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Substituent Effects on the Photogeneration and Selectivity of Triaryl Vinyl Cations

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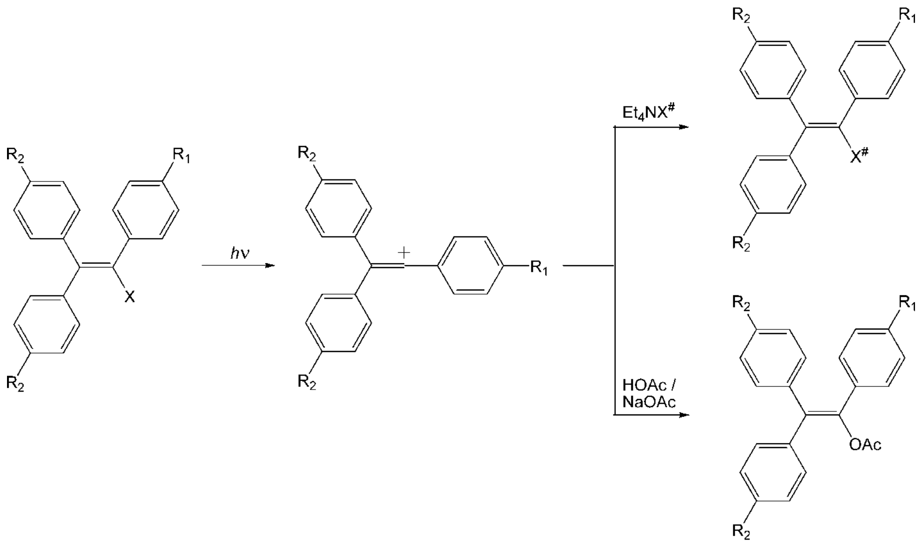

Photoreactivity Selectivity

The photochemical reactions of a series of triaryl vinyl halides **1X** in acetic acid and in acetonitrile have been studied using product analysis as a function of the time of irradiation. The quantum efficiencies of formation of the products derived from the photogenerated vinyl cations $\mathbf{1}^+$ depend on the α-aryl substituent, the *β*-aryl substituent, the leaving group X (= bromide or chloride), and the temperature at which the irradiations are carried out. Hammett correlation or noncorrelation of the α-aryl substituent effects with (excited-state) substituent constants indicates that the ions $\mathbf{1}^+$ are formed directly from the excited states of **1X** by heterolytic cleavage of the carbon−halogen bond. Homolytic cleavage, yielding radicals $\mathbf{1}^\bullet$, is a parallel process: the partitioning into ion and radical occurs in the excited state. This conclusion is corroborated by the leaving group effect and the temperature effect. By performing the photochemical reactions of **1X** in the presence of HOAc and/or NaOAc as well as the labeled common halide ion $^{82}Br^-$ or $^{36}Cl^-$, the relative reactivities of the cations $\mathbf{1}^+$ toward these nucleophiles were determined. The selectivities follow the Reactivity−Selectivity Principle. The temperature effect data show that the reactions of the cations with the anionic nucleophiles are (de)solvation controlled and their reactions with the neutral nucleophile activation controlled.

Introduction

Photolysis of vinyl halides in appropriate media has become a versatile method to generate vinyl cations under mild reaction conditions.[1] The method has been used to prepare a score of vinyl cations with a variety of α-substituents ranging from electron-donating to electron-withdrawing groups and with a small number of *β*-substituents. Triaryl vinyl cations have been at the forefront of this research. These ions are also thermally accessible, albeit only at high reaction temperatures.[2] The nature of photogenerated triaryl vinyl cations has been shown to be the same as that of the ions involved in thermal nucleophilic

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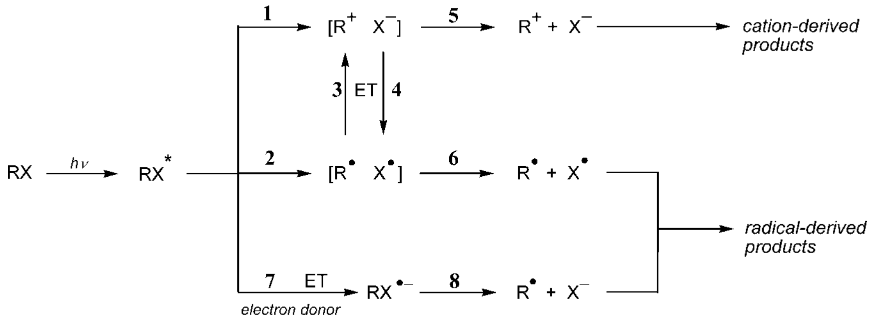
SCHEME 1



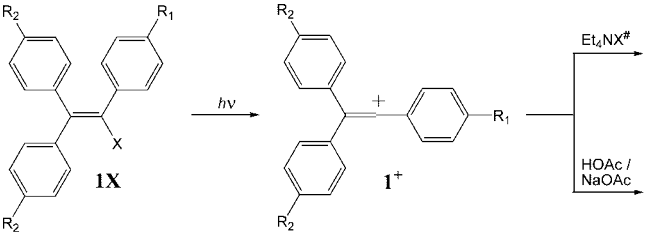
Mechanism	Pathways of ion formation	Pathways of radical formation
A	2 - 3 - 5	2 - 6
B	1 - 5	2 - 6
C	1 - 5	1 - 4 - 6

substitution reactions, i.e., free (not ion-paired), "cold" (thermally relaxed, i.e., solvated) vinyl cations: the extent of β-aryl rearrangement[3] as well as the selectivity toward different nucleophiles are the same in photochemically[4] and thermally[5] induced reactions. Also, triaryl vinyl cations have been observed in flash photolysis studies by both optical absorption and electrical conductivity measurements.[6,7]

Upon irradiation of vinyl halides, in general, both ion- and radical-derived products are produced. In the course of time, several mechanisms have been proposed for their formation (Scheme 1).

Initially, these routes were (A) homolysis of the carbon−halogen bond yielding a radical pair (pathway 2), followed either by electron transfer yielding an ion pair (pathway 3) or by dissociation into free radicals (pathway 6),[8] and (B) heterolysis of the carbon−halogen bond forming an ion pair directly (pathway 1), in parallel with homolysis (pathway 2).[4a] Recently, (C) initial heterolysis of the carbon−halogen bond forming an ion pair (pathway 1), followed either by dissociation into ions (pathway 5) or by electron transfer yielding a radical pair (pathway 4), has been proposed.[9] In the presence of a suitable electron donor, vinyl radicals can also be formed by photoinduced electron transfer (pathway 7) followed by halide ion loss from the radical anion (pathway 8).[10]

SCHEME 2



a: $R_1 = R_2 = H$; X = Br, Cl
b: $R_1 = CH_3$; $R_2 = H$; X = Br
c: $R_1 = OCH_3$; $R_2 = H$; X = Br
d: $R_1 = R_2 = OCH_3$; X = Br, Cl
e: $R_1 = OCH_3$; $R_2 = Cl$; X = Br

Thus, the partitioning into ion and radical occurs in the radical pair in mechanism A, in the excited state in mechanism B, and in the ion pair in mechanism C.

In this paper, we report substituent effects on the photochemical generation and selectivity of the triaryl vinyl cations **1**$^+$ produced from the triaryl vinyl halides **1X** depicted in Scheme 2. The compounds **1aX**−**1eX** were selected because (a) their $E \rightleftarrows Z$ isomerization is a degenerate process and (b) in their cations 1,2-aryl shifts across the double bond are either degenerate or do not occur.[2,3,4a] This ensures that the reaction mixtures are not unnecessarily complex. The series **1aBr**−**1bBr**−**1cBr** gives information about α-aryl substituent effects, the series **1cBr**−**1dBr**−**1eBr** about β-aryl substituent effects, and the series **1aBr**−**1aCl** and **1dBr**−**1dCl** about leaving group effects. All compounds were irradiated in two solvents, acetic acid and acetonitrile/1 M

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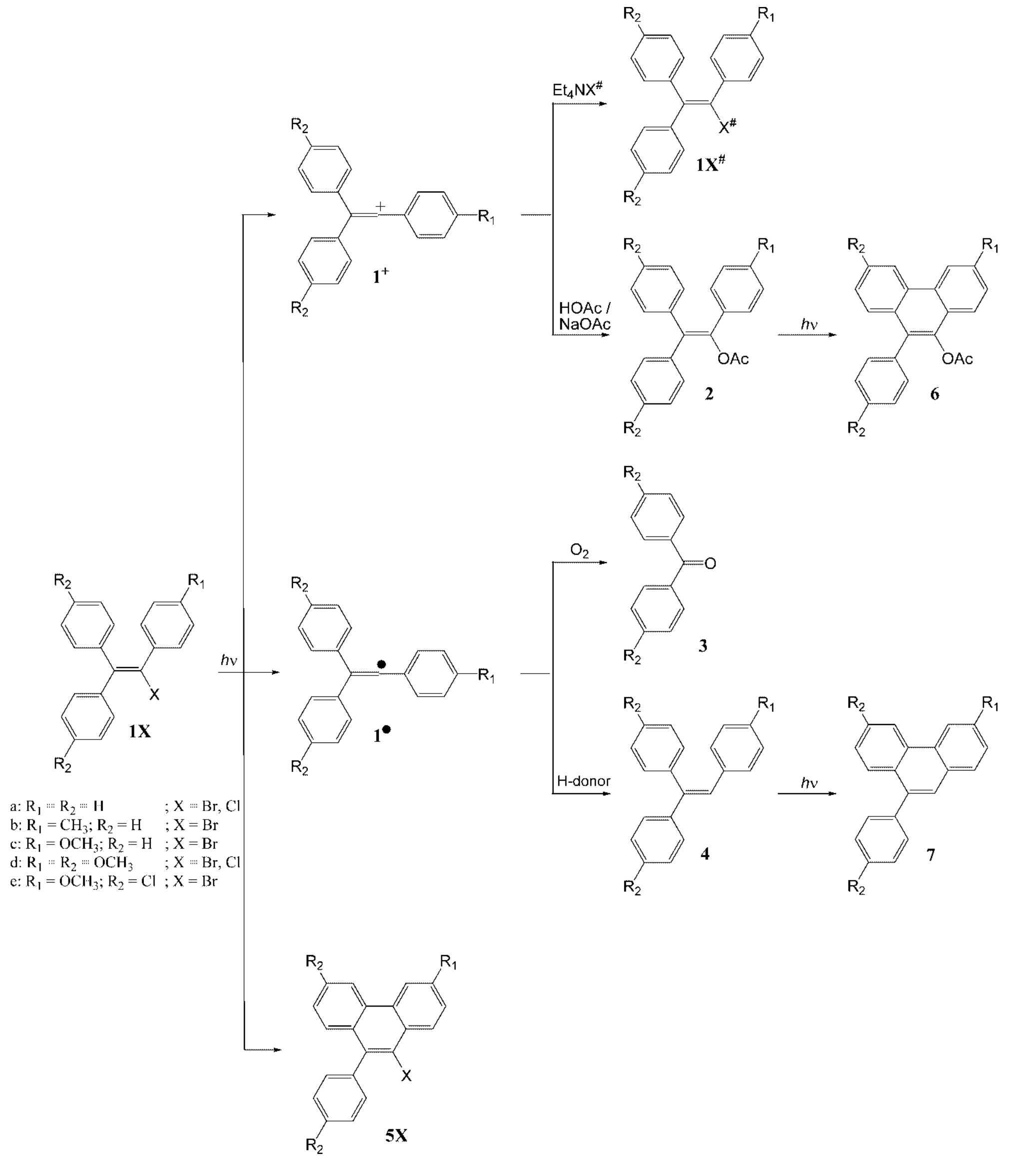
SCHEME 3



acetic acid. Also, the effect of the temperature at which the irradiations are carried out (23 vs 60 °C) was investigated for compounds **1aBr** and **1dBr**. Together, these effects allow discrimination between mechanisms A, B, and C.

