many electronically excited vinylic halides yield vinylic cations in appreciable yields, next to the corresponding vinyl radicals. Such cations are difficult to obtain via thermal generation; prolonged reaction times at elevated temperatures and use of good leaving groups and/or strongly stabilizing α-substituents are required.[2] Therefore, the photochemical production of vinylic cations at ambient temperatures is worth pursuing. This allows investigation of their reactivity under mild reaction conditions[1] as well as their application in synthesis.[3,4]

Two aspects are still topics of discussion: the nature of the photogenerated vinyl cations in the absence of stabilizing α-substituents and the mechanism of formation of the C−X bond cleavage products.

Thus far, most photochemical studies have employed vinyl halides with cation-stabilizing groups at the α-position, such as phenyl and anisyl.[1] The resulting cations behave in the same way as their corresponding thermally generated species, which means that the same product-yielding intermediate is involved in both reactions, i.e., a linear free vinyl cation.[5,6] Except with special substrates, primary vinyl cations cannot be thermally generated.[7] Several examples of photochemical generation of primary vinyl cations have been reported.[8] Formation of such destabilized cations is expected to be accompanied by rearrangements, producing more stable vinyl cations.[2,9] Indeed, in a combined experimental gas-phase and theoretical study, Apeloig et al. showed that the primary β-phenyl vinyl cation I_1 isomerizes without barrier by a 1,2-hydride shift across the double bond to the α-phenyl vinyl cation I_2.[10] In line with this, Lee and Ko proposed rearrangement from I_1 to I_2 in the condensed phase upon silver-assisted solvolysis of (*E*)- and (*Z*)-bromostyrene.[11] Another possibility for I_1 to stabilize itself would be a 1,2-phenyl shift,[9] leading to the vinylenebenzenium ion

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CHART 1. Mechanism of Dissociative Photobehavior of Vinyl Halides, Involving Consecutive Formation of Radicals and Ions (Mechanism 1)
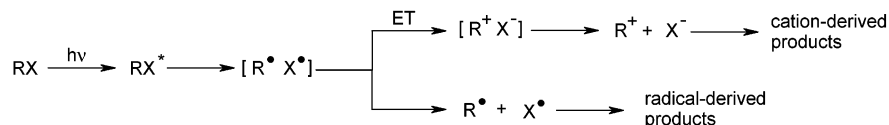
CHART 2. Mechanism of Dissociative Photobehavior of Vinyl Halides, Involving Parallel Formation of Ions and Radicals (Mechanism 2)
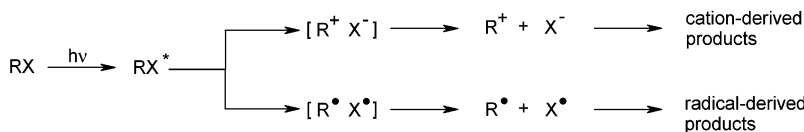
I_3. The cations I_1–I_3, next to the vinyl radical I_4, can be surmised as intermediates in the photochemistry of (*E*)-bromostyrene (**1E**).
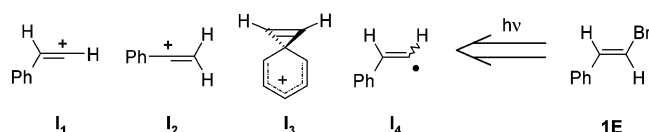

The mechanism of the photochemical formation of vinylic cations from vinylic halides is still not clear. The proposal of Kropp[12] envisions the formation of vinylic cations via vinylic radicals. These radicals are formed by homolytic carbon–halogen bond cleavage and yield cations by subsequent electron transfer (ET) to the halogen atom (mechanism 1, Chart 1).

This mechanism has found widespread acceptance,[13–15] but some observations do not easily fit this proposal. First, calculations indicate that the electron-transfer step is energetically feasible for species with a good cation-stabilizing group at the α-position, but it is too endot-

hermic to occur for species R lacking such substituents.[16] Nevertheless, such vinyl halides do give cation-derived products.[8] Second, the hypothesis of consecutive formation of vinylic radicals and cations predicts a ratio of radical to cationic products from excited vinylic bromides or chlorides, which is determined by the relative reduction potentials of bromine and chlorine in the solvent used. This has been investigated in detail for the photochemistry of β-alkenyl-β-halostyrenes[18] and 1-aryl-2-(2,2′-biphenyldiyl)vinyl halides[19] and found to be counterfactual: in all these cases, as in the compounds studied by Kropp,[1a,12] the bromo derivatives rather than the chlorides gave rise to the highest efficiency of ion product. To accommodate all observed phenomena another reaction mechanism has been proposed (mechanism 2, Chart 2). in which vinylic cations R^+ and vinylic radicals $R^{\bullet}$ are formed in parallel from the excited vinylic halide.[19]

In this paper, we report a study of the photochemistry of one of the simplest vinyl bromides excitable with 254 nm light, (*E*)-bromostyrene (**1E**) and two of its isotopomers: (*E*)-1-bromo-2-deutero- and (*E*)-1-bromo-1-deutero-2-phenylethene (**1E-2D** and **1E-1D**). The aim of the study is 2-fold: (1) to demonstrate the intermediacy of a vinyl cation and to probe its nature, by monitoring scrambling of the deuterium label and by ab initio calculations, and (2) to resolve the mechanism of formation of the cationic (I_1–I_3) and radical (I_4) intermediates and their stable products upon C–Br bond cleavage, by measuring the effect of the solvent polarity, activation energies and isotope effects (IEs) on the product formation.
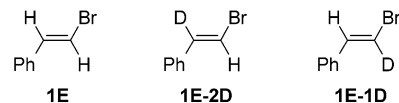
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(16) The driving force of the ET reaction $R^+Br^- \rightarrow R^{\bullet}$ $Br^{\bullet}$ can be estimated by comparing the driving force for R = benzyl (for which experimental data in acetonitrile are available) and R = styryl. The driving force of the ET reaction for R = benzyl is +12 kcal/mol.[17] The gas-phase enthalpy of formation of the vinylic cation from the vinylic radical is calculated to be 23 kcal/mol more positive than that of the enthalpy of formation of the benzyl cation from the corresponding radical (PM3 calculations). Therefore, for the unstabilized vinylic cation, the ET is calculated to be exothermic by about 11 kcal/mol.

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Results and Discussion

Reactive Intermediates. Product Composition. In a wide range of solvents (methanol, acetonitrile, acetic acid, 2,2,2-trifluoroethanol, 1,4-dioxane, *n*-pentane, and hexane), irradiation of (*E*)-bromostyrene (**1E**) at 254 nm under argon yields three primary photoproducts: (*Z*)-bromostyrene (**1Z**), phenylacetylene (**2**), and styrene (**3**) (Scheme 1).[20] Regularly, traces of oxidation products, such as benzaldehyde and methyl benzoate (in methanol), are detected; the amount varies per experiment but is always small (<0.3%). Under an air atmosphere, these products are formed with significant efficiencies at the expense of the formation of **3**. In the alkane solvents several secondary products are detected. One of them was identified as 1,2-dibromo-1-phenylethane, the Markovnikov product of HBr addition to **1**.

