# Photochemical Formation and Electrophilic Reactivities of Vinyl Cations. Influence of Substituents, Anionic Leaving Groups, Solvents, and Excitation Wavelength on Photoheterolysis and Photohomolysis of 1-(*p*-R-Phenyl)-2-(2,2'-biphenyldiyl)vinyl Halides

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Using product analysis and time-resolved laser flash photolysis techniques, the photochemistry at  $\lambda_{exc} \approx 250$ and 310 nm (exc = excitation) of 1-(p-R-phenyl)-2-(2,2'-biphenyldiyl)vinyl halides (R = H, Me, MeO) inmethanol and acetonitrile at room temperature was studied. The title compounds undergo photoheterolysis and photohomolysis to give vinyl cations  $=C^+-$  (carbenium ions) and vinyl radicals  $=C^{+}-$ . The cation: radical ratio increases with electron-donating strength of the substituent R,  $H \le MeO$ , and with anionic leaving group power of the halide,  $F^- < Cl^- < Br^- < I^-$ , indicating that the cleavage of the C-X bond to yield cation and halide anion proceeds, in the rate-determining step, by heterolysis and not by homolysis followed by electron transfer in the radical pair. The cation: radical ratio is solvent dependent: e.g., for the vinyl bromide with R = MeO and with  $\lambda_{exc}$  = 308 nm, in CH<sub>2</sub>Cl<sub>2</sub> as solvent, only radical is observed, in comparison with only cation in the much more polar solvent acetonitrile. In acetonitrile-methanol mixtures, the absolute yields of both cation and radical go through a maximum as the methanol content is increased, however, the cation: radical ratio decreases continuously with increasing [MeOH]. For a particular R, the quantum yield for C-X bond cleavage is higher at  $\approx 250$  than at  $\approx 310$  nm. Also, the cation: radical ratio is wavelength-dependent: at  $\lambda_{exc} \approx 310$  nm there is relatively more heterolysis than at  $\lambda_{exc} \approx 250$  nm. Rate constants for reaction of the cations with nucleophiles were determined in acetonitrile. Those for reaction of the cation with R = MeO (lifetime in acetonitrile 7 µs) with anionic nucleophiles such as the halides are at the diffusion limit in this solvent,  $\approx 2 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$ , whereas those for reaction with water, alcohols, and cyclic ethers are of the order  $10^5 - 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The less stabilized cation (R = Me) reacts with alcohols faster by the factor  $\approx 100$ , and it decays in acetonitrile  $\approx 100$  times more rapidly. Also, 1-(p-R-phenyl)-2dimethylvinyl bromides (R = H, Me, MeO) were photolyzed in acetonitrile. In the case of R = MeO, the cation p-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-C<sup>+</sup>=CMe<sub>2</sub> was seen (lifetime 770 ns), and its reactivity with alcohols (k values of  $10^6 - 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) and halides (k values of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) was determined. The vinyl radicals =C<sup>-</sup> react with O<sub>2</sub> to yield vinylperoxyl radicals = $C-O_2$ • which have absorption maxima at  $\approx 390$  nm.

# Introduction

Vinyl cations have been proposed as reactive intermediates in an increasing number of useful reactions. However, detailed studies of vinyl cations have been hampered by the difficulty of creating these intermediates in thermal reactions. In contrast with the situation for saturated carbocations, which carry the positive charge formally on an sp<sup>2</sup> hybridized carbon atom, with vinyl cations the positive charge is formally on an sp carbon, and strenuous reaction conditions and super leaving groups are often needed for their production.<sup>3</sup> These requirements are not present in photochemical generation of vinyl cations.<sup>4</sup> UVirradiation of, e.g., triarylvinyl bromides results in the facile formation of these intermediates in high yields at room temperature. The vinyl cations formed in this way have been shown to follow the same reactivity pattern as the corresponding thermally synthesized vinyl cations, thereby proving these species are identical.5,6

Up to now the formation of vinyl cations via photoheterolysis has been investigated mainly via product analysis in continuous irradiation experiments.<sup>4,7</sup> In contrast with the wealth of information obtained via time-resolved studies of saturated carbocations,<sup>8,9</sup> the study of unsaturated cations via laser flash techniques thus far has been limited to a few cases.<sup>10,11</sup> Subjects of these studies were mainly the identification and reactivity of the transient vinyl ions.