Almost all irradiations were performed in the presence of HOAc and/or NaOAc and the labeled (#) common halide ion $Br^-[^{82}Br]$ or $Cl^-[^{36}Cl]$ as nucleophiles. This procedure probes the selectivity of the photochemically formed triaryl vinyl cations $\mathbf{1}^+$ toward selected pairs of nucleophiles, including the (labeled) common halide ion. The method was initially introduced[5] to deal with the common ion rate depression which often hampers thermal kinetic studies of triaryl vinyl cation formation.[2a,11] It has become a powerful supplement to the more common mechanistic tools to investigate the mechanistic pathway from substrate to nucleophilic photosubstitution product. It also provides insight into the selectivity of carbocations of the type $\mathbf{1}^+$ toward different kinds of nucleophiles.

Results and Discussion

Photoproducts. Irradiation ($\lambda_{exc} = 313$ nm) of the 1-halo-1,2,2-triarylethenes **1X** in acetic acid/sodium acetate/labeled tetraethylammonium halide or in acetonitrile/acetic acid/labeled tetraethylammonium halide gives the mixture of products depicted in Scheme 3: the isotopically labeled 1-halo-1,2,2-triarylethenes **1X#**, the 1-acetoxy-1,2,2-triarylethenes **2**, the benzophenones **3**, the triarylethenes **4**, the 9-halo-10-arylphenanthrenes **5X**, the 9-acetoxy-10-arylphenanthrenes **6**, and the 9-arylphenanthrenes **7**.

Examination of the product concentrations as a function of time of irradiation revealed that **1X#**, **2**, **3**, **4**, and **5X** are primary photoproducts, while **6** and **7** are secondary ones. Products **1X#** and **2** are formed through the intermediacy of the vinyl cations $\mathbf{1}^+$ reacting with (labeled) X^- and HOAc/OAc^-, respectively. Products **3** and **4** are formed through the intermediacy of the vinyl radicals $\mathbf{1}^\bullet$ reacting with O_2 (with the vinyl peroxyl radical $\mathbf{1O_2}^\bullet$ as a further intermediate[12]) and with a H-atom donor, respectively. **5X** is the (*cis*-stilbene-type) photocyclization[13] product of **1X**. The secondary products **6** and **7** result from photocyclization of the primary products **2** and **4**. Formation

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TABLE 1. Quantum Yields of the Photoreactions of the Vinyl Bromides 1aBr−1eBr in Acetic Acid and in Acetonitrile (λ_{exc} = 313 nm; T = 23 °C) and Selectivities of the Vinyl Cations 1a$^+$−1e$^+$ toward Br$^-$ and OAc$^-$ or HOAc

entry	substrate	solvent	$10^2\Phi_d$	$10^2\Phi_c$	$10^2\Phi_{ox}$	$10^2\Phi_{OAc}$	$10^2\Phi_{ex}$	$10^2\Phi_{ion}$	S_{NaOAc}	S_{HOAc}
1	**1aBr**	HOAc[a]	11.2	3.0	0.45	6.8	7.5	14.3	1.4	280
2	**1bBr**		8.6	1.8	0.41	5.6	11.9	17.5	2.6	520
3	**1cBr**[b]		5.6	2.0	0.1[c]	1.5	28	29.5	23	4600
4	**1dBr**[b]		2.9	0.6	0.15[c]	0.97	20	21	25.5	5100
5	**1eBr**		4.8	2.8	0.56	2.6	27	29.6	13	2600
6	**1aBr**	CH_3CN[d]	17.3	2.3	1.2	2.0	34	36		240
7	**1bBr**		17.2	1.3	1.1	1.5	66	68		620
8	**1cBr**		6.0	1.9	0.71	0.30	81	81		3800
9	**1dBr**		2.9	0.39	0.21	0.145	47.6	48		4700
10	**1eBr**		5.4	3.0	0.83	0.24	50	50		2900

[a] Added nucleophiles present: [$Et_4NBr^{\#}$] = 71 × 10^{-3} M; [NaOAc] = 87 × 10^{-3} M. [b] Reported in ref 4a. [c] Φ_{red}; Φ_{ox} not reported. [d] added nucleophiles present: [$Et_4NBr^{\#}$] = 71 × 10^{-3} M; [HOAc] = 1.0 M.

of **6** from **5X** by nucleophilic aromatic photosubstitution[14] is a relatively insignificant reaction route,[4a] and so is the formation of **7** from **5X** by reductive dehalogenation.[1c] All irradiations were performed in the presence of atmospheric oxygen, which is necessary to quantitatively convert the dihydrophenanthrenes formed initially in the photocyclization process of **1X** and **2** into the easily monitorable phenanthrenes **5X** and **6**. Under these conditions, almost the only products derived from the vinyl radicals **1**$^\bullet$ are the benzophenones **3**; the reduction products **4** (and **7**) are at best observed in trace amounts.

In the irradiations in acetonitrile/1.0 M HOAc, no Ritter products resulting from the reaction of **1**$^+$ with acetonitrile are detected. Also, no products resulting from ipso-substitution, in which the *p*-methoxy group is replaced by one of the nucleophiles,[15] are found in the irradiations of the α-(*p*-methoxyphenyl) compounds **1cBr**, **1dBr**, **1eBr**, and **1dCl**.

Photoreactivity. (a) Kinetics. The rates of disappearance of starting material and of formation of products as a function of the intensity of the absorbed light were determined under the same reaction conditions as used for the product studies. The kinetics for photochemically induced simultaneous isotope exchange and product-forming reactions are represented by eqs 1–3.[4b]

$$\ln\left(\frac{[RX]_t}{[RX]_0}\right) = -k_d t = -\Phi_d t \frac{I_0}{[RX]_0} \tag{1}$$

$$[\text{product}]_t = \Phi_p \frac{I_0}{k_d}(1 - e^{-k_d t}) \tag{2}$$

$$\ln\left(\frac{\{n_\infty/n_\infty - n_t\}}{e^{tk_d} - \{n_\infty/n_\infty - n_t\}\{e^{tk_d} - 1\}}\right) = \Phi_{ex} I_0 t \frac{[RX]_0 + [Et_4NX]_0}{[RX]_0[Et_4NX]_0} \tag{3}$$

In these equations, $[RX]_t$ and $[RX]_0$ represent the concentration of vinyl halide **1X** in the photolysis mixture at times t and 0; k_d stands for the rate constant of disappearance of **1X** (an algebraic magnitude which does not include the isotopic exchange and other (formally) degenerate processes); Φ_d is the quantum yield of disappearance of starting material, and I_0 is the intensity of the light absorbed by **1X** at time $t = 0$. Φ_p is the quantum yield of product formation. Φ_{ex} is the quantum yield for the isotope exchange, and n_t and n_∞ are the specific radioactivities of **1X**$^{\#}$ at time t and at equilibrium.

The quantum yields of disappearance of starting material and of formation of products under various conditions are listed in Tables 1, 4, and 5. In these tables, Φ_d is the quantum yield of disappearance of starting material (as above); Φ_c the quantum yield of formation of the photocyclization product **5X**; Φ_{ox} the quantum yield of formation of the (substituted) benzophenone **3**; Φ_{red} the quantum yield of formation of the reduction products **4** and **7** combined; Φ_{OAc} the quantum yield of formation of compounds **2**, obtained by monitoring the formation of both the vinyl acetate **2** itself and its secondary photoproduct, the phenanthrene acetate **6**; and Φ_{ex} the quantum yield of the isotope-exchange reaction, i.e., the formation of the labeled product **1X**$^{\#}$ (as above). Φ_{ion} is the quantum yield of formation of the photoproducts derived from **1**$^+$, i.e., **1X**$^{\#}$, **2** (and **6**), and thus $\Phi_{ion} = \Phi_{ex} + \Phi_{OAc}$.

Also listed are two selectivity constants: S_{NaOAc} is the selectivity of the vinyl cations **1**$^+$ in their reactions with the common halide ion and acetate ion (eq 4a), and S_{HOAc} is the selectivity of the cations **1**$^+$ in their reactions with the common halide ion and acetic acid (eq 4b).

$$S_{NaOAc} = \frac{k_{ex}}{k_{OAc}} = \frac{\Phi_{ex}}{\Phi_{OAc}} \frac{[NaOAc]}{[Et_4NX]} \tag{4a}$$

$$S_{HOAc} = \frac{k_{ex}}{k_{OAc}} = \frac{\Phi_{ex}}{\Phi_{OAc}} \frac{[HOAc]}{[Et_4NX]} \tag{4b}$$

Table 1 shows the quantum yields of the photoreactions of the vinyl bromides **1aBr**−**1eBr**. The data show that the formation of ion-derived products as expressed by Φ_{ion} is more efficient in the more polar[16] medium acetonitrile than in acetic acid. This solvent effect does not discriminate between mechanisms A and B in Scheme 1. Polar solvents favor electron transfer within the radical pair (mechanism A) but also direct heterolysis of the electronically excited state (mechanisms B and C). They disfavor electron transfer within the ion pair initially formed in mechanism C. Therefore, the larger values of Φ_{ox} in acetonitrile than in acetic acid accompanying the larger values of Φ_{ion} do not agree with the latter mechanism.