Product **1Z** results from *E/Z*-isomerization around the C=C bond, product **2** from the loss of hydrogen bromide, and product **3** from replacement of the bromine atom by a hydrogen atom. Production of hydrogen bromide in the formation of **2** is noticeable from the decrease in pH during the reaction, as well as from the formation of products derived from attack of HBr on the starting material **1E** or product **1Z**.

Photochemical dehydrohalogenation of vinyl halides has previously been shown to proceed via an intermediate vinyl cation.[18,21] Product **2** is therefore concluded to be cation-derived, which is confirmed by the isotope scrambling study presented below. No products from nucleophilic attack of the solvent to the intermediate vinyl cation are obtained. This is in contrast with the behavior of photogenerated α-aryl and α-alkenyl vinyl cations,[18] but in line with that of the *p*-methoxystyryl cation[22] and of α-cyano- and α-formylstyryl cations.[21] Apparently, proton loss from C_β of vinyl cations, lacking a cation-stabilizing group (i.e., alkenyl or aryl) at the α-position, is so fast that nucleophilic attack cannot compete. Previously, the large propensity for loss of a β-proton in the photochemistry of vinyl halides has been attributed to the formation of "hot" vinylic cations.[12,23] We propose that the exclusive formation of elimination products in the case of unstabilized and destabilized vinyl cations in the photochemistry of vinyl halides can be fully explained by proton abstraction by the leaving halide anion from a "cold" cation within a tight ion pair.

This proton abstraction within the solvent cage is facile because of the high kinetic basicity of the bromide anion (Scheme 2, pathway A). This phenomenon is not uncommon and well documented, even for more stable carbocations.[24] This interpretation is corroborated by the results of the irradiation of (*E*)-styryl(phenyl)iodonium tetrafluoroborate (**4**), a compound similar to **1** with neutral

SCHEME 1
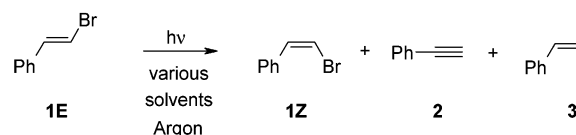
SCHEME 2. Mechanisms of Reaction of I_1 upon Photochemical Formation from 1 (A), from 4 in TFE (B) and from 4 in Methanol (C)
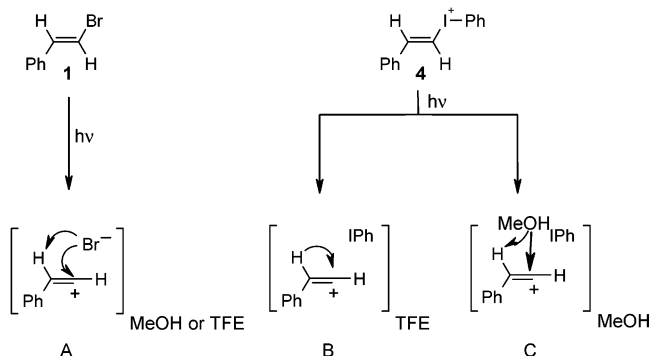
iodobenzene as the leaving group instead of bromide.[25] In 2,2,2-trifluoroethanol (TFE), **4** mainly yields acetophenone as cation-derived product (via rearrangement followed by solvent addition) next to traces of the elimination product **2** and the products of direct nucleophilic addition of the solvent to I_1 (Scheme 2, pathway B). In methanol, the main cation-derived photoproducts from **4** are the β-methoxystyrenes, next to **2** and only a trace of rearranged product. In this case, methanol, I_1, and iodobenzene are formed together within a solvent cage due to precomplexation of methanol to **4** (Scheme 2, pathway C).[25,26] Methanol is a stronger base than TFE, thus yielding elimination product **2**, but also a stronger nucleophile yielding the β-methoxystyrenes. The presence of methanol in the solvent cage thus advances proton abstraction and nucleophilic substitution at the expense of rearrangement. In principle, the same is true for the bromide anion in the ion pair of Scheme 2, path A, so here also nucleophilic substitution by internal return within the solvent cage is very well possible. However, since this will reform β-bromostyrene and largely with retention of configuration this mode of reactivity goes unnoticed in the photochemistry of **1**. In fact, this may even explain the relatively low quantum yield of disappearance of **1** (~0.3) compared to **4** (~1), because the internal return is a photon wasting pathway of reaction. Thus, although the same carbocation is formed in the photochemistry of **1** and **4** in TFE and methanol, its reactivity is quite different and is controlled by the nature of the leaving group.

The styryl cation I_1, not encumbered by an anion, has also been prepared in methanol by the nuclear decay of tritium technique. In that case also, rearrangement and substitution are important processes.[27]

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SCHEME 3
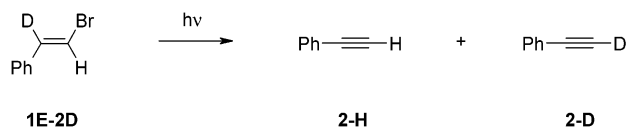
TABLE 1. Percentage of Deuterium in Photoproduct 2 upon Irradiation of 1E−2D in Solvents of Varying Polarity

	$E_T(30)^{a,30}$	2-D (%)
n-pentane	31.0	8.0 ± 0.2
methanol	55.4	16.5 ± 0.8
acetonitrile	45.6	18.1 ± 0.9
acetic acid	51.7	18.7 ± 0.8
TFE	59.8	21.5 ± 1.0

^{a} In kcal/mol.

Replacement of bromide by hydrogen, forming **3**, is a well-known photochemical reaction of vinyl halides and was concluded to occur via an intermediate vinyl radical.[19] This is in line with the sensibility of the formation of **3** toward oxygen. Scavenging of the vinyl radical I_4 thus occurs by hydrogen atom transfer from the solvent, yielding **3**, or by oxygen, yielding the vinyl peroxyl radical $I_4O_2{}^{\bullet}$,[19,28] and ultimately oxidation products.

Isotope Scrambling. Deuterium scrambling studies were performed using 1-bromo-2-deutero-2-phenylethene (**1E-2D**). Since rearrangements are only expected in the chemistry of vinyl cations, and not in the chemistry of vinyl radicals,[29] scrambling was monitored soley in the cation-derived product **2**. The extent of deuterium scrambling was analyzed using GC−MS. The low detection limit of this technique (compared to ^{1}H or ^{2}H NMR, necessary to study scrambling in **3** and **1Z**) allows scrambling to be studied at low conversion. Upon irradiation of **1E-2D** in various, even apolar, solvents, deuterium scrambling does occur, leading to deuterated **2** (Scheme 3, Table 1). The amount of scrambling is independent of the conversion of the photoreaction.

The occurrence of rearrangement confirms that **2** is formed via a cationic intermediate. The dependence of the amount of scrambling on the solvent polarity is also indicative of the ionic origin of **2**. The percentages qualitatively correlate with the $E_T(30)$ values, with more deuterium scrambling in the more polar solvents. This is probably caused by the increased lifetime of the ion pair (Scheme 2A) in such solvents, giving more time for the rearrangement to occur.