In this paper we present a combined continuous irradiation and laser flash photolysis approach to the study of 1-(p-R-phenyl)-2-(2,2'-biphenyldiyl)vinyl halides**1X**.<sup>12</sup> Quantum yieldshave been determined for the products resulting from irradiationat 254 and 313 nm, and laser flash light of 248 and 308 nmwas used for the time-resolved study of the transient vinylcations and radicals. Also, laser flash photolysis results for 1-(*p*-R-phenyl)-2,2-dimethylvinyl bromides**2Br**are reported.

The present paper emphasizes (a) the photoreactivity of the vinyl halides 1X and 2Br (yields of cations and radicals and those of the corresponding stable products) as a function of their structure, (b) the photoreactivity of 1X as a function of reaction conditions such as the wavelength of excitation and solvent, and (c) the reactivity of the cations photogenerated from 1X and 2Br, with nucleophiles.

### **Experimental Section**

a. Synthesis of Starting Materials. The vinyl bromides 1aBr-1cBr were prepared from the corresponding ethene compounds 1aH-1cH via bromination in CCl<sub>4</sub> followed by dehydrobromination in glacial acetic acid as described<sup>13</sup> for 1aBr. The ethene compounds were synthesized according to literature<sup>14</sup> procedures. The vinyl chlorides 1aCl-1cCl were

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prepared from the corresponding ethene compounds via chlorination with  $Cl_2$  in  $CCl_4$  and dehydrochlorination in NaOAc/ HOAc.<sup>13</sup> The vinyl fluoride **1cF** was prepared via fluorination of 9-benzoylfluorene with diethylaminosulfur trifluoride<sup>15</sup> and dehydrofluorination with 1,8-diazabicyclo[5.4.0]undec-7-ene, and the vinyl iodide **1cI** from **1cBr** by heating this compound with CuI and KI in hexamethylphosphoramide.<sup>16</sup> The vinyl bromides **2aBr-2cBr** were prepared from their corresponding ethene compounds via bromination in CCl<sub>4</sub> followed by dehydrobromination in *t*-BuOH/*t*-BuOK as described for **2aBr**.<sup>17</sup>

**b.** Photolysis Procedure and Product Analysis. The experimental setup of the continuous irradiation experiments as well as the sampling procedure has been described previously<sup>6</sup> and so have the kinetics.<sup>18</sup> For actinometry, the photolysis of 3-nitroanisole in an aqueous 0.1 M NaOH solution was used.<sup>19</sup> 254-nm excitation was achieved with a Hanau TNN 15/32 low-pressure mercury lamp, 313 nm, with a Hanau TQ 81 high-pressure mercury lamp combined with a filter solution.<sup>6</sup>

The concentrations of the vinyl halides **1X** in methanol (MeOH, spectroscopic grade) were always 0.5 mM. The solutions were argon or oxygen saturated by bubbling with argon or oxygen, respectively, for 30 min prior to and during the irradiation. Control experiments in the dark showed that no thermal product formation occurs under the reaction conditions employed. The analysis for disappearance of starting material and formation of products was carried out by means of HPLC calibrated with standard solutions of the starting material and products. All irradiations were performed at room temperature and at least in duplicate. The values of the quantum yields reported are average values; the error (deviation from the mean) is 5-10%.