(b) α-Aryl Substituent Effects. Within the series **1aBr**, **1bBr**, and **1cBr** (R_1 = H, CH_3, OCH_3), a clear increase in Φ_{ion},

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TABLE 2. Correlations and Noncorrelations of Quantum Yields of Ion Formation from 1aBr, 1bBr, and 1cBr with Ground- And Excited-State Substituent Constants

	solvent		σ_{ex}[a]	σ^*[b]	$\sigma^{h\nu}$[c]	$\sigma^{\bullet h\nu}$[d]	σ_p[e]	σ^+[f]	$\sigma_{jj}^{\bullet}$[g]
subst const		*p*-H	0	0	0	0	0	0	0
		p-CH_3	−0.13	−0.08	−0.53	0.74	−0.17	−0.31	0.15
		p-OCH_3	−0.39	−0.78	−1.17	0.33	−0.27	−0.78	0.23
Φ_{ion}	HOAc	ρ	−0.80	−0.36	−0.27	0.10	−1.08	−0.40	1.25
		standard dev	0.04	0.07	0.05	0.42	0.44	0.05	0.55
		corr coeff R^2	0.998	0.963	0.967	0.049	0.858	0.986	0.840
Φ_{ion}	CH_3CN	ρ	−0.81	−0.31	−0.29	0.36	−1.33	−0.42	1.57
		standard dev	0.47	0.30	0.12	0.35	0.25	0.21	0.25
		corr coeff R^2	0.750	0.522	0.857	0.509	0.966	0.810	0.974
$k_{ion} = \Phi_{ion}/\tau$	HOAc	ρ_τ	−3.10	−1.42	−1.03	0.32	−4.13	−1.55	4.78
		standard dev	0.25	0.23	0.23	1.63	1.84	0.23	2.27
		corr coeff R^2	0.994	0.974	0.954	0.036	0.835	0.977	0.816
$k_{ion} = \Phi_{ion}/\tau$	CH_3CN	ρ_τ	−3.10	−1.37	−1.05	0.58	−4.38	−1.57	5.09
		standard dev	0.26	0.46	0.06	1.57	1.15	0.02	1.47
		corr coeff R^2	0.993	0.899	0.997	0.120	0.936	0.999	0.922

[a] Taken from ref 20b. [b] Taken from ref 20d. [c] Taken from ref 21. [d] Taken from ref 23. [e] Taken from ref 26. [f] Taken from ref 22. [g] taken from ref 24.

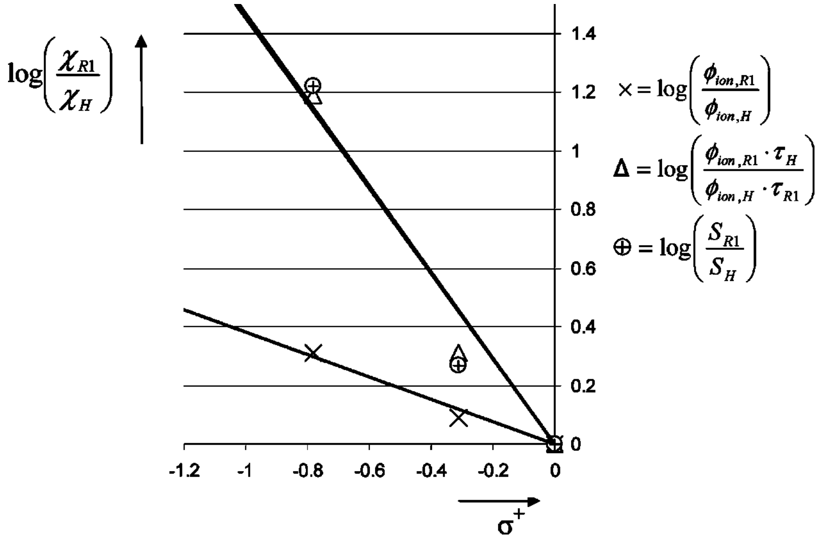

FIGURE 1. Hammett plot of the efficiency (×) and rate (Δ) of photolytic formation and selectivity (⊕) of the vinyl cations **1a**$^+$, **1b**$^+$, and **1c**$^+$ in acetic acid.

the quantum yield of formation of ion-derived products, with increasing electron-donating ability of the α-aryl substituent is observed in both media (Table 1, entries 1−3 and 6−8). The formation of radical-derived photoproducts as expressed by Φ_{ox} is in all cases a minor process with, if any, a small oppositely directed α-aryl substituent effect. There is no complementarity between the decrease in Φ_{ox} and the increase in Φ_{ion}.

The α-aryl substituent effects on Φ_{ion} (and on Φ_{ox}) invite a Hammett treatment.[17] This is, however, not as straightforward for photochemical reactions as it is for thermal ones because the usual substituent constants represent electronic effects in the ground rather than in the excited state.[18] Moreover, the Hammett equation pertains to rate (or equilibrium) constants and not to quantum yields. The relationship between the rate constant k_r of a photochemical reaction and its quantum yield Φ_r is given by eq 5, with τ the lifetime of the reactive excited state. Therefore, ideally lifetimes should be taken into account. As for all other vinyl halides investigated,[1d] the reactive excited state in the present case is a singlet species.[19]

$$k_r = \Phi_r/\tau \qquad (5)$$

Two sets of photochemical substituent constants based on pK_a* values (σ_{ex} and σ^*) have been suggested to correlate reactions occurring from the lowest excited singlet state.[20] The inherent problems of this approach have been reviewed by McEwen and Yates,[21] who proposed a $\sigma^{h\nu}$ scale based on the effects of aryl substituents on the rates of photohydration of styrenes and phenylacetylenes. This concept was tested against literature data and gives good correlations for photoreactions for which actual rates are known, but not if only quantum yields are available. This $\sigma^{h\nu}$ scale is an excited-state equivalent of the Brown−Okamoto ground-state σ^+ scale,[22] which reflects

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(19) The photoreactions of **1aBr** in acetic acid are neither sensitized by xanthone nor quenched by 1,3-cyclohexadiene. In the presence of the latter (0.5 M), instead significant amounts of the otherwise rarely found reduction products **4a** and **7a** ($\Phi_{red} = 9.7 \times 10^{-2}$) are produced. Probably 1,3-cyclohexadiene first acts as electron donor (Scheme 1, pathways 7 and 8) and next as hydrogen-atom donor.

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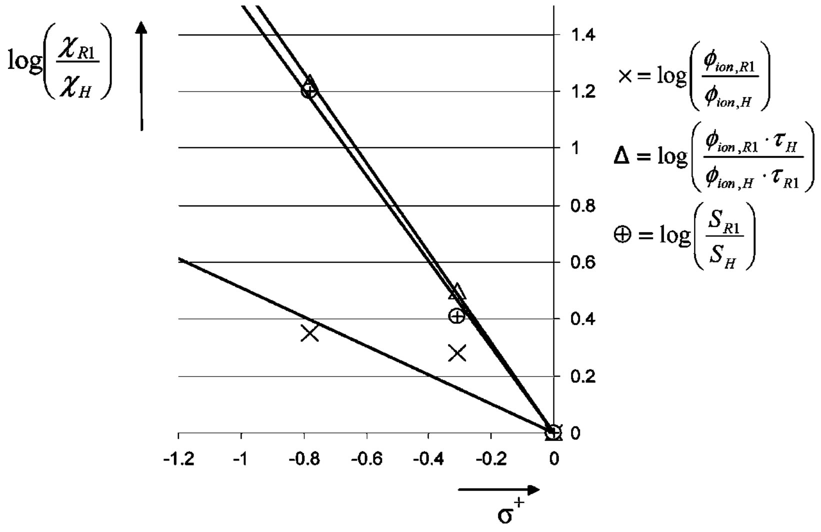

FIGURE 2. Hammett plot of the efficiency ($\times$) and rate (Δ) of photolytic formation and selectivity ($\oplus$) of the vinyl cations **1a**$^+$, **1b**$^+$, and **1c**$^+$ in acetonitrile.

direct resonance interaction with a cationic reaction center. Fleming and Jensen subsequently proposed a $\sigma^{\bullet hv}$ scale for excited-state radical cleavage reactions based on the photochemical fragmentation of benzyl phenyl thioethers.[23] This $\sigma^{\bullet hv}$ scale is an excited-state equivalent of the ground-state $\sigma^{\bullet}$ scales.[24]

Several authors have tested the kinetic data they obtained for various photoreactions against excited-state as well as against ground-state substituent constants and have drawn their mechanistic conclusions.[25]

In Table 2, we report the correlations of the kinetic data in Table 1 for the nucleophilic photosubstitution reactions of the compounds **1aBr**, **1bBr**, and **1cBr** with the excited-state substituent constants σ_{ex}, σ^*, σ^{hv}, and $\sigma^{\bullet hv}$ as well as with the ground-state substituent constants σ_p, σ^+, and $\sigma^{\bullet}$.[27] Considering that our data refer to three compounds only, the values of Φ_{ion} in acetic acid correlate well with σ^+, σ_{ex}, σ^*, and σ^{hv} but not with σ_p, $\sigma^{\bullet}$, or with $\sigma^{\bullet hv}$. In acetonitrile, the correlation coefficients are smaller: the lines level off because with $\Phi_{ion} = 0.81$ for **1cBr** the limiting value of 1.0 is approached.

Regrettably, the correlations of k_{ion} ($= \Phi_{ion}/\tau$ according to eq 5) with the various substituent constants cannot be studied directly. Triaryl vinyl halides do not fluoresce, and consequently, their singlet excited-state lifetimes elude measurement. Correction of the quantum yields of ion formation from **1aBr**, **1bBr**, and **1cBr** with the lifetimes of the corresponding, structurally related, styrenes (styrene, $\tau = 7.5$ ns, *p*-methylstyrene, $\tau = 4.5$ ns, and *p*-methoxystyrene, $\tau = 1.2$ ns)[21] allows us to study the correlations of k_{ion} with the various substituent constants indirectly.[28] This approach gives values of $\log\{(\Phi_{ion,R1}/\Phi_{ion,H})(\tau_H/\tau_{R1})\}$, serving as approximation for $\log\{k_{ion,R1}/k_{ion,H}\}$.

Again, the best correlations are found with σ^+, σ_{ex}, and σ^{hv}, now in both media employed (see Table 2). There is no good correlation with σ_p or $\sigma^{\bullet}$ and not even a semblance of a correlation with $\sigma^{\bullet hv}$. In Figures 1 and 2, the effect of the lifetime correction on the quantum yields is shown for the correlations with σ^+.

It was also tested whether any Hammett correlation is present with Φ_{ox}, the quantum yield of vinyl radical formation. Neither Φ_{ox} nor Φ_{ox}/τ correlates with σ^+, σ_{ex}, σ^{hv}, σ_p, or $\sigma^{\bullet}$. The only correlations found were $\rho_{ox}(\sigma^*) = +0.29 \pm 0.02$ ($R^2 = 0.996$) and $\rho_{ox,\tau}(\sigma^{\bullet hv}) = +0.24 \pm 0.02$ ($R^2 = 0.995$) in acetonitrile. Thus, no connection exists between the (lack of) Hammett correlations for the ion- and radical-formation process.

Almost the same α-aryl substituent effects as for compounds **1a**−**cBr** have been observed for the nucleophilic photosubstitution reactions of a series of 1-aryl-2-(2,2′-biphenyldiyl)vinyl bromides (**8Br**) in deoxygenated methanol[12,29] (Scheme 4, Table 3).

In contrast to the vinyl cations **1**$^+$, the vinyl cations **8**$^+$ are not subject to 1,2-aryl shifts across the double bond. These shifts are prevented by the rigid fluorenyl moiety at the β-carbon atom.[10] In the series of compounds **8Br**, therefore, also the effects of electron-withdrawing α-aryl substituents such as *p*-bromo- and *p*-cyanophenyl could be and were investigated. A Hammett treatment of the values of Φ_{ion} of the five compounds **8Br** using the same seven sets of substituent constants as used with the compounds **1a**−**cBr** shows only correlation with σ^+ and σ^*. Singlet excited-state lifetimes are not available for *p*-bromo- and *p*-cyanostyrene. Therefore $\Phi_{ion}/\tau = k_{ion}$ can only be calculated for **8aBr**, **8bBr**, and **8cBr** but not for **8dBr** and **8eBr**. The values of Φ_{ion}/τ for **8a**−**cBr** correlate with σ_{ex} and σ^{hv} as well as with σ^+ and σ^*. No correlation exists with σ_p and certainly not with $\sigma^{\bullet}$ or $\sigma^{\bullet hv}$.