Three different mechanisms for deuterium scrambling in the styryl cation should be considered. First, a 1,2-hydride shift converts I_1 into another styryl cation I_2 (Scheme 4, route A). The driving force for this reaction is the well-known stabilizing effect of a phenyl group at the α-position of a carbocation, as well as the (small) destabilizing effect of a phenyl group at the β-position of a vinyl cation.[31] Loss of H^+ or D^+ from I_2 yields **2-D** or

2-H. Second, partial migration of the phenyl ring across the carbon−carbon double bond yields the vinylene benzenium ion I_3 (route B), which is energetically more stable than I_1. Loss of either hydrogen or deuterium, yielding **2-D** or **2-H**, can occur directly from I_3 because a significant part of the positive charge resides on the vinylic carbon atoms. Alternatively, I_3 can reopen, giving either the I_1-**1D** or I_1-**2D**. Proton or deuterium loss from these intermediates yields **2-D** or **2-H**. Third, α-H loss from I_1 initially yields an vinylidene carbene (route C). Alkylidene carbenes are known to quickly rearrange to alkynes.[32] α-Elimination from I_1 leads to exclusive formation of **2-D**.

Routes A and B predict about equal amounts of **2-H** and **2-D** to be formed.[33] Route C predicts exclusively **2-D**. Since in all of the solvents used the percentage of scrambling is lower than 50%, direct loss of D^+ from I_1-**2D** must be a significant pathway, in competition with the operating scrambling pathway.

Cation I_2 (involved in route A) can be independently prepared by photolysis of 1-bromo-1-phenylethene (**5**).[34] Upon irradiation of **5** in methanol, we observed 1-methoxy-1-phenylethene (**6**) as primary nucleophilic substitution product (Scheme 5). Not even traces of **6** are found in the photochemistry of **1E** in methanol. Formation of vinyl ether **6** in the photochemistry of **5** in methanol and its absence in the photochemistry of **1E** in methanol exclude the intermediacy of I_2 in the formation of **2-D** and thus route A.

If route C were the actual mechanism of formation of the rearrangement product **2-D**, it should be a readily accessible reaction path for all styryl cations bearing an α-hydrogen atom. The reaction path should be especially important for styryl cations with electron-withdrawing groups attached to the phenyl ring or to the double bond, which increase the acidity of the α-hydrogen atom. However, no elimination product is formed in the photosolvolysis of compound **7** in methanol (Scheme 6).[35] Moreover, using deuterated methanol, the formation of the vinyl ethers was shown not to occur via an intermediate alkylidene carbene (inserting into the H(D)−O bond of the solvent[32]). So, route B remains as the only plausible mechanism for the formation of **2-D** in the photochemistry of **1E−2D**.

MO Calculations on $C_8H_7{}^+$. Having proven the presence of I_1 and the absence of I_2 in the condensed-phase photochemistry of **1E**, it is of interest to investigate why upon formation of I_1 in the gas phase only products derived from I_2 are formed.[10] Medium effects may well stabilize the cation I_1 and make it a metastable intermediate in solution, similar to the situation of the parent

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(33) This statement is only valid if the isotope effect for H^+ loss equals one, which is unlikely. However, the primary IE will be normal (larger than one), preferentially forming **2-D**, whereas our experiments give more **2-H** (Table 1). So, the conclusion that a considerable part of **2** is formed by direct β-D^+ loss from I_1-**2D** still holds.

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SCHEME 4.   Mechanisms of Deuterium Scrambling of the Styryl Cation I_1, Involving a 1,2 D-Shift (A), a 1,2 Phenyl-Shift (B), or α-Elimination (C)
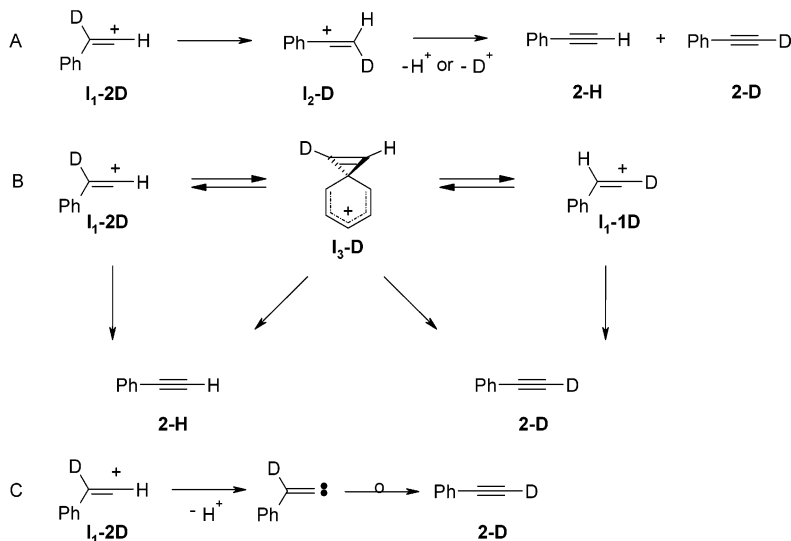
SCHEME 5
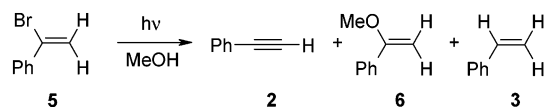
vinyl cation, where the more delocalized bridged structure is observed in the gas phase[36] and the charge-localized open stucture in the condensed phase.[37] The relative stabilities of the selected isomeric geometries I_1–I_3 of $C_8H_7^+$ are calculated at the B3LYP/6-31G(d,p) level of theory in the gas phase and in a dielectric continuum with $\epsilon_r = 78$ (Table 2).

Intermediate I_2 with its vinylic hydrogen atoms orthogonal to the plane of the phenyl ring is calculated to be the global minimum, and all energies are reported with respect to its energy. In accordance with the previous study on $C_8H_7^+$,[10] no minimum energy structure is found for isolated I_1 at the B3LYP/6-31G(d,p) level of theory. Inclusion of electron correlation is necessary for this result. At the HF/6-31G(d,p) level of theory, I_1 is a local minimum. A B3LYP/6-31G(d,p) geometry of I_1 was obtained from the HF/6-31G(d,p)-optimized geometry by freezing the H–C_β=C_α bond angle and reoptimization of the geometry at the B3LYP/6-31G(d,p) level. A frequency calculation of the thus-obtained geometry has real frequencies for all optimized coordinates. This indicates that the 1,2-hydride shift, yielding I_2, is the only barrierless pathway to stabilize I_1. Rotation of the phenyl ring out of the plane, and subsequent anchimeric interaction of the phenyl ring with the positively charged carbon atom, yielding I_3, therefore must occur with an activation barrier. I_3 is 16.0 kcal/mol more stable than I_1, but 24.0 kcal/mol less stable than I_2. This is in line with results for triarylvinyl cations, where the open structure usually is more stable and the phenonium ion is either a transition state or a local minimum, as in this case.[38]

Our results using the SCRF-IPCM model to account for solvent polarity are in line with a recent study of the parent vinyl cation.[39] In that case, the dielectric was shown to influence the relative stabilities of the open and bridged species, but the order of stabilities does not change. The stabilization by the dielectric correlates qualitatively with the extent of charge delocalization. For $C_8H_7^+$ the largest changes in relative stabilities upon solvation are calculated for I_1, the cation with a localized charge (Table 1, column 6). The cations with a π-delocalized positive charge (I_2 and I_3) only benefit to a minor extent from the dielectric.

Computation of the two extreme pathways for the hydride shift (within the plane of the phenyl ring, or perpendicular to this plane) is performed by means of a relaxed PES scan, by stepwise variation of the H–C_β=C_α bond angle (Figure 1).