Equipment. HPLC analyses were carried out with a system consisting of a (Kipp 9208) pump, a (Kipp 9202) UV detector (254 nm), and a (Chrompack) Si 60-5 4.6 mm  $\times$  25 cm column. The eluents used were 0.1-3% THF in hexane. UV spectra were recorded in hexane on a (Cary 219) spectrophotometer; NMR spectroscopy was performed in CDCl<sub>3</sub> or CCl<sub>4</sub> with a Jeol JNM-PS100 or a Bruker WM300 spectrometer. Both the low-resolution electron impact (EI) mass spectrometry and the high-resolution EI mass spectrometer with the ion source operating at 70 eV electron beam energy at an ion chamber temperature of 420 K.

Identification of Products. The nucleophilic substitution products  $10CH_3$  were identified on the basis of their NMR, mass, and UV spectra. Compound  $1cOCH_3$  was synthesized independently by methylation of 9-benzoylfluorene. The reduction products were identified via comparison with authentic 1aH-1cH which are precursors in the synthesis of vinyl halides 1X.

c. Laser Photolysis Method. After deoxygenation by bubbling with argon, solutions of 1X or 2Br (OD/cm  $\approx 0.2-$ 2) in acetonitrile (MeCN) or MeOH were flowed through a 2 mm (in the direction of the laser beam) by 4 mm (in the direction of the analysis light) Suprasil quartz cell (flow rates  $\approx 1-2$ mL/min) and photolyzed with 20-ns pulses of 248- or 308-nm light (ca. 2-40 mJ/pulse) from a Lambda-Physik EMG103MSC excimer laser. The light-induced optical transmission changes (which typically corresponded to peak optical density changes  $(\Delta OD)$  of 0.01-0.1, depending on substrate concentration and pulse power; the rise time was 1-2 ns) were digitized by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73<sup>+</sup> computer which also process controlled the apparatus and on-line preanalyzed the data. Final data analysis was performed on a Microvax I connected to the LSI. The pulse width of 20 ns means that species with a lifetime less than this cannot be detected. Nondetection of species thus does not mean they are not formed. In case two species with different lifetimes are produced, the measured concentration ratio depends, of course, on time.

## **Results and Discussion**

1. Product Analysis Results. a. Methanol as Solvent. In argon-saturated MeOH, irradiation of compounds 1X, which are thermally stable under the reaction conditions, yields the nucleophilic substitution products  $1OCH_3$  and the reduction products 1H (Scheme 1, eq 1a). Upon photolysis in oxygen-saturated MeOH, in addition to compounds  $1OCH_3$ , fluorenone (3) is formed instead of compounds 1H (Scheme 1, eq 1b).

The formation of **1H** and **3** is mutually exclusive. If the argon-saturated solution is deliberately not *completely* deoxygenated, initially only **3** is formed and later only **1H**, as shown in Figure 2. This indicates that **1H** and **3** are both formed via capture of a common precursor, presumably the vinyl radical,<sup>12,20</sup> see eq 7. Clearly its capture by oxygen is much more efficient than hydrogen transfer from the solvent MeOH. An alternative explanation would be that fluorenone is a secondary (photo)product of compounds **1H** with oxygen. This was refuted by irradiating compound **1cBr** (0.5 mM) in the presence of **1cH** nor formation of **3** over and above the amount of **3** formed in the irradiations of **1cBr** in the absence of **1cH** was observed.

In the experiments in the presence of oxygen oxidation products complementary to fluorenone were also detected. For example, in the case of compound **1bBr**, the methyl ester of *p*-methylbenzoic acid was found in a ratio 0.6:1 with respect to fluorenone; in the case of **1cBr** benzoic acid was isolated in a ratio 0.12:1 relative to fluorenone.

The disappearance of starting material (RX) and the formation of products (P) as a function of time of irradiation was studied with calibrated HPLC at both  $\lambda_{exc} = 254$  nm and  $\lambda_{exc} = 313$ nm in both deoxygenated and oxygen-saturated MeOH. The kinetic data fit the previously reported<sup>18</sup> eqs 2 and 3.

$$\ln[RX]_{t} [RX]_{0} = -k_{d}t = -\Phi_{d}tI_{0} [RX]_{0}$$
(2)

$$[P]_{t} = \Phi_{P} I_{0} (1 - e^{-k_{d} t}) / k_{d}$$
(3)

In these equations,  $[RX]_t$  represents the concentration of the vinyl halide (RX) in the reaction mixture at time t,  $k_d$  stands



Figure 1. Disappearance of starting material 1aBr (circles) and formation of nucleophilic substitution product 1aOCH<sub>3</sub> (triangles) during irradiation ( $\lambda = 254$  nm) of 1aBr in partially deoxygenated MeOH.