Overall, only with respect to σ^+ is a correlation found for both Φ_{ion} and Φ_{ion}/τ for the compounds **1a**−**cBr** as well as for the compounds **8Br**. The $\rho(\sigma^+)$ values for the vinyl bromides **8Br** in methanol are $\rho(\sigma^+) = -0.58 \pm 0.09$ ($R^2 = 0.927$) and $\rho_{\tau}(\sigma^+) = -1.69 \pm 0.31$ ($R^2 = 0.967$), respectively. These values almost equal those of $\rho(\sigma^+) = -0.40$(HOAc), -0.42(CH_3CN),

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(26) Hansch, C.; Leo, A.; Taft, W. *Chem. Rev.* **1991**, *91*, 165–195.

(27) Several $\sigma^{\bullet}$ scales exist.[24] The data in Table 2 and the text pertain to Jiang's recently established $\sigma_{jj}^{\bullet}$ scale.[24]

(28) The quite similar substituent effects on the singlet lifetimes of excited phenylacetylenes[21] and (2-arylcyclopropyl) methylacetates support the use of these model compounds: Hixson, S. S.; Franke, L. A.; Gere, J. A.; Xing, Y. D. *J. Am. Chem. Soc.* **1988**, *110*, 3601–3610.

(29) Verbeek, J. M.; Lodder, G. Unpublished results.

SCHEME 4

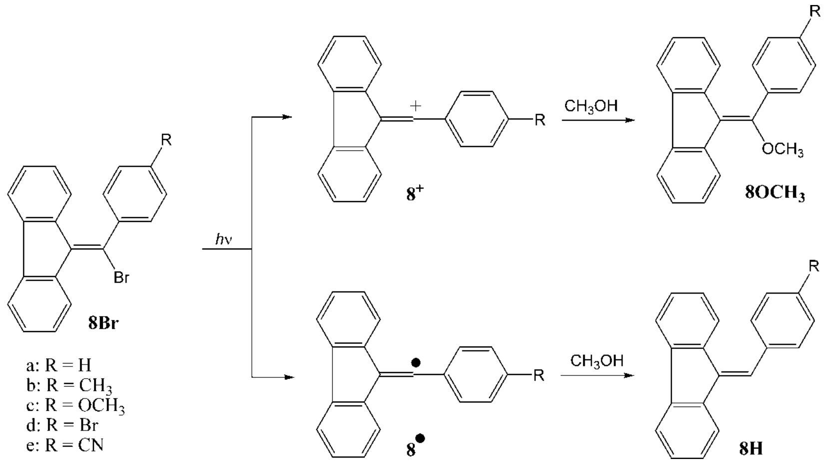

TABLE 3. Quantum Yields of the Photoreactions of the Vinyl Bromides 8Br in Deoxygenated Methanol (λ_{exc} = 254 nm; T = 0 °C)

R	p-H [a]	p-CH$_3$[a]	p-OCH$_3$[a]	p-Br[b]	p-CN[b]
$10^3\Phi_{ion}$[c]	35	42	109	20	16
$10^3\Phi_{red}$[d]	15	7	10	17	12

[a] Data from ref 12. [b] Data from ref 29. [c] Formation of **8OCH$_3$**. [d] Formation of **8H**.

and $\rho_\tau(\sigma^+) = -1.55$(HOAc), -1.57(CH$_3$CN) for the vinyl bromides **1a−cBr** listed in Table 2.

The correlation of the quantum yields (lifetime-uncorrected and -corrected) of ion formation from both **1a−cBr** and from **8Br** with σ^+, and in some cases with σ_{ex}, σ^*, and $\sigma^{h\nu}$, but not with σ_p, $\sigma^\bullet$, or $\sigma^{\bullet h\nu}$, indicates that both the vinyl cations $\mathbf{1}^+$ and $\mathbf{8}^+$ are formed directly from the excited states of **1Br** and **8Br** by heterolytic cleavage of the C−Br bond and not by homolytic cleavage giving initially the vinyl radical(pair)s $\mathbf{1}^\bullet$ or $\mathbf{8}^\bullet$, which subsequently give electron transfer to the ions (Scheme 1: pathway 1 and not pathways 2 and 3). This is in accordance with mechanisms B and C, but not with mechanism A. The overall noncorrelation of the quantum yields (lifetime-uncorrected and -corrected) of radical formation with any set of substituent constants shows that radical formation and ion formation are not consecutive processes. This points to mechanism B rather than to mechanism C (or A).

The $\rho_\tau(\sigma^+)$ values of -1.6 and -1.7 for the photochemical formation of the vinyl cations $\mathbf{1}^+$ and $\mathbf{8}^+$ are small compared to the $\rho_\Delta(\sigma^+)$ value of -4.6 for the thermal acetolysis of triaryl vinyl bromides.[30] This difference is easily explained in terms of the transition states involved: early, with little charge separation, in the photochemical process ("on the descent" from the excited state) and late, with more charge separation, in the thermal process ("on the ascent" from the ground state).

(c) *β*-Aryl Substituent Effects. In the series **1cBr**, **1dBr**, and **1eBr** (R$_2$ = H, OCH$_3$, Cl) the Φ_{ion} values do not increase with the electron-donating ability of the β-aryl substituent (Table 1, entries 3−5 and entries 8−10). Here too, however, rate constants (k_r) rather than quantum yields matter. Although the substituent effects on the lifetimes of α-aryl-substituted styrenes, which we used in the discussion of the α-aryl substituent effects, can obviously not be used quantatively to correct the β-aryl substituent effects on Φ_{ion}, their relative magnitude ($\tau_{styrene}$ = 6 $\tau_{p\text{-methoxystyrene}}$) offsets the about 50% higher values of Φ_{ion} for **1cBr** than for **1dBr**. This brings the β-aryl substituent effect on the rates of the photochemical cation formation in the same direction as the α-aryl substituent effect: a slight increase with increasing electron-donating abilities within the series **1c−eBr**.

Thermal β-aryl substituent effects on vinyl cation formation are also small;[2a] e.g., at both 120.3 and 141.5 °C **1dBr** acetolyzes thermally about 3 times faster than **1cBr**.[11] Still, that thermal substituent effect is larger than the photochemical one, reflecting again the late transition state in the former and the early transition state in the latter process.

(d) Leaving Group Effects. Table 4 lists the quantum yields of the photoreactions of the vinyl chlorides **1aCl** and **1dCl**. Comparison of Φ_{ion} for the formation of cation $\mathbf{1a}^+$ from **1aBr** (Table 1, entries 1 and 6) with those from **1aCl** (Table 4, entries 1 and 3) as well as of Φ_{ion} for the formation of cation $\mathbf{1d}^+$ from **1dBr** (Table 1, entries 4 and 9) with those from **1dCl** (Table 4, entries 2 and 4) shows that the bromine compounds form vinyl cations more efficiently than the chlorine compounds, both in acetic acid and in acetonitrile.[31] This leaving group effect is larger for the formation of the less stable triphenyl vinyl cation $\mathbf{1a}^+$ (4−6-fold) than for the formation of the more stable tris(p-methoxyphenyl) vinyl cation $\mathbf{1d}^+$ (1−2-fold). Thus, the leaving group effect on Φ_{ion} is attenuated by the stability of the vinyl cations produced.

Thermally, at 141.5 °C, **1dBr** acetolyzed about 10 times faster than **1dCl**.[11] Once more, the effect of a structural variation is stronger for the thermal than for the photochemical process: the transition state for the latter reaction is earlier than that for the former.

The same leaving group effect on Φ_{ion} (Br > Cl) has been found in kinetic studies of the photosolvolysis of compounds **8a−cBr/Cl**[12] and of α-alkenyl-substituted vinyl bromides and chlorides.[32] The effect parallels the anionic leaving group abilities of the halides and indicates that C−X bond cleavage occurs heterolytically, as in mechanisms B and C. For mechanism A, the reverse effect (Cl > Br) would be expected, in parallel with the electron affinities of the halogen atoms.

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(30) Rappoport, Z.; Gal, A. *J. Org. Chem.* **1972**, *37*, 1174–1181.

(31) Leaving group effects Br > Cl can be discussed qualitatively in terms of Φ_{ion}. Singlet lifetimes of bromine compounds are smaller than those of corresponding chlorine compounds (see, for instance: Durand, A.-P.; Brown, R. G.; Worrall, D.; Wilkinson, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 365–370.). Therefore, the leaving group effect on $\Phi_{ion}/\tau = k_{ion}$ should be larger than that on Φ_{ion}, but in the same direction.

(32) Krijnen, E. S.; Zuilhof, H.; Lodder, G. *J. Org. Chem.* **1994**, *59*, 8139–8150.

TABLE 4. Quantum Yields of the Photoreactions of the Vinyl Chlorides 1aCl and 1dCl in Acetic Acid and in Acetonitrile (λ_{exc} = 313 nm; *T* = 23 °C) and Selectivities of the Vinyl Cations $1a^+$ and $1d^+$ toward Cl^- and OAc^- or HOAc

entry	substrate	solvent	$10^2\Phi_d$	$10^2\Phi_c$	$10^2\Phi_{ox}$	$10^2\Phi_{OAc}$	$10^2\Phi_{ex}$	$10^2\Phi_{ion}$	S_{NaOAc}	S_{HOAc}
1	**1aCl**	HOAc[a]	5.4	3.1		2.6	0.80	3.4	0.35	70
2	**1dCl**		8.4	5.1	0.7	3.3	15.9	19	5.9	1200
3	**1aCl**	CH_3CN[b]	8.6	3.4	trace	0.78	5.4	6.2		100
4	**1dCl**		4.1	3.2	0.67	0.32	25.8	26		1130

[a] Added nucleophiles present: [$Et_4NCl^{\#}$] = 71 × 10^{-3} M; [NaOAc] = 87 × 10^{-3} M. [b] Added nucleophiles present: [$Et_4NCl^{\#}$] = 71 × 10^{-3} M; [HOAc] = 1.0 M.

In early reports on the photoreactivity of vinyl bromides and chlorides, the ratio of ion-derived vs radical-derived products was used to discuss leaving group effects on the photochemistry of vinyl halides. This ratio was found to be larger for the bromine than for the chlorine compounds in the case of halomethylene cyclohexanes[8,33] but smaller in the case of diaryl vinyl halides.[34] Still, both effects were considered to be in line with mechanism A (Scheme 1) in which first the carbon—halogen bond cleaves homolytically and vinyl cations are formed subsequently by electron-transfer within the initially formed radical pair.

In the case of compounds **1X**, the ratio of ion- to radical-derived products is larger for **1dBr** than for **1dCl** (229 vs 39 in acetonitrile), but the opposite is true for **1aBr** and **1aCl** (30 vs almost infinite; **1aCl** forms virtually no radical-derived product). Clearly, great care should be taken in attributing mechanistic consequences to such product ratios.