Both pathways have no barrier. Hopping from the "perpendicular" to the "in-plane" path occurs somewhere in the region where the two cross, as indicated by the dashed line in Figure 1. It is important to note that initially the energy gain for the 1,2-hydride shift is only small and that the energy gain becomes larger toward the end of the reaction path.

A transition state on the reaction path from I_1 to I_2 is expected to be reagent-like because of the large exothermicity of the reaction (even in a dielectric). To study whether the presence of a dielectric makes cation I_1 a metastable species, the I_1-like part of the lowest energy path was recalculated with incorporation of the SCRF-IPCM method (Figure 1). Clearly, the PES for the 1,2-hydride shift is flatter in the presence of a dielectric, but the rearrangement from I_1 yielding I_2 still occurs without barrier.

Specific interactions between a carbocation and its counterion have previously been shown to be crucial for a correct description of alkyl carbocations in solution.[40,75]

(36) (a) Kanter, E. P.; Vager, Z.; Both, G.; Zajfman, D. *J. Chem. Phys.* **1986**, *85*, 7487. (b) Vager, Z.; Naaman, R.; Kanter, E. P. *Science* **1989**, *244*, 426.
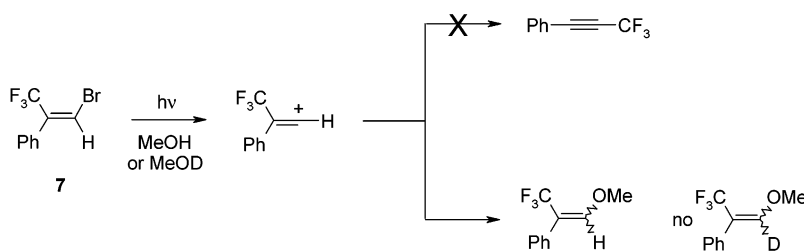(37) Lucchini, V.; Modena, G. *J. Am. Chem. Soc.* **1990**, *112*, 6291.
(38) Yamataka, H.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1998**, *63*, 9105.

(39) Bagno, A.; Modena, G. *Eur. J. Org. Chem.* **1999**, 2893.
(40) (a) Fărcaşiu, D.; Hâncu, D.; Haw, J. F. *J. Phys. Chem. A* **1998**, *102*, 2493. (b) Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem. A* **1998**, *102*, 10436. (c) Fărcaşiu, D.; Norton, S. H.; Hâncu, D. *J. Am. Chem. Soc.* **2000**, *122*, 668.
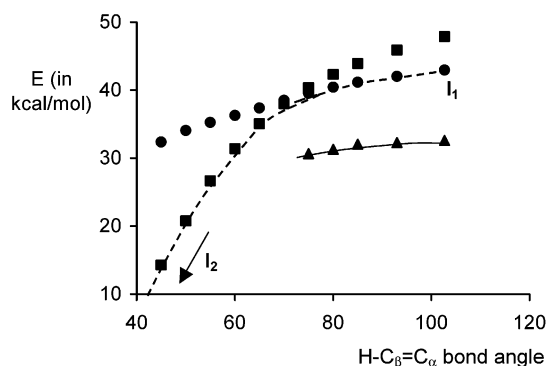
SCHEME 6

TABLE 2. Relative Stabilities (in kcal/mol) of Species I_1–I_3 at the B3LYP/6-31G(d,p) Computational Level in the Gas Phase, with Their Number of Imaginary Frequencies, and in a Dielectric Continuum Using the SCRF-IPCM Model

species	symmetry	energy + ZPE	no. of imaginary frequencies	energy in dielectric	energy change
I_1	C_s	40.8	a	32.6	8.2
I_2	C_{2v}	0^b	0	0^b	0^b
I_3	C_{2v}	24.0	0	22.6	1.4

^{a} Not a stationary point (see text). ^{b} By definition.

FIGURE 2. Geometry of the I_1–LiH_2^- ion-pair at 3.0 Å distance.

FIGURE 1. Energetics for 1,2-hydride shift from I_1 to I_2, perpendicular to (■) and in the plane of (●) the phenyl ring, by variation of the $H-C_\beta=C_\alpha$ bond angle. The I_1-like part of the lowest energy path is recalculated with inclusion of a dielectric continuum (▲).

Of a series of anions tested, lithium dihydride (LiH_2^-) efficiently describes anion–carbocation interactions, provided the distance between the ions is sufficiently large to prevent spontaneous proton abstraction.[75] Unfortunately, DFT methods do not give satisfactory results upon inclusion of counterions because of preferential proton abstraction.[75] Thus, electron correlation was accounted for using MP2 corrections.[41,42]

Addition of a lithium dihydride counterion at 3.0 Å distance[43] results in a metastable species for I_1! Optimization of all coordinates, except for the interionic distance, gives the geometry depicted in Figure 2. The cation I_1 in the ion-pair I_1–LiH_2^- has characteristics intermediate between those expected for the free ion and the

corresponding radical I_4: the NBO charge on the C_8H_7 entity is +0.60 and the C_β–C_α–H bond angle is 142°, indicating hybridization of the formally charged carbon atom intermediate between sp and sp².

Specific interactions between an anion and I_1 are thus capable of stabilizing I_1 enough to make it a metastable species. The presence of a dielectric is expected to stabilize it even more, since this has been shown to flatten the PES for hydride migration for the bare ion (cf. Figure 1). Moreover, as charge separation increases upon addition of a dielectric continuum, I_1 will have more ionic character in the ion pair, which will result in a more linear $C_\beta=C_\alpha$–H bond and a better description of I_1 in the condensed phase. Excessive computational costs of such calculations refrained us from verifying this.

Mechanism of Photolysis. Nature of the Reactive Excited State. Upon irradiation at $\lambda_{exc} = 313$ nm[44] of a solution of (E)-bromostyrene (**1E**; 2 mM) in methanol, using xanthone as sensitizer, **1Z** is the only product up to a conversion of 40% of **1E**. This result is in line with our previous results in the study of α-alkenyl vinyl halides which give exclusive E/Z-isomerization from their triplet-excited state as well.[18] Therefore, the reactive state for C–Br bond dissociation is an excited singlet state.[45]

The UV spectrum of **1E** exhibits an absorption maximum at 257 nm ($\epsilon = 1.92 \times 10^4$ M^{-1} cm^{-1}). Its position and extinction coefficient are equal within experimental error in methanol, acetonitrile, and n-pentane. The solvent-polarity independence of the λ_{max} and the high extinction coefficient indicate that the initially excited state is most likely of $\pi\pi^*$ type. In any case, both observations rule out a $\pi \rightarrow \sigma^*$ transition, since (a) a $\pi\sigma^*$ state has a substantial dipole moment, due to the shift

(41) Electron correlation by MP2 was successfully applied in previous studies of counterion effects on the structure of carbocations (see ref 40).

(42) Calculations of the bare cation I_1 on the MP2(fc)/6-31G(d,p) level of theory give essentially the same features as the DFT calculations. No local minimum is calculated for I_1, which isomerizes barrierless to I_2.

(43) Defined as the distance between C_α and the nearest hydrogen atom of LiH_2^-.

(44) At this wavelength no light is absorbed by the vinyl halide.