Figure 2. Formation of reduction product 1aH (circles) and oxidation product 3 (triangles) and their sum (squares) during irradiation ( $\lambda = 254$  nm) of 1aBr in partially deoxygenated MeOH.

for the rate constant of disappearance of RX, t is the time of irradiation,  $\Phi_d$  is the quantum yield of decomposition of RX, and  $I_0$  represents the intensity of the light absorbed by the starting material at time t = 0 in Einstein  $L^{-1} s^{-1}$ . [P]<sub>t</sub> is the concentration of product P in the photolysis mixture at time t,  $\Phi_P$  is the quantum yield of formation of product P. In Figures 1 and 2 the disappearance of vinyl bromide **1aBr** (R = OMe) and the formation of products **1aOCH<sub>3</sub>**, **1aH**, and **3** are

SCHEME 1

TABLE 1: Quantum Yields<sup>a</sup> of the PhotochemicalReactions of Compounds 1X in Argon-Saturated Methanol

	-				
compd	$\lambda_{\rm exc}$ (nm)	$10^3 \phi_{\rm D}$	$10^{3}\phi_{\rm OMe}$	$10^3 \phi_{\rm H}$	$\phi_{\mathrm{OMe}}/\phi_{\mathrm{H}}{}^{b}$
1aBr	254	140	109	10	11
	313	22	19	2	10
1bBr	254	51	42	7	6
	313	8	8	1	8
1cBr <sup>c</sup>	254	66	35	15	2
	313	8	5	2	3
1aCl	254	12	9	2	5
	313	1.4	1.4	0.2	7
1bCl	254	7	4	2	2
1cCl	254	11	4	5	1
	313	0.5	0.2	0.1	2
1cF	254	0.7	0	0.04	
	313	0	0	0	
1cI	254	110	81	5	16
	313	90	23	3	8

 ${}^{a}\phi_{\rm D}$  is the quantum yield of disappearance of starting material,  $\phi_{\rm OMe}$  the quantum yield of formation of vinyl ether product, and  $\phi_{\rm H}$  the quantum yield of formation of reduction products.  ${}^{b}$  This ratio corresponds to the heterolysis/homolysis ratio.  ${}^{c}$  Reported in ref 12.

graphically represented. From the slopes of such graphs the quantum yields for disappearance of 1X ( $\Phi_d$ ), formation of nucleophilic substitution product 1OCH<sub>3</sub> ( $\Phi_{OMe}$ ), formation of reduction product 1H ( $\Phi_H$ ), and formation of oxidation product 3 ( $\Phi_{Ox}$ ) were obtained. The values are reported in Tables 1 (reactions in *deoxygenated MeOH*) and 2 (reactions in oxygenated MeOH) and 2 (reactions were also performed in oxygenated MeCN containing 1 M MeOH and 10 mM Et<sub>4</sub>N<sup>82</sup>Br (see Table 2).

Effect of Oxygen. In the presence of oxygen the cationderived products 10CH<sub>3</sub> are still present but the radical-derived products 1H decrease and fluorenone (3) is formed instead (eq 1a versus 1b). The quantum yields of formation of the nucleophilic substitution products 10CH3 are somewhat smaller in oxygen-containing solutions than in deoxygenated irradiation mixtures, whereas the quantum yields of formation of fluorenone are somewhat larger than those of the reduction products 1H. The decrease in  $\Phi_{OMe}$  is generally exactly matched by the increase in  $\Phi_{Ox}$  relative to  $\Phi_H$  (Table 2 versus Table 1). This most probably results from the fact that the substitution products **10CH<sub>3</sub>** are slightly photolabile in the presence of  $O_2$  and are converted into 3 in a secondary photoreaction. The related enol ether compound 9-(methoxymethylene)fluorene has been reported to be very susceptible to photooxidation.<sup>21</sup> Also photolysis of p-chlorobenzyl chloride in MeOH yields products