The (virtual) nonformation of radical-derived products from **1aCl** does not support mechanism A, in which vinyl cation formation occurs through the intermediacy of a vinyl radical (Scheme 1, pathways 2 and 3), but is in accordance with mechanisms B and C, in which vinyl cation formation occurs directly from the excited state (pathway 1). The formation of radical-derived product from **1dCl**, where electron transfer in the ion pair [$\mathbf{1d^+}$ $\mathbf{Cl^-}$], forming the radical pair [$\mathbf{1d^\bullet}$ $\mathbf{Cl^\bullet}$] (pathway 4), should be less favorable than in the ion pair [$\mathbf{1a^+}$ $\mathbf{Cl^-}$], (not) forming the radical pair [$\mathbf{1a^\bullet}$ $\mathbf{Cl^\bullet}$], points at mechanism B, in which the formation of ion and radical formation are parallel processes, rather than at mechanism C.

(e) Temperature Effects. In Table 5, the effect on the quantum yields of the photoreactions of the temperature at which the irradiations were carried out (60 vs 23 °C) is reported for compound **1aBr** with (entry 1 vs 2) and without (entry 6 vs 5) added nucleophiles as well as for compound **1dBr** with (entry 8 vs 7) and without (entry 10 vs 9) added nucleophiles, always in acetic acid. At 60 °C, as at 23 °C, no thermal reaction occurs. The dependence of the quantum yields on the reaction temparature provides the activation parameters given in Table 6. Because quantum yields are ratios of reaction rate constants (see eq 5), the calculated activation parameters are differences of activation energies/enthalpies, not absolute values. However, temperature hardly affects the photophysical decay of excited states,[35] and the photochemical decay only constitutes a small contribution to the lifetimes τ.[36] Therefore, the overall lifetimes are only weakly affected by the temperature and the calculated activation energies/enthalpies effectively pertain to the reaction rates k_r.

None of the photoreactions of the triaryl vinyl halides **1X** is a single-step process: the vinyl cation $\mathbf{1^+}$ is an intermediate in the nucleophilic photosubstitution, the vinyl radical $\mathbf{1^\bullet}$ in the photooxidation, and the dihydrophenanthrene in the photocyclization.[13] Consequently, the activation parameters pertain to the rate determining step of each reaction.

The enthalpy of activation for the photoacetolysis of **1aBr** (= formation of $\mathbf{1a^+}$) and its activation energy for photooxidation (= formation of $\mathbf{1a^\bullet}$) in acetic acid without any additives are both zero (Table 6, entry 2). As it is difficult to envision a cation ⇄ radical transition to be entirely entropy controlled without any enthalpy contribution, this lack of an activation barrier shows that both the vinyl cation $\mathbf{1a^+}$ and the vinyl radical $\mathbf{1a^\bullet}$ are formed directly from the excited state of **1aBr** without either one of them being an intermediate in the formation of the other (intermediate defined by Jencks as a species with a significant lifetime and having barriers for its breakdown to both reactants and products[37]). This disagrees with mechanism A, which involves a radical → ion conversion (Scheme 1, pathway 3), as well as with mechanism C, which involves an ion → radical conversion (pathway 4). It supports mechanism B, in which cation (pathways 1 and 5) and radical formation (pathways 2 and 6) are parallel processes.

As the triphenyl vinyl cation $\mathbf{1a^+}$ is formed photochemically with zero enthalpy of activation, the same surely also applies to the more stabilized vinyl cation $\mathbf{1d^+}$. Indeed, determination of the capturing nucleophile in the following section shows that all other activation parameters for the ionic photoprocesses of **1aBr** and **1dBr** (Φ_{OAc} and Φ_{ex}) listed in Table 6 (entries 1, 3, and 4) pertain to the second step of the product formation process, the (thermal) reaction of the vinyl cation with a nucleophile.

In the case of the photolysis of (*E*)-bromostyrene in methanol, for which mechanism C has been established by means of isotope effects, the activation energies for the formation of ion- and radical-derived photoproducts were also quite similar, but—due to the absence of a carbocation-stabilizing α-aryl substituent—much larger (6.7 and 6.1 kcal·mol^{-1})[9a] than here. It was argued that two entirely different photoprocesses from the same excited state are unlikely to have virtually the same activation energies. The activation energies (6.7 ≈ 6.1 kcal·mol^{-1}) were attributed to the ion-pair formation (Scheme 1, pathway 1), and the activation energy for the electron-transfer process converting the ion pair into a radical pair (pathway 4) was considered to be lower than that. Valid as the argument

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(33) Sonawane, H. R.; Nanjundiah, B. S.; Panse, M. D. *Tetrahedron Lett.* **1985**, 3507–3510.

(34) (a) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1982**, *47*, 2323–2328. (b) Šket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752–756.

(35) Birks, J. B. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1973; Vol. 1, Chapter 1.

(36) For instance, in the case of **1aBr** $(\Phi_d + \Phi_{ex})_{23} = 0.187$, i.e. more than 80% of the decay is photophysical. Therefore, the overall lifetime is not (significantly) affected by the temperature. As $(\Phi_d + \Phi_{ex})_{60}/(\Phi_d + \Phi_{ex})_{23} = 1.4$ the effect of increasing the temperature from 23 to 60 °C on τ is estimated to be less than 10% (40% of 20%), i.e., $\tau_{23}/\tau_{60} < 1.1$. Insertion of that information, eq 5, and the temperatures into the Eyring equation shows that the contribution of the lifetimes to the calculated activation energies/enthalpies is less than 0.5 kcal·mol^{-1}, i.e., within the random error.

(37) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161–169.

TABLE 5. Quantum Yields of the Photoreactions of 1aBr and 1dBr under Various Conditions in Acetic Acid (λ_{exc} = 313 nm) and Selectivities of the Vinyl Cations $1a^+$ and $1d^+$ toward Br^- and OAc^- or HOAc

entry	substrate	additives	T (°C)	$10^2\Phi_d$	$10^2\Phi_c$	$10^2\Phi_{ox}$	$10^2\Phi_{OAc}$	$10^2\Phi_{ex}$	$10^2\Phi_{ion}$	S_{NaOAc}	S_{HOAc}
1	**1aBr**	*a,b*	60	15.1	4.5	0.56	8.1	11.0	19	1.7	340
2		*a,b*	23	11.2	3.0	0.45	6.8	7.5	14.3	1.4	280
3		*a*	23	11.7	3.4	0.53	5.7	7.8	13.5		340
4		*b*	23	9.6	2.8	0.33[c]	4.5		4.5		
5			23	8.2	3.1	0.56	4.0		4.0		
6			60	11.2	3.7	0.56	4.5		4.5		
7	**1dBr**	*a,b,d*	23	2.9	[e]	0.15[f]	0.97	20	21	25.5	5100
8		*a,b,d*	60	5.1	[e]	[e]	1.58	31	33	23.7	4700
9			23	2.7	0.5	0.42	0.15		0.15		
10			60	3.6	0.6	0.55	0.57		0.57		

[a] $[Et_4NBr^{\#}] = 71 \times 10^{-3}$ M. [b] [NaOAc] = 87×10^{-3} M. [c] Traces of the reduction products **4a** and **7a** were also found. [d] Reported in ref 4a. [e] Not reported. [f] Φ_{red}; Φ_{ox} not reported.

TABLE 6. Activation Parameters (±0.5 kcal·mol^{-1}) for the Photoreactions of 1aBr and 1dBr in Acetic Acid

			Φ_{OAc}		Φ_{ex}		Φ_{ox}		Φ_c	
entry	substrate	additives	E_a	$\Delta H^{\ddagger}$	E_a	$\Delta H^{\ddagger}$	E_a	$\Delta H^{\ddagger}$	E_a	$\Delta H^{\ddagger}$
1	**1aBr**	*a*	0.9	0.3	2.1	1.5	1.1	0.5	2.2	1.6
2			0.6	0.0			0.1	−0.5	0.9	0.3
3	**1dBr**	*a,b*	2.6	2.0	2.3	1.7	*c*	*c*	*c*	*c*
4			7.1	6.5			1.4	0.8	1.0	0.4

[a] $[Et_4NBr^{\#}] = 71 \times 10^{-3}$ M; [NaOAc] = 87×10^{-3} M. [b] Reported in ref 4a. [c] Not reported.

about the equality of the activation energies for the formation of ion- and radical-derived photoproducts is for measurable activation energies, it cannot be applied when these activation enthalpies/energies are 0, as is the case here for the photochemical formation of the vinyl cations $\mathbf{1}^+$ and vinyl radicals $\mathbf{1}^\bullet$.

Selectivity. (a) Capturing Nucleophile. The selectivity for the irradiation of **1aCl** in acetic acid/sodium acetate/tetraethylammonium chloride[^{36}Cl] is less than unity: $S_{NaOAc} = 0.35$ (Table 4, entry 1). This value catches the eye because it is most unlikely that OAc^- is more reactive than Cl^- toward $\mathbf{1a}^+$; that would constitute a reversal of the normal order of nucleophilicity ($Cl^- > OAc^-$).[38] It suggests that the triphenyl vinyl cation $\mathbf{1a}^+$ reacts efficiently with acetic acid even in the presence of acetate. This is in contrast to the more stable 1-(*p*-methoxyphenyl)-2,2-diphenylvinyl cation $\mathbf{1c}^+$, for which it has been shown that the capturing nucleophile in the (photo)acetolysis reaction is acetate ion rather than acetic acid.[4a] That acetic acid and not acetate ion is the capturing nucleophile in the photoacetolysis of **1aBr** in acetic acid is confirmed by irradiations of **1aBr** with only one or neither of the nucleophiles NaOAc and $Et_4NBr[^{82}Br]$ present (Table 5, entries 2 vs 3 and 4 vs 5): Φ_{OAc} is virtually independent of the presence of NaOAc.

The change from acetic acid as capturing nucleophile in the photoacetolysis of the α-phenyl-substituted compound **1aBr** to NaOAc in the photoacetolysis of the α-(*p*-methoxyphenyl)-substituted compounds **1cBr** and **1dBr** is reflected in the values of the activation parameters listed in Table 6. Because the vinyl cations $\mathbf{1}^+$ are formed with zero $\Delta H^{\ddagger}$ (vide supra) all activation parameters for the acetolysis and exchange processes listed in Table 6 pertain to the reaction of the vinyl cations with the nucleophiles Br^-, OAc^-, and HOAc. The values of the enthalpy of activation ($\Delta H^{\ddagger}$) for the reactions with the anionic nucleophiles Br^- (1.5 kcal·mol^{-1} for **1aBr** and 1.7 kcal·mol^{-1} for **1dBr**) and OAc^- (2.0 kcal·mol^{-1} for **1dBr**) are virtually independent of the nature of the vinyl cation ($\mathbf{1a}^+$ or $\mathbf{1d}^+$). The $\Delta H^{\ddagger}$ values for the reaction with the solvent acetic acid, however, show a pronounced substituent effect: 0.0 kcal·mol^{-1} for the triphenyl vinyl cation $\mathbf{1a}^+$ and 6.5 kcal·mol^{-1} for the more stable tris(*p*-methoxyphenyl) vinyl cation $\mathbf{1d}^+$. That is consistent with the reaction of the vinyl cations $\mathbf{1}^+$ with the solvent acetic acid being activation-controlled. The activation energies of the reactions of the vinyl cations $\mathbf{1}^+$ with the anionic nucleophiles Br^- and OAc^- on the other hand are at 2.1−2.6 kcal·mol^{-1} almost equal and within the 2−4 kcal·mol^{-1} range[39] associated with Ingold's "collapse theory". These small but distinct activation energies represent the need for (partial) desolvation of the ions to get sufficiently close to each other to commence the release of bond energy in excess.[39a,40a] That is consistent with the ionic combination reactions being (de)solvation-controlled.