(45) Alternatively, the reactive state may be an upper triplet state. See: (a) Scaiano, J. C.; Arnold, B. R.; McGympsey, W. G. *J. Phys. Chem.* **1994**, *98*, 5431–5434. (b) Elisei, F.; Latterini, L.; Aloisi, G. G.; D'Auria, M. *J. Phys. Chem.* **1995**, *99*, 5365–5372. (c) Latterini, L.; Elisei, F.; Aloisi, G. G.; D'Auria, M. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2765–2770.

TABLE 3. Effect on the Product Ratio 2/3 of the Wavelength of Irradiation of 1E (2.24 mM) in *n*-Pentane at Room Temperature

λ (in nm)	2/3
240	0.38 ± 0.06
254	0.32 ± 0.08
270	0.36 ± 0.02
295	0.42 ± 0.01

TABLE 4. Quantum Yields of Disappearance (Φ_{dis}) of 1E (1 mM) and the Product Ratio 2/3 in Different Solvents at Room Temperature

solvent	Φ_{dis}	2/3
methanol	0.33 ± 0.01	0.52 ± 0.08
acetonitrile	0.30 ± 0.02	0.59 ± 0.05
hexane	0.22 ± 0.02	0.65 ± 0.08
1,4-dioxane	0.25 ± 0.01	0.59 ± 0.14

TABLE 5. Activation Energies (in kcal/mol) for the Formation of Photoproducts from 1E in *n*-Pentane

	1Z	2	3
E_a	3.0 ± 0.4	6.7 ± 0.2	6.1 ± 0.3

of charge from the π system to the C–Br bond, and would be stabilized in polar solvents, and (b) $\pi\sigma^*$ transitions are local symmetry-forbidden in the planar equilibrium geometry of **1E** (the overlap between the π-system and the orthogonal σ^* C–Br orbital is near-zero),[46] and so the $\pi\sigma^*$ absorption intensity will be extremely small in the solution UV spectra.[47] Likewise, the high ϵ_{max} value is also strong evidence against an n → σ^* transition, which is the lowest energy transition in alkyl halides. In these compounds, n → σ^* transitions have substantially lower ϵ values ($\epsilon_{max}(CH_3Br) = 265$ M^{-1} cm^{-1}) at much shorter wavelengths ($\lambda_{max}(CH_3Br) = 202$ nm).[48] Since no significant change in the strength of the C–Br bond is expected upon a π → π^* transtition, the reactive state is presumably not the one which is initially excited in the direct irradiation experiments with 254 nm light. We propose the reactive state to be a $\pi\sigma^*$ state, in analogy with vinyl bromide,[49] and in contrast with the alkyl bromides.[15] Since homolytic photocleavage of vinyl halides as in mechanism 1 (Chart 1) was proposed in analogy with the photochemical behavior of alkyl halides, the fact that these two classes of species have different lowest excited singlet states may result in different photocleavage modes.

Effect of Wavelength of Excitation. The photochemistry of **1E** in *n*-pentane at room temperature was studied at wavelengths of excitation ranging from 240 to 295 nm (the absorption onset is at 303 nm; Table 3).

The lack of sensitivity of the photoreaction to the wavelength of irradiation contrasts with the photochemistry of other vinyl halides.[18,19,21] Apparently, only one excited state plays a role in the photochemical C–Br bond cleavage from **1E**, yielding cation-derived (**2**) as well as radical-derived (**3**) products. Mechanism 2 suggests parallel formation of both vinylic radicals and vinylic cations from electronically excited vinylic halides. Since the formation of radicals and ions requires very different charge distributions in the reactive excited state, it is unlikely that they will simultaneously be formed from a single excited state. The absence of wavelength dependence therefore argues against mechanism 2 (Chart 2).

Effect of Solvent Variation. The photoreactivity of **1E** changes only slightly upon variation of the solvent (Table 4). The quantum yields of disappearance (Φ_{dis}) are somewhat higher in the polar solvents methanol and acetonitrile than in the nonpolar solvents hexane and 1,4-dioxane. This trend is not expected for a reaction which

starts with formation a radical pair (as in mechanism 1, Chart 1), but is in line with predictions for a reaction involving initial formation of an ion pair next to a radical pair (as in mechanism 2, Chart 2).

Mechanism 1 (Chart 1) predicts a substantial solvent effect on the relative efficiency of formation of cation- and radical-derived products. A simple relation is expected: the more polar the solvent, the more ionic products. However, no clear relation between the ratio **2/3** and the polarity of the solvent is observed. This implies that if ET is one of the reaction steps of the initially formed intermediate, it cannot be the only one next to diffusion apart (as in mechanism 1). For mechanism 1, no obvious other reaction is available for the radical pair. The vinylic radicals are stable enough to diffuse in competition with ET.

Effect of Variation of the Reaction Temperature. The amounts of **1Z**, **2**, and **3** formed were measured by means of product analysis of the reaction mixture after fixed irradiation times at reaction temperatures varying from −80 to +20 °C. Lowering of the temperature yields lower amounts of all products. At −60 to −80 °C, **1Z** is the only observed product. Analysis of Arrhenius plots using the data between −40 and +20 °C yields the data collected in Table 5.

The activation energies of the formation of photoproducts from **1E** should give important information. Especially in an apolar solvent, such as *n*-pentane, mechanisms 1 and 2 (Charts 1 and 2) are expected to give very different activation energies for the formation of cation-derived **2** and radical-derived **3**.

The activation barriers for formation of **2** and **3** are equal within experimental error. This observation disagrees with mechanisms 1 and 2 (Charts 1 and 2). In the case of mechanism 1, an endothermic ET step (this step is especially endothermic in *n*-pentane) forms the cation-derived product **2**, after intial homolysis. In this mechanism, a significantly higher activation energy on the formation of **2** than on the formation of **3** is thus expected. It is extremely unlikely that the formation of an ion pair and a radical pair from a single excited state, as in the case of mechanism 2, have equal activation energies.

The activation barrier for *E*/*Z*-isomerization is measured to be only 3.0 kcal/mol. The value of the activation energy for *E*/*Z*-isomerization is clearly different from those leading to products following from C–Br bond

(46) Klessinger, M.; Michl, J. *Lichtabsorption und Photochemie Organischer Moleküle*; VCH: Weinheim/New York, 1989; p 30.
(47) $\pi\sigma^*$ states are generally hard to observe for organic compounds: Michl, J.; Bonačić-Koutecký, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990; p 44.
(48) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell: London, 1991; p 462.
(49) Reference 47, pp 380–386.

CHART 3. Mechanism of Dissociative Photobehavior of Vinyl Halides Involving Consecutive Formation of Ions and Radicals (Mechanism 3)
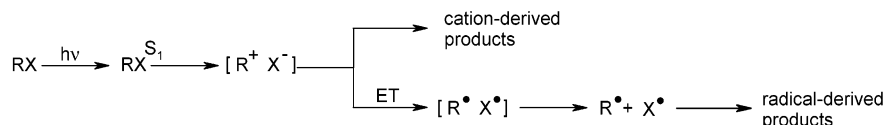
	1Z	2	3
α-secondary IE[a]	1.03 ± 0.02	1.27 ± 0.11	1.39 ± 0.13
β-secondary IE[b]	1.03 ± 0.01	1.11 ± 0.02	0.88 ± 0.05

[a] Relative rates of formation of products from **1E** and **1E-1D**. [b] Relative rates of formation of products from **1E** and **1E-2D**.

cleavage. This demonstrates that *E/Z*-isomerization occurs via a separate process, not involving C−Br bond cleavage.