The thermal nucleophilic substitution of **1dBr**[5] occurs via the S_N2 (C^+) mechanism,[40b,41] a rarely observed variation on the S_N1 mechanism in which the cation−nucleophile reaction is rate determining under solvolytic conditions. The activation data ($\Delta H^{\ddagger}$ is larger for the reaction of the stabilized tris(*p*-methoxyphenyl) vinyl cation $\mathbf{1d}^+$ with the weakly nucleophilic solvent acetic acid than for the ionic combination reactions of $\mathbf{1d}^+$ with Br^- and OAc^-) show that the same happens photochemically. The reactions of the less stable triphenyl vinyl cation $\mathbf{1a}^+$ are the second steps of an S_N1 process: $\Delta H^{\ddagger}$ is larger for the ionic combination reactions of $\mathbf{1a}^+$ with Br^- and OAc^- than for its reaction with the solvent HOAc.[42]

(b) Selectivity. When the selectivities S (S_{HOAc} and S_{NaOAc} only differ by a constant concentration factor) of the vinyl cations $\mathbf{1a}-\mathbf{c}^+$ listed in Table 1 are subjected to Hammett treatment with reference to σ^+, the same ρ_S values are obtained

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(38) Richard, J. P.; Toteva, M. M.; Crugeiras, J. *J. Am. Chem. Soc.* **2000**, *122*, 1664–1674.

(39) (a) Hawdon, A. R.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1952**, 2499–2503. (b) Bunton, C. A.; del Pesco, T. W.; Dunlop, A. M.; Yang, K. U. *J. Org. Chem.* **1971**, *36*, 887–897.

(40) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, 1969; Chapter 7, (a) pp 494−496; (b) p 470.

(41) Kinetic evidence for such a process has recently been obtained in the case of the bis(*p*-methoxyphenyl)methyl cation: Mayr, H.; Minegishi, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4493–4495.

(42) Minegishi, S.; Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2005**, *127*, 2641–2649.

in acetic acid ($\rho_{\mathrm{S,HOAc}}(\sigma^+) = -1.60$ (±0.31; $R^2 = 0.963$)) and in acetonitrile ($\rho_{\mathrm{S,CH3CN}}(\sigma^+) = -1.55$ (±0.10; $R^2 = 0.996$)) (Figures 1 and 2). The presence of OAc$^-$ in acetic acid but not in acetonitrile makes no difference in this respect, even though OAc$^-$ is the main capturing nucleophile leading to **2c** for the vinyl cation **1c**$^+$, whereas HOAc is the main capturing nucleophile leading to **2a** for the vinyl cation **1a**$^+$. The (de)solvation-controlled reaction with OAc$^-$ occurs with almost constant efficiency over the investigated range, about 1.1×10^{-2} for **1a**$^+$ (Table 5, the difference between Φ_{OAc} in entries 2 and 3) and about 1.5×10^{-2} for **1c**$^+$ (Table 1, entry 3), and consequently does not contribute significantly to the $\rho_{\mathrm{S}}(\sigma^+)$ values. These are solely determined by the reactions with Br$^-$ and HOAc.

Vinyl cations have also been generated by laser flash photolysis, and actual rates of their reactions with several nucleophiles have been measured.[6,7,12] According to eq 4b, $\rho_{\mathrm{S}}(\sigma^+) = \rho_{\mathrm{Br^-}}(\sigma^+) - \rho_{\mathrm{HOAc}}(\sigma^+)$, and, of course, one wishes to compare the $\rho_{\mathrm{S}}(\sigma^+)$ values obtained in the continuous irradiation experiments of the vinyl bromides **1a−cBr** reported here with values of $\rho_{\mathrm{Br^-}}(\sigma^+) - \rho_{\mathrm{HOAc}}(\sigma^+)$ for the reactions of the vinyl cations **1**$^+$ with bromide ion and acetic acid, respectively. Using the flash photolysis method, a value of $\rho_{\mathrm{Br^-}}(\sigma^+) = +2.0$ (cation-reactivity results in sign inversion compared with cation formation) was obtained for the reaction of ions **1b**$^+$ and **1c**$^+$ with Br$^-$ in acetonitrile.[43a] A value of $\rho_{\mathrm{HOAc}}(\sigma^+)$, however, could not be determined:[43] Stern−Volmer plots for the reaction of **1c**$^+$ with acetic acid are nonlinear, and low concentrations of HOAc in acetonitrile actually increase the lifetime of **1c**$^+$ rather than decrease it.[44] The value of $\rho_{\mathrm{HOAc}}(\sigma^+)$ can, however, be estimated as $+3.6$ ($= -\rho_{\mathrm{S}}(\sigma^+) + \rho_{\mathrm{Br^-}}(\sigma^+)$). This agrees well with the value of $\rho_{\mathrm{EtOH}}(\sigma^+) = +3.4$ reported by Kobayashi and Schnabel for the reaction of a series of multisubstituted triaryl vinyl cations with another protic nucleophile, ethanol.[6c]

The values of $\rho_{\mathrm{S}}(\sigma^+)$ for the cations **1a−c**$^+$ are the same as those listed in Table 2 for the α-aryl substituent effect on their rate of photochemical formation Φ_{ion}/τ, $\rho_\tau(\sigma^+)$ (Figures 1 and 2). The same equality, $\rho_{\mathrm{S}}(\sigma^+) = \rho_\tau(\sigma^+)$, has been found in irradiations of vinyl bromides **8Br** in methanol in the presence of Et$_4$NBr[^{82}Br].[12,29] Apparently, the difference in energy content of the transition states for the reactions of the vinyl cations **1**$^+$ with Br$^-$ and HOAc ($\rho_{\mathrm{S}}(\sigma^+) = \rho_{\mathrm{Br^-}}(\sigma^+) - \rho_{\mathrm{HOAc}}(\sigma^+)$) is subject to the same electronic substituent effect as the energy content of the transition states for the photochemical formation of the vinyl cations **1**$^+$ ($\rho_\tau(\sigma^+)$). In the case of diarylmethyl cations, it has been shown that bond making in the transition state is 50−65% advanced for the reaction with the protic nucleophile water and ~25% advanced for the reaction with Br$^-$.[45] If similar values would apply for the reaction of the vinyl cations **1**$^+$ with Br$^-$ and HOAc the equality of $\rho_{\mathrm{S}}(\sigma^+)$ and $\rho_\tau(\sigma^+)$ would put the (early) transition state of the photochemical formation of the cations **1**$^+$ at 25−40% on the reaction coordinate.

(c) Reactivity−Selectivity. The selectivities S for the reactions of the vinyl cations **1**$^+$ with Br$^-$ vs NaOAc/HOAc listed in Table 1 (last two columns) follow the so-called Reactivity−Selectivity Principle (RSP)[46,47] both within the series **1aBr**, **1bBr**, **1cBr** (α-aryl substituent effect) and **1cBr**, **1dBr**, **1eBr** (β-aryl substituent effect): the better stabilized vinyl cation is the more selective in both media employed.

The selectivity data in Table 4 (last two columns) show that the same applies for the selectivities S of the vinyl cations **1a**$^+$ and **1d**$^+$ (photogenerated from **1aCl** and **1dCl)** for their reactions with Cl$^-$ vs NaOAc/HOAc: **1d**$^+$ is more selective than **1a**$^+$.

On the other hand, for the selectivities $S_{\mathrm{Br^-/Cl^-}}$ of the vinyl cations **1a**$^+$ and **1d**$^+$ toward the two anionic nucleophiles Br$^-$ and Cl$^-$ (calculated by dividing the S_{HOAc} values obtained in the photolyses of **1aBr** and **1aCl**, respectively, **1dBr** and **1dCl**),[48] a different picture emerges. In acetic acid $S_{\mathrm{Br^-/Cl^-}} = 4$ for both **1a**$^+$ and **1d**$^+$. Similarly, in acetonitrile $S_{\mathrm{Br^-/Cl^-}} = 4$ for **1d**$^+$ and 2.5 for **1a**$^+$. This appears to be an adherence to Ritchie's constant selectivity rule recalled in eq 6, with k_{Nu} the reaction rate of the cation with the nucleophile, k_0 a parameter only depending on the identity of the cation (usually the rate of the reaction of the cation with the solvent, originally k_{H2O}), and N^+ a parameter depending only on the identity of the nucleophile and the solvent.[49]

$$\log\left[\frac{k_{\mathrm{Nu}}}{k_0}\right] = \mathrm{N}^+ \qquad (6)$$

The Ritchie equation has recently been extended by Mayr and co-workers for $k_{\mathrm{Nu}} < 10^8$ M^{-1} s^{-1} to eq 7, with k_{Nu} the reaction rate (in M^{-1} s^{-1}) of the cation with the nucleophile at 20 °C, s_{E} an electrophile-specific slope parameter ($s_{\mathrm{E}} = 1$ for reactions of carbocations with nucleophiles), s_{N} a nucleophile-specific slope parameter, E a nucleophile-independent electrophilicity parameter, and N an electrophile-independent nucleophilicity parameter.[42,46g,50]

$$\log k_{\mathrm{Nu}} = s_{\mathrm{E}} s_{\mathrm{N}}(E + N) \qquad (7)$$

The Ritchie N^+ values for Br$^-$ and Cl$^-$ are 2.2 and 1.2, respectively;[38] i.e., $N^+_{\mathrm{Br^-}} - N^+_{\mathrm{Cl^-}} = 1.0$. According to eq 6 this should give a value of $\log S_{\mathrm{Br^-/Cl^-}} = 1.0$, which is in good agreement with the value of $\log S_{\mathrm{Br^-/Cl^-}} = 0.6$ we calculate from the selectivities in our competition experiments, taking the difference in solvent (H$_2$O vs HOAc) into account. Mayr's $N_{\mathrm{Br^-}}$ and $N_{\mathrm{Cl^-}}$ values are not available for the solvents we use, but in the solvents for which they have been reported, $N_{\mathrm{Br^-}} - N_{\mathrm{Cl^-}} \approx 1.5$,[42] still within one log unit of the number (0.6) we find.

The selectivity behavior of carbocations in general and the discrepancy between the RSP and Ritchie behavior in particular have been the subject of considerable research, and perhaps more exceptions than adherences to the RSP have been reported.

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(43) (a) Lodder, G. Unpublished results. (b) Krijnen, E. S. Ph.D. Thesis, University of Leiden, The Netherlands, 1992.

(44) A lifetime extension by acetic acid has also been observed in a flash photolysis study of the vinyl cation **8c**$^+$.[12] Alcohols have been reported to exert a similar effect on the retinyl cation: Pienta, N. J.; Kessler, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 2419–2428.

(45) Van Pham, T.; McClelland, R. A. *Can. J. Chem.* **2001**, *79*, 1887–1897.

(46) (a) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69–132. (b) Giese, B. *Angew. Chem.* **1977**, *89*, 162–173. (c) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461–3480. (d) Arnett, E. M.; Molter, K. E. *Acc. Chem. Res.* **1985**, *18*, 339–346. (e) Richard, J. P. *Tetrahedron* **1995**, *51*, 1535–1573. (f) Richard, J. P.; Amyes, T. L.; Toteva, M. M. *Acc. Chem. Res.* **2001**, *34*, 981–988. (g) Mayr, H.; Ofial, A. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 1844–1854.

(47) (a) Johnson, C. D.; Stratton, B. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1903–1907. (b) Denton, P.; Johnson, C. D. *J. Chem. Soc., Perkin Trans. 2* **1995**, 477–481.

(48) This approach presumes that Φ_{OAc} is independent of the leaving group (Br/Cl).

(49) (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348–354. (b) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239–2250.

(50) (a) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66–77. (b) Minegishi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 286–295. (c) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174–5181. (d) Phan, T. B.; Breugst, M.; Mayr, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3869–3874.

Therefore, the term "Reactivity−Selectivity Principle" is questionable as the word "principle" is misleading, but this is the term used by most authors.[46,47,49–53] Ta-Shma and Rappoport have first shown that in many cases which follow the RSP the reaction with the less reactive nucleophile is activation-controlled and the reaction with the more reactive nucleophile is diffusion-controlled.[51] Jencks, Richard, and co-workers have reported several more cases following that pattern[52] but have also pioneered the concept that in other cases that follow the RSP the reaction with the less reactive nucleophile is activation-controlled and the reaction with the more reactive nucleophile is (de)solvation-controlled.[53]

We propose that our selectivity results are fully consistent with the reaction of the vinyl cations **1**$^+$ with acetic acid being activation controlled and that with the anionic nucleophiles Br$^-$ and OAc$^-$ being (de)solvation controlled. This is based on the activation data in Table 6 and the analysis of the capturing nucleophile and supported by the α-aryl substituent effect on the selectivities. Flash photolysis studies have shown that the reaction of the 1-(*p*-methoxyphenyl)vinyl cation **1c**$^+$ with Br$^-$ in acetonitrile is not diffusion controlled: the reaction rate ($k = 2 \times 10^9$ M^{-1} s^{-1})[7] is an order of magnitude lower than that for the reaction of the vinyl cation **8c**$^+$ with Br$^-$ ($k = 1.7 \times 10^{10}$ M^{-1} s^{-1}).[12] McClelland, Steenken, and co-workers have observed the influence of nucleophile solvation on the rates of cation−nucleophile reactions in flash photolysis studies.[45,54a,b] Moreover, they measured a rate 3−4 orders of magnitude below the diffusion-limited value for the reaction of **1c**$^+$ with Br$^-$ ($k = 6 \times 10^6$ M^{-1} s^{-1}) in TFE and also found that that even **1a**$^+$, the least stabilized vinyl cation in the series **1**$^+$, reacts with Br$^-$ at a rate ($k = 8.2 \times 10^8$ M^{-1} s^{-1}) at least an order of magnitude below the diffusion-limited value in 1,1,1,3,3,3-hexafluoro-2-propanol.[54c]

Conclusions

In this study, we have been concerned with the photoreactivity of a series of triaryl vinyl halides **1X**, as well as with the selectivity of the photogenerated vinyl cations **1**$^+$.

Photoreactivity. The α- and *β*-aryl substituent effects, the leaving group effect, and the temperature effect on the photoreactivity of the compounds **1X** were investigated and interpreted in terms of the mechanisms A, B, and C (Scheme 1). The *β*-aryl substituent effect does not allow mechanistic conclusions, but the α-aryl substituent effect, the leaving group effect, and the temperature effect all argue against mechanism A, which involves initial homolytic C−X bond scission to a radical pair followed by electron tranfer to form an ion pair, and against mechanism C, which involves initial heterolytic C−X bond scission to an ion pair followed by electron tranfer to form a radical pair. The effects support mechanism B, in which ion-pair and radical-pair formation are parallel processes: the partitioning into ion and radical occurs in the excited state. Mechanistically, the photochemistry of α-aryl-substituted vinyl halides such as **1X** thus occupies a position in between benzyl halides, which follow mechanism A or B,[55] and α-H- and α-alkyl-substituted vinyl halides, which follow mechanism C.[9] This reflects the both benzylic and vinylic nature of the reaction center of the compounds **1X**. The mechanism directing the photoreactivity of vinyl compounds depends on structural effects as it does for aromatic compounds.[14]

Selectivity. The activation data for the reactions of the vinyl cations **1**$^+$ with Br$^-$, OAc$^-$, and HOAc are consistent with Ingold's "collapse theory".[39a,40a] The reactions of the vinyl cations **1**$^+$ with the anionic nucleophiles Br$^-$ and OAc$^-$ are (de)solvation controlled and their reaction with acetic acid is activation controlled. Therefore, the selectivities of the vinyl cations **1**$^+$ toward bromide ion and acetic acid follow the Reactivity−Selectivity Principle.[46,47]

Experimental Section

Procedure. The experimental setup as well as the sampling and workup procedure have been described previously,[4a] and so have the kinetics[4b] and the 3-nitroanisole actinometry.[56,57] Irradiation at $\lambda_{\mathrm{exc}} = 313$ nm was achieved using a Hanau TQ 81 high-pressure mercury arc in combination with a filter solution.[4a]

The concentration of the vinyl halides **1X** was always 4.7×10^{-3} M. If NaOAc was present in the reaction mixture it was so in a concentration of 87×10^{-3} M. The (labeled) tetraethylammonium halide Et$_4$NBr[^{82}Br] or Et$_4$NCl[^{36}Cl] used in the irradiation mixtures was invariably that with the halide in common with the substrate; if present it was so in a concentration of 71×10^{-3} M. In the irradiation mixtures of compounds **1X** in acetonitrile spiked with acetic acid, the latter was present in a concentration of 1.0 M.

For all systems studied, control experiments in the dark showed that neither product formation nor radioactive halide exchange occurs thermally under the reaction conditions employed. The counting procedures for ^{82}Br[4a] and ^{36}Cl[58] have been reported previously, and so has the analysis of the disappearance of starting material and the formation of products by means of HPLC (Chrompack Si 60-5 4.6 mm × 25 cm column, eluents 0−7.5% THF in hexane) calibrated with standard solutions of the starting material and products.[4a,58]

All irradiations were performed in triplicate. The values of the quantum yields and selectivity constants reported are average values; the error (i.e., deviation from the mean) is 5−10%. An error of 5% in the quantum yields leads to an error of 0.5 kcal·mol^{-1} in the activation parameters.

Purification of Reagents and Solvents. Sodium acetate, tetraethylammonium bromide, and tetraethylammonium chloride were analytical grade and used as such. Acetonitrile was spectroscopic grade. Hexane (technical quality) and THF (from CaH$_2$) were distilled before use. Acetic acid was prepared by refluxing analytical glacial acid with 1% acetic anhydride and distilling and collecting the middle fraction.[59]

Synthesis of Starting Materials. 1-Bromo-1,2,2-triphenylethene (**1aBr**) was commercially available and used as such. The other vinyl

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bromides (**1bBr**−**1eBr**) were prepared by bromination−dehydrobromination[60] in CCl_4 of the corresponding ethylene compounds **4b**−**e**, which in turn were synthesized by the procedure described in ref 61. The vinyl chlorides were also prepared from the corresponding ethylene compounds, **1aCl** according to ref 62 and **1dCl** according to ref 61. The spectral data of 1-chloro-1,2,2-triphenylethene (**1aCl**),[63] 1-chloro-1,2,2-tris(*p*-methoxyphenyl)ethene (**1dCl**),[64] 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**1cBr**),[59] and 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (**1dBr**)[59] have been reported.

1-Bromo-1-(*p*-methylphenyl)-2,2-diphenylethene (1bBr)[65]: UV (hexane) λ_{max} 215 nm (ϵ 13500), 234 (22800), 267 (7000), 298 (10100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 6.95−6.97 (m, 4H), 7.04−7.07 (m, 3H), 7.20 (d, 2H, $J = 8$ Hz), 7.27−7.31 (m, 1H), 7.36 (d, 4H, $J = 4$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 126.8, 127.4, 127.8, 128.1, 128.7, 129.5, 130.2, 130.3 (Attached Proton Test[66] (APT) −); δ 122.5, 137.8, 138.1, 141.2, 143.0, 143.9 (APT +); MS (EI, 70 eV): *m/z* (relative intensity) 350, 348 (M^+, 39, 38), 269 ($M^+ - Br$, 100); HRMS (EI, 70 eV) *m/z* 348.0517 ($C_{21}H_{17}Br$ requires 348.0514).

1-Bromo-1-(*p*-methoxyphenyl)-2,2-bis(*p*-chlorophenyl)ethene (1eBr): UV (hexane) λ_{max} 214 nm (ϵ 19800), 220 (21100), 245 (25400), 307 (12900); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.77 (s, 3H), 6.71−7.06 (AA′BB′, 4H), 6.84−7.23 (AA′BB′, 4H), 7.26−7.35 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.2, 113.6, 128.2, 128.5, 131.1, 131.5, 131.6 (APT −); δ 123.6, 132.8, 132.9, 133.5, 139.4, 140.2, 141.9, 159.4 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 438, 436, 434, 432 (M^+, 5, 22, 45, 30), 357, 355, 353 ($M^+ - Br$, 11, 67, 100), 320, 318 ($M^+ - Br - Cl$, 3, 14); HRMS (EI, 70 eV) *m/z* 431.9686 ($C_{21}H_{15}OBrCl_2$ requires 431.9684).

Tetraethylammonium bromide$[^{82}Br]$ was prepared by neutron irradiation of Et_4NBr,[5] tetraethylammonium chloride$[^{36}Cl]$ according to the method described in ref 67.

Identification of Products. The photoproducts were separated from the irradiation mixtures according to the method reported in ref 4a. The photoproducts were identified on the basis of their NMR, mass, and UV spectra and their HPLC retention times and by comparison with authentic samples. Of the photoproducts, benzophenone (**3a**), 4,4′-dimethoxybenzophenone (**3d**), 4,4′-dichlorobenzophenone (**3e**), and triphenylethene(**4a**) were commercially available. 1,1-Diphenyl-2-(*p*-methoxyphenyl)ethene (**4c**) and tris(*p*-methoxyphenyl)ethene (**4d**) were intermediate products in the synthesis of the starting materials **1cBr** and **1dBr/Cl**.

1-Acetoxy-1,2,2-triphenylethene (**2a**) and 1-acetoxy-1,2,2-tris(*p*-methoxyphenyl)ethene (**2d**) were prepared according to ref 68. The remaining vinyl acetates **2** were synthesized in an analogous fashion. The spectral data of **2a** and **2d**[68] as well as of 1-acetoxy-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**2c**)[69] have been reported.