On the basis of the above results, we propose mechanism 3 (Chart 3) for the photodissociation of the C−Br bond in **1E**. Upon excitation with light of 254 nm followed by internal conversion, the S_1 ($\pi\sigma^*$) state is populated. In this state a direct heterolysis of the C−Br bond occurs, yielding an ion pair consisting of a vinylic cation and a bromide anion.[50] The ion pair can undergo one of three processes: (1) proton abstraction from the vinylic cation to yield phenylacetylene (**2**), (2) rearrangement of the vinylic cation to a more stable species (see labeling experiments), and (3) electron transfer from the bromide anion to the electron-deficient vinyl cation. The components of the resulting radical pair diffuse apart and the vinyl radical yields **3** as stable product by abstraction of a hydrogen atom from the solvent.

Mechanism 3 (Chart 3) agrees with the solvent effects. The formation of ionic species in the first reaction step accounts for the higher quantum yields of disappearance in polar solvents. Since no clear relation between the ratio **2/3** and the polarity of the solvent is observed, the vinylic cation in the tight ion pair must be so unstable that diffusion cannot compete with ET. Branching between proton loss and ET occurs, which is hardly affected by the solvent polarity. This conclusion is in line with the absence of nucleophilic substitution products. Mechanism 3 also agrees with the activation energies for **2** and **3**. Formation of the ion pair is the rate-determining step and the subsequent ET step leading to formation of **3** is almost without barrier. Therefore, cation-derived **2** and radical-derived **3** are formed with equal activation energies, even in *n*-pentane.

Isotope Effects. Deuterium isotope effects on the formation of the $E \rightarrow Z$ isomerization product **1Z**, the cation-derived product **2** and the radical-derived product **3** in the photolysis **1E**, **1E−1D**, and **1E−2D** in methanol are measured as the relative rates of formation of these products from **1E** and its deuterated analogues (Table 6).

The α- and β-deuterium IE on the appearance of **2** are both normal, as expected for its formation via initial

heterolysis of the carbon−bromine bond. In this process, the hybridization of the reaction center changes from sp^2 to sp, which leads to an α-secondary deuterium IE > 1.[51] The difference in hyperconjugative stabilization of the incipient vinyl cation by β-hydrogen and β-deuterium leads to a β-secondary IE > 1.[51] The magnitudes of the effects compare well with literature values for the thermal formation of vinyl cations. In solvolytic generation of primary allenyl cations α-IEs ranging from 1.20 to 1.28 (Table 6, 1.27) have been measured.[7b,52] A β-deuterium IE of 1.25 (Table 6, 1.11) is reported for the thermal formation of a vinyl cation from CH$_3$(L)C= C(OTf)CH$_3$ (L = H or D) with the β-deuterium and the leaving group in a cis-orientation (as is the case for **1E-2D**).[53]

The IEs on the formation of **2** can be understood within the framework of all three mechanisms. For mechanism 2 (Chart 2) as well as mechanism 3 (Chart 3), the observed IEs are explained by initial heterolysis of the carbon−bromine bond using the same arguments as used for the IEs on the thermal formation of vinyl cations. In mechanism 1, the formation of the cation from the radical in a secondary, ET step, may be accompanied by a substantial normal IE on the formation of the cation-derived product.

The α- and β-deuterium IE on the appearance of the radical-derived product **3** are both large, but the first one is normal, while the second one is inverse. These IEs cannot be understood within the framework of mechanism 1 or 2, which involve vinyl radical formation via direct homolysis of the C−Br bond. Upon formation of the styryl radical from (*E*)-bromostyrene, there is hardly any change in hybridization of the reaction center.[54] Also hyperconjugative stabilization of the radical is not possible, due to the spatial orientation of the C$_\beta$−H bond and the orbital in which the unpaired electron resides. Therefore, both the α- and β-secondary IE on the formation of the vinyl radical **1·** are expected to be close to unity. Since the IEs on the formation of **3** are significantly different from 1, mechanisms involving direct formation of the vinyl radical (i.e., mechanisms 1 and 2) can be discarded. The question now is: Can mechanism 3, involving formation of the vinyl radical via ET from the intially produced vinyl cation, explain the observed IEs?

If we assume that all steps in mechanism 3 are irreversible, the IEs on the formation of **2** as well as **3** will originate from the ET step and the proton loss step. Although this is less correct these two steps will be considered separately, and only the effect of the ET step

(50) Direct heterolytic C−X cleavage has been earlier proposed for the photochemical formation of triphenylmethyl cations from triphenylmethyl chloride: (a) Manring, L. E.; Peters, K. S. *J. Phys. Chem.* **1984**, *88*, 3516. (b) Peters, K. *Annu. Rev. Phys. Chem.* **1987**, *38*, 253.

(51) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley & Sons: New York, 1980; Chapter 6.

(52) Schiavelli, M. D.; Germroth, T. C.; Stubbs, J. W. *J. Org. Chem.* **1976**, *41*, 681.
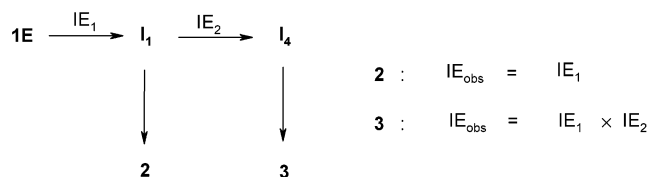
(53) Stang, P. J.; Hargrove, R. J.; Dueber, T. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 843.

(54) Galli, C.; Guarnieri, A.; Koch, H.; Mecarelli, P.; Rappoport, Z. *J. Org. Chem.* **1997**, *62*, 4072.

SCHEME 7. Schematic Representation of the Influence of IEs of the Separate Steps on the Observed IE in a Reaction Involving Two Consecutive Rate-Determining Steps, According to Mechanism 3

SCHEME 8

α-IE: $L_\alpha = D$, $L_\beta = H \Rightarrow \Delta ZPE = +21$ cal/mol

β-IE: $L_\beta = H$, $L_\alpha = D \Rightarrow \Delta ZPE = -192$ cal/mol

on the IEs will be discussed here because we find this treatment more instructive. The effect of the proton loss step on the IEs is discussed in the Supporting Information. There also an analytical solution of the problem is presented which describes the likely situation that the overall measured IEs originate from the IEs on the ET step as well as the IEs on proton loss. All reasonings lead to the same conclusions.

In general, IEs on the formation of products in a reaction involving subsequent reaction steps will be the product of the IEs of all steps. So, for a reaction involving two consecutive rate-determining steps, the observed IE (IE$_{obs}$) on the first product equals the IE of the first reaction step, and IE$_{obs}$ for the second product equals the product of the IEs of the first and the second step (Scheme 7).

If we accept mechanism 3 to be correct, we predict both the α- and β-IE on the formation of the cation (IE$_{obs}$ = IE$_1$) to be normal. Concerning the α-deuterium IE on the formation of the radical, for IE$_{obs}$ to be larger than that of the cation, IE$_2$ must be >1. Similarly for the β-IE on the formation of the radical, for IE$_{obs}$ to be smaller than IE$_{obs}$ on formation of the cation IE$_2$ must be <1. In other words, the IEs on the formation of the radical-derived product, are explained by mechanism 3 provided that the IE on the ET step which leads from I_1 to its corresponding radical (I_4) is normal for the α-D- and inverse for the β-D-species.

Deuterium is an inductive electron donating substituent as is demonstrated by its negative Hammett σ_I constant (−0.0011).[55] This means that I_1 is slightly better stabilized by an α-deuterium than by an α-hydrogen atom. Because this stabilization will be less important in the radical, the ET step is predicted to be more exothermic for the hydrogen compound than for the deuterium compound. Since rates of ET increase with increased exothermicity,[56] the rate of ET is predicted to be higher for the hydrogen compound than for the deuterium compound: a normal IE!

For the β-IE the distance between the position of deuteration and the positive carbon center is too large, for the inductive effect to play a role. The β-C−H bond is however weakened in I_1, due to the hyperconjugative stabilization of the cation by this bond. The potential energy curve for this carbon−hydrogen bond will therefore be shallow. Because hyperconjugative stabilization is absent in I_4, the potential energy curve will be steeper in this case. This causes a larger difference between the ZPEs for hydrogen and deuterium in the radical than in
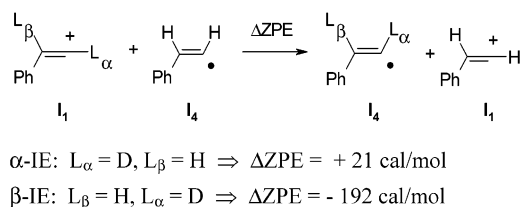
the cation. Therefore, the ET step will be energetically more favorable for the deuterium than for the hydrogen compound, and the rate will be higher for the first than for the latter: an inverse IE!

The differences in ZPEs on the ET step can also be calculated using quantum chemical methods. For this purpose, semiempirical MO programs using the PM3 parametrization set have proven to give adequate qualitative and semiquantitative results.[57,58] The changes in ZPEs for α- and β-deuterium substitution on the ET step were calculated as depicted in the isodesmic reaction in Scheme 8.

The changes in the calculated ZPEs are qualitatively in agreement with the predicted IEs on the ET step as discussed above. The change in ZPE in the isodesmic equation for the α-IE is positive, indicating that I_1-**1D** is stabilized relative to I_1. On the other hand, the change in ZPE in the isodesmic equation for the β-IE is negative, indicating that I_1-**2D** is *de*stabilized with respect to I_1.[59] In conclusion, the IEs on the formation of the radical-derived compound **3** can be interpreted in terms of mechanism 3!

The IEs on *E/Z*-isomerization (Table 6, column 2) provide information about the pathways for *E/Z*-isomerization of vinyl halides. Although the lowest triplet excited state of **1E** exclusively yields E/Z-isomerization products, it is not necessarily an intermediate in the formation of **1Z** from **1E** upon direct excitation. Next to direct E/Z isomerization from the lowest excited singlet state, internal return within the cation−anion (I_1−Br$^-$) pair or the radical−radical pair (I_4−Br$^\bullet$) can, in principle, yield **1Z** as well. Both the α- and the β-secondary IE for *E/Z* isomerization of **1E** are close to unity, and very different from the respective IEs for the formation of the cation- and radical-derived product. This indicates that **1Z** is neither a cation- nor a radical-derived product. Thus, internal return from either the ion pair or the radical pair is not an important pathway for *E/Z*-isomerization. This leaves direct isomerization from the triplet or the singlet excited state as options.

Secondary IEs on *E/Z*-isomerization have been studied both experimentally[60,61] and theoretically.[61] In most of

(55) Young, W. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1969**, *91*, 4581.

(56) Marcus, R. A. *Int. J. Chem. Kinet.* **1981**, *13*, 865.

(57) B3LYP or MP2 ab intio data cannot be calculated in this way, because at these levels of theory the styryl cation does not correspond to a local minimum. Also see the calculations section.

(58) (a) Zuilhof, H.; Lodder, G. *J. Phys. Chem.* **1992**, *96*, 6957. (b) Zuilhof, H.; Lodder, G. *J. Phys. Chem.* **1995**, *99*, 8033. (c) Hammerich, O.; Nielsen, M. F.; Zuilhof, H.; Mulder, P. P. J.; Lodder, G.; Reiter, R. C.; Kage, D. E.; Rice, C. V.; Stevenson, C. D. *J. Phys. Chem.* **1996**, *100*, 3454.

(59) This conclusion holds as long as the stability of I_4 is not significantly affected by deuteration. This is a plausible assumption as previously argued.

(60) (a) Caldwell, R. A.; Misawa, H. *J. Am. Chem. Soc.* **1987**, *109*, 6869. (b) Courtney, S. H.; Balk, M. W.; Philips, L. A.; Webb, S. P.; Yang, D.; Levy, D. H.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 6697. (c) Brouwer, A. M.; Cornelisse, J.; Jacobs, H. J. C. *J. Photochem. Photobiol. A: Chem.* **1988**, *42*, 313.

these studies large normal secondary IEs (1.4−2.0) have been measured for rotation around the C=C bond and significant activation barriers (up to 12.8 kcal/mol) have to be overcome. In one case a low activation barrier (0.33 kcal/mol) for rotation (for the photoisomerization of *cis*-stilbene in hexane), was observed, as well as an IE equal to unity.[62] It was concluded that the magnitude of the IE is related to the activation energy for isomerization. Our small value for the IE on *E*/*Z*-isomerization thus is in agreement with the small observed activation energy (3.0 kcal/mol) for this reaction.

Conclusions

Upon UV-photolysis of (*E*)-bromostyrene in various solvents, a cation- and a radical-derived product are formed. Photolysis of specifically deuterated (*E*)-bromostyrene results in scrambling of the deuterium label in the elimination product. Together with the solvent dependence of the amount of scrambling this demonstrates unequivocally that a cationic intermediate is involved in the formation of this product. The scrambling occurs via a vinylene benzenium ion.

Although the primary vinyl cation, formed upon C−Br heterolysis, does not exist in the gas phase, calculations show stabilization by the counterion and by the solvent. It is therefore a metastable species in solution, in agreement with our experiments.

The mechanism of the dissociative photochemistry of (*E*)-bromostyrene involves direct heterolytic carbon−bromine bond cleavage from the lowest excited $\pi\sigma^*$ singlet state. Radical-derived products are formed by electron transfer within the initially formed ion pair. This is shown by (1) the higher Φ_{dis} for polar than for apolar solvents, (2) the equal activation energies for the formation of the radical- and the cation-derived product, and (3) the α- and β-deuterium isotope effects on the formation of styrene. Previously proposed mechanisms starting either with homolytic cleavage followed by electron transfer or with parallel homolytic and heterolytic cleavage cannot explain these observations.

E/*Z*-isomerization occurs in a separate process and does not involve C−Br bond cleavage. This reaction may proceed via the singlet excited state, the triplet excited state, or both.

Experimental Section

Chemicals. (*E*)-Bromostyrene (**1E**) was purchased as a 13:1 *E*/*Z*-mixture. The *Z*-isomer was removed by repetitive crystallization from hexane (mixed isomers) at −60 °C, which yielded **1E** in a purity >99.3% (0.6% (*Z*)-bromostyrene; **1Z**). To obtain UV transparent and gas−liquid chromatography (GC) pure solvents, they were distilled before use.