1-Acetoxy-1-(*p*-methylphenyl)-2,2-diphenylethene (2b): UV (hexane) λ_{max} 229 nm (ϵ 20600), 257 (7800), 260 (7600), 267 (9500), 290 (15000); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.97 (s, 3H), 2.26 (s, 3H), 6.96 (d, 2H, $J = 8$ Hz), 7.07−7.16 (m, 7H), 7.22−7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 21.3, 127.0, 127.3, 128.0, 128.1, 128.7, 128.8, 129.0, 130.8 (APT −); δ 131.4, 132.9, 138.0, 139.9, 140.2, 144.0, 169.8 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 328 (M^+, 11), 286 (M^+ − ketene, 100); HRMS (EI, 70 eV) *m/z* 328.1468 ($C_{23}H_{20}O_2$ requires 328.1463).

1-Acetoxy-1-(*p*-methoxyphenyl)-2,2-bis(*p*-chlorophenyl)ethene (2e): UV (hexane) λ_{max} 239 nm (ϵ 19800), 263 (8800), 266 (9500), 301 (16300); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.00 (s, 3H), 3.77 (s, 3H), 6.72 (d, 2H, $J = 9$ Hz), 6.98 (d, 2H, $J = 9$ Hz), 7.12−7.16 (m, 6H), 7.26−7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 55.2, 113.7, 128.5, 128.6, 130.3, 130.5, 132.1 (APT −); δ 127.5, 128.6, 133.1, 133.3, 138.1, 138.3, 144.7, 159.6 169.6 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 416, 414, 412 (M^+, 2, 8, 14), 374, 372, 370 (M^+ − ketene, 10, 63, 100); HRMS (EI, 70 eV) *m/z* 412.0638 ($C_{23}H_{18}O_3Cl_2$ requires 412.0633).

The compounds **5X**, **6**, and **7** were prepared by independent photocyclization[13] in acetic acid of the corresponding compounds **1X**, **2**, and **4**. For some of the phenanthrene derivatives **5X**, **6**, and **7**, spectral data have already been reported:[4a] 10-bromo-3-methoxy-9-phenylphenanthrene (**5cBr**), 9-bromo-3,6-dimethoxy-10-(*p*-methoxyphenyl)phenanthrene (**5dBr**), 10-acetoxy-3-methoxy-9-phenylphenanthrene (**6c**), 9-acetoxy-3,6-dimethoxy-10-(*p*-methoxyphenyl)phenanthrene (**6d**), 3-methoxy-9-phenylphenanthrene (**7c**), 3,6-dimethoxy-9-(*p*-methoxyphenyl)phenanthrene (**7d**), and 9-phenylphenanthrene (**7a**).[70]

9-Bromo-10-phenylphenanthrene (5aBr)[71]: UV (hexane) λ_{max} 201 nm (ϵ 22700), 225 (16500), 251 (32100), 258 (39700), 271 (19000), 281 (15100), 290 (13700), 303 (11800); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.74 (multiple multiplets (mm), 10H), 8.53 (d, 1H, $J = 8$ Hz), 8.71−8.75 (dd, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.6, 126.8, 127.0, 127.4, 127.6, 127.7, 127.9, 128.4, 129.0, 130.0 (APT −); δ 123.6, 129.7, 130.5, 131.0, 132.6, 139.7, 141.0 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 334, 332 (M^+, 35, 36), 253 ($M^+ - Br$, 25), 252 ($M^+ - Br - H$, 38), 51 (C_4H_3, 100); HRMS (EI, 70 eV) *m/z* 332.0207 ($C_{20}H_{13}Br$ requires 332.0201).

10-Bromo-3-methyl-9-phenylphenanthrene (5bBr): UV (hexane) λ_{max} 208 nm (ϵ 39100), 230 (34700), 252 (58300), 259 (76400), 274 (24700), 282 (16000), 293 (16000), 305 (17400); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.66 (s, 3H), 7.33−7.65 (mm, 9H), 8.40 (d, 1H, $J = 8$ Hz), 8.52 (s, 1H), 8.71 (d, 1H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9, 122.4, 122.6, 126.6, 126.9, 127.6, 127.9, 128.4, 128.8, 129.4, 130.1 (APT −); δ 123.5, 128.5, 131.0, 132.7, 137.3, 138.6, 141.1 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 348, 346 (M^+, 90, 92), 267 ($M^+ - Br$, 43), 252 ($M^+ - Br - CH_3$, 100); HRMS (EI, 70 eV) *m/z* 346.0354 ($C_{21}H_{15}Br$ requires 346.0357).

9-Bromo-3-chloro-6-methoxy-10-(*p*-chlorophenyl)phenanthrene (5eBr): UV (hexane) λ_{max} 243 nm (ϵ 34100), 253 (39100), 261 (40000), 284 (13600), 304 (10200), 316 (10700), 349 (1500), 366 (1400); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.04 (s, 3H), 7.22−7.78 (mm, 8H), 7.92 (d, 1H, $J = 2$ Hz), 8.39 (d, 1H, $J = 9$ Hz), 8.56 (d, 1H, $J = 2$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 104.0, 118.3, 122.4, 127.6, 128.8, 129.1, 130.8, 131.6 (APT −); δ 123.7, 125.2, 130.2, 130.9, 131.3, 132.7, 133.9, 135.4, 138.9, 159.3 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 436, 434, 432, 430 (M^+, 4, 26, 57, 33), 419, 417, 415 ($M^+ - CH_3$, 4, 8, 5), 391, 389, 387 ($M^+ - CH_3 - CO$, 5, 10, 7), 303, 301 ($M^+ - CH_3 - Br - Cl$, 7, 20), 275, 273 ($M^+ - CH_3 - Br - Cl - CO$, 33, 100); HRMS (EI, 70 eV) *m/z* 429.9532 ($C_{21}H_{13}OBrCl_2$ requires 429.9527).

9-Chloro-10-phenylphenanthrene (5aCl). UV (hexane) λ_{max} 210 nm (ϵ 31900), 224 (24400), 251 (46200), 258 (57700), 272 (18300), 280 (11900), 291 (11200), 303 (12200); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33−7.35 (m, 2H), 7.41−7.43 (m, 2H), 7.44−7.59 (mm, 4H), 7.65−7.69 (m, 2H), 8.47 (q, 1H), 8.63−8.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.5, 122.6, 125.9, 126.6, 127.0, 127.3, 127.4, 127.5, 127.7, 128.4, 130.1 (APT −); δ 129.3, 129.4, 129.7, 130.9, 132.3, 136.7, 138.6 (APT +); MS (EI, 70 eV) *m/z* (relative

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intensity) 290, 288 (M$^+$, 31, 93), 253 (M$^+$ − Cl, 78), 252 (M$^+$ − Cl − H, 100); HRMS (EI, 70 eV) *m/z* 288.0714 ($C_{20}H_{13}Cl$ requires 288.0706).

9-Chloro-3,6-dimethoxy-10-(*p*-methoxyphenyl)phenanthrene (5dCl): UV (hexane) λ_{max} 207 nm (ϵ 20900), 214 (17800), 240 (23900), 253 (31000), 260 (30700), 289 (11100), 304 (6500), 314 (6900), 354 (1100), 372 (1100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.86 (s, 3H), 3.98 (s, 3H), 4.03 (s, 3H), 6.92–7.40 (mm, 7H), 7.97 (q, 1H), 8.05 (d, 1H, $J = 9$ Hz), 8.37 (d, 1H, $J = 9$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.2, 55.4, 55.5, 104.5, 104.6, 113.7, 116.4, 116.9, 127.6, 129.1, 131.4 (APT −); δ 121.6, 124.5, 127.4, 127.7, 130.1, 131.6, 133.8, 158.0, 158.6, 159.0 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 380, 378 (M$^+$, 34, 100), 363 (M$^+$ − CH_3, 12); HRMS (EI, 70 eV) *m/z* 378.1021 ($C_{23}H_{19}O_3Cl$ requires 378.1023).

9-Acetoxy-10-phenylphenanthrene (6a): UV (hexane) λ_{max} 211 nm (ϵ 29000), 220 (19300), 248 (38000), 254 (44900), 270 (13100), 276 (10100), 286 (6200), 299 (8500); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.06 (s, 3H), 7.30−7.89 (mm, 11H), 8.70−8.73 (dd, 2H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 122.2, 122.7, 122.9, 126.3, 126.9, 127.1, 127.2, 127.7, 128.3, 130.2 (APT −); δ 126.4, 129.2, 129.4, 131.1, 131.9, 135.6, 142.3, 169.4 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 312 (M$^+$, 17), 270 (M$^+$ − ketene, 100); HRMS (EI, 70 eV) *m/z* 312.1146 ($C_{22}H_{16}O_2$ requires 312.1150).

10-Acetoxy-3-methyl-9-phenylphenanthrene (6b): UV (hexane) λ_{max} 235 nm (ϵ 16700), 250 (28600), 256 (34200), 272 (11700), 279 (9600), 289 (7700), 300 (8100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.12 (s, 3H), 2.69 (s, 3H), 7.39−7.66 (mm, 9H), 7.83 (d, 1H, $J = 8$ Hz), 8.59 (s, 1H), 8.77 (d, 1H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 22.1, 122.1, 122.6, 122.7, 126.1, 126.7, 127.1, 127.6, 128.2, 128.9, 130.3 (APT −); δ 124.3, 128.3, 131.2, 132.1, 135.7, 136.8, 137.0, 142.4, 169.5 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 326 (M$^+$, 14), 284 (M$^+$ − ketene, 100); HRMS (EI, 70 eV) *m/z* 326.1303 ($C_{23}H_{18}O_2$ requires 326.1307).

9-Acetoxy-3-chloro-6-methoxy-10-(*p*-chlorophenyl)phenanthrene (6e): UV (hexane) λ_{max} 235 nm (ϵ 26000), 251 (26100), 257 (25800), 271 (13200), 282 (12300), 298 (9100), 310 (8500), 346 (1500), 363 (1100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.11 (s, 3H), 4.03 (s, 3H), 7.25−7.49 (mm, 7H), 7.78 (d, 1H, $J = 9$ Hz), 7.96 (d, 1H, $J = 2$ Hz), 8.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 55.6, 104.2, 118.3, 122.4, 124.0, 127.5, 128.3, 128.7, 131.7 (APT −); δ 121.1, 125.4, 129.7, 130.5, 132.2, 133.7, 133.9, 142.7, 159.3, 169.2 (APT +); MS (EI, 70 eV) *m/z* (relative intensity) 414, 412, 410 (M$^+$, 2, 14, 19), 372, 370, 368 (M$^+$ − ketene, 12, 68, 100); HRMS (EI, 70 eV) *m/z* 410.0485 ($C_{23}H_{16}O_3Cl_2$ requires 410.0476).

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Supporting Information Available: ^{1}H and ^{13}C NMR (APT) spectra of compounds **1bBr**, **1eBr**, **2b**, **2e**, **5aBr**, **5bBr**, **5eBr**, **5aCl**, **5dCl**, **6a**, **6b**, and **6e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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