(*E*)-1-Bromo-1-deutero-2-phenylethene (**1E-1D**) was synthesized in two steps from phenylacetylene (**2**). First, **2** (11 g; 0.11 mol) was converted into phenylacetylene-*d* (**2-D**) by exchanging twice with a suspension of CaO (1.5 g; 27 mmol) and D$_2$O (10 mL; 0.5 mol) at 40 °C for 20−24 h, followed by filtration, extraction with ether, drying over MgSO$_4$, and removal of solvent.[63] Yield: 99%, with >98% deuterium incorporation. Phenylacetylene-*d* (2.5 g; 42 mmol) in hexane (10 mL), to which benzoyl peroxide (0.18 g; 0.85 mmol) was added was converted into **1E-1D** by addition of hydrogen bromide at 60 °C.[64] The HBr gas, produced by addition of bromine to tetralin, was continuously bubbled through the solution under vigorous stirring. The reaction was stopped when GC analysis showed no **2-D** left, and the reaction mixture was worked up by extraction with water/diethyl ether, drying of the organic layer over MgSO$_4$ and vacuum distillation: yield 18%; purity 97.8% (2.0% **1Z-1D**); deuterium incorporation >96%.

(*E*)-1-Bromo-2-deutero-2-phenylethene (**1E-2D**) was synthesized from benzaldehyde-*d* in THF at −78 °C according to a literature procedure.[65] An 11:1 *Z*/*E*-mixture was obtained in 70% yield. Irradiation at λ = 313 nm in acetone afforded a 3:2 *Z*/*E*-mixture, from which **1E-2D** was isolated by preparative GC; deuterium incorporation 96%.

1-Bromo-1-phenylethene (**5**) was prepared by bromination of styrene in CCl$_4$, followed by elimination of HBr using NaOH in ethanol.[66] Column chromatography, on silica gel using petroleum ether as eluent, yielded **5** in >95% purity (remainders: 1-bromo-2-phenylethene and phenylacetylene).

The identity of the deuterated starting materials and the photoproducts was established by comparison (^{1}H NMR, GC, GC/MS) with reference compounds. All reference compounds were commercially available, except for 1-methoxy-1-phenylethene (**6**), which was prepared by a literature procedure.[25,67]

Photochemical Experiments. The photochemical reactions were carried out under argon, in three different setups. For the quantum yield determinations and measurements of the isotope effects a 65 mL cylindrical Pyrex reaction vessel was used in which a quartz tube was immersed. This tube contained a Hanau TNN-15/32 low-pressure mercury arc (254 nm light), which was placed in a filter solution, consisting of 0.190 M NiSO$_4$ and 0.4 mM K$_2$CrO$_4$ in water. For irradiations at λ = 313 nm (sensitization experiments) the lamp used was a Hanau TQ-81 high-pressure mercury arc with a quartz cover glass, surrounded by a glass spiral tube through which cooling water was circulated. As filter solution in the quartz tube a solution consisting of 0.025 M potassium biphthalate, 1.0 M NiSO$_4$, and 0.25 M CoSO$_4$ in water was used.

For actinometry at λ = 254 nm the photohydrolysis of 3-nitroanisole (3.5 mM) in a 0.1 M NaOH water/methanol (9:1) solution, which occurs with a quantum yield of 0.22,[68] was performed under the same conditions, except the atmosphere (air instead of argon). The disappearance of starting material **1E** (conversions up to 20%) and appearance of products **1Z**, **2**, and **3** were studied as a function of time, using an internal standard (*n*-decane or 1-dodecanol) and the kinetics described earlier.[6] This was done by taking aliquots (0.50−1.00 mL) from the reaction mixture at appropriate times, followed by analysis by means of GC.

For the measurements of the effects of the temperature a somewhat different device was used. The volume of the reaction vessel was larger (180 mL), and an evacuated double-walled quartz tube was used to isolate the cooling water for the lamp from the cold reaction mixture (down to −40 °C). Low solution temperatures were achieved by placing the whole setup in a Dewar flask filled with diethyl ether. Solid carbon dioxide was added to the ether until the desired temperature was reached. Reaction times were up to 6 min, over which

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period no noticeable variation in the solution temperature occurred, with conversions up to 10%.

The effect of wavelength variation was studied using the light from a light source consisting of a 1000 W Hanovia Hg/Xe high-pressure short-arc lamp and an Oriel monochromator (5 nm bandwidth), impinging on a 3 mL quartz cuvette. Conversions were up to 10%, as determined using *n*-decane as internal standard. All experiments were performed in triplicate, unless noted otherwise. GC analyses were at least in duplicate.

Equipment. The GC analyses were carried out using a gas chromatograph fitted with a capillary CP SIL5-CB column (50 m, ∅ = 0.25 mm) and a flame ionization detector. Hydrogen was used as the carrier gas at an inlet-pressure of 72 kPaLow resolution mass spectra were obtained with a GC/MS setup consisting of a gas chromatograph, fitted with a CP-SIL 19 CB column (25m, ∅ = 0.32 mm) using helium as carrier gas, coupled with a mass spectrometer using electron impact and chemical ionization with methanol.

Calculations. All ab initio calculations were performed using the GAUSSIAN 94 (Rev. D4)[69] or GAUSSIAN 98 (Rev. A5)[70] set of programs on an IBM 6000/RISC computer. On all calculated structures, except for those from the coordinate driving calculations, frequency calculations were performed to check whether they are minimum energy structures, transition states, or higher-order saddle points. The calculations were performed on the B3LYP/6-31G(d,p) level of theory. This method was chosen because the Hartree−Fock (HF) method is known to overestimate ring strain energies (due to the absence of electron correlation in this method). However, explicit inclusion of electron correlation by second-order Møller−Plesset perturbation theory (MP2) underestimates the ring strain energy for the parent vinyl cation.[71] Higher order electron correlation is computationally too costly. Moreover, MP types of post-HF calculations frequently give dubious results for open shell systems, due to significant spin contamination. Therefore density functional theory (DFT), which has implicit electron correlation and usually gives little spin contamination with unrestricted calculations of open shell systems is the method of choice. The B3LYP method was selected because of its proven accuracy in the prediction of vinyl cation energetics.[72] The 6-31G(d,p) basis set was chosen, because it contains polarization functions on both carbon and hydrogen atoms to accurately describe bridging involving both these atoms.

Charge densities and bond orders were calculated using the NBO 3.1 program,[73] as implemented in GAUSSIAN 98, and for the reported charges the hydrogens are summed into the heavy atoms.

All calculations using a dielectric to mimic the solvent were performed with the SCRF-IPCM method,[74] using the solvent parameters for water. Single-point calculations were performed on the gas-phase B3LYP/6-31G(d,p)-optimized geometries.

As B3LYP calculations have been shown to give erroneous results for calculations involving counterions, the MP2(fc) method was used in this case.[75]

The calculations on the equilibrium IEs were performed on an IBM RS/6000 platform, using the PM3 parametrization set as implemented in MOPAC 93.[76] After pre-optimization, the final structures were obtained by optimization with the eigenvector following method. With the thus obtained geometries, frequency calculations were performed, and the effect of isotopic substitution on the zero-point energies was determined.

Supporting Information Available: Discussions of the effect of the proton loss step on the IEs and of the effect of the ET as well as the proton loss step on the IEs. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0264877

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