TABLE 2: Quantum Yields<sup>a</sup> of the Photochemical Reactions of Compounds 1X in Oxygen-Saturated Methanol or Acetonitrile<sup>b</sup>

		$10^3\phi_{\rm D}$		$10^3 \phi_{ m OMe}$		$10^3 \phi_{\mathrm{ox}}$		10 <sup>3</sup> d	10 <sup>3</sup> ሌ
compd	$\lambda_{\rm exc} ({\rm nm})$	MeOH	MeCN	MeOH	MeCN	MeOH	MeCN	MeCN	MeCN
1aBr	254 313	100 18	22 2.3	55 14	1.4	22 1	6.6 0.7	22 2.9	23
1bBr	254 313	50 8		33 7		17 1		2.7	<i></i>
1cBr	254 313	62° 9°	43 5.3	28° 5°	8.4 1.7	22° 2°	8 0.6	6 0.9	14 2.6
1bCl	254 313	7 0.4		3 0.4		3 0.02			
1cI	254 313	150 130		59 26		39 20			

 ${}^{a} \phi_{D}$  is the quantum yield of disappearance of starting material,  $\phi_{OMe}$  the quantum yield of formation of vinyl ether products,  $\phi_{ox}$  the quantum yield of formation of fluorenone,  $\phi_{ex}$  that for exchange of <sup>79,81</sup>Br by <sup>82</sup>Br, and  $\phi_{ion}$  that for ionization of the bromides. <sup>b</sup> In the presence of 1 M MeOH and 10 mM Et<sub>4</sub>N<sup>82</sup>Br. <sup>d</sup> Reported in ref 12.

which result from photooxidation of the primarily formed p-chlorobenzyl methyl ether.<sup>22</sup> Indeed, upon independent irradiation of **1aOCH**<sub>3</sub> in oxygenated MeOH fluorenone is formed. Also formed is the methyl ester of p-methylbenzoic acid, which one expects as the product complementary to fluorenone upon photooxidation of the enol ether **1bOCH**<sub>3</sub>. However, in the irradiation mixtures of **1bBr** the methyl ester is present in a larger amount that could result from partial photooxidation of the vinyl ether **1bOCH**<sub>3</sub> alone. Another pathway to those products is esterification of the corresponding acid formed in the scavenging of the vinyl radical with oxygen.

The small effect of oxygen on the overall photoreactivity at both wavelengths of excitation means that oxygen quenching<sup>23</sup> of the reactive excited states populated at 254 and 313 nm is not an important process. This means that those states must be very short lived. One expects this to be the case for the S<sub>2</sub>, T<sub>2</sub>, and S<sub>1</sub> states but possibly not for the T<sub>1</sub> state. The excited state leading to the products is therefore probably not the lowest triplet state, a conclusion also reached on the basis of flash photolysis result (see below).

Effect of Wavelength of Excitation. The quantum yield data reported in Tables 1 and 2 show a pronounced effect of the excitation wavelength on the photoreactivity of compounds 1X in MeOH. The formation of both the vinyl cation-derived products 10CH<sub>3</sub> and the vinyl radical-derived products 1H and 3 is more efficient upon irradiation at 254 nm than at 313 nm. There is the possibility that such a wavelength dependence<sup>24</sup> is not inherent to the compounds under study but caused by selective excitation at the lower wavelength of an impurity which acts as a sensitizer,<sup>25,26</sup> by irradiation into a charge-transfer absorption band<sup>27</sup> of 1X with MeOH, or by wavelength-sensitive photolability or interconversion of the photoproducts. However, benzene, toluene, or acetone is not effective as a photosensitizer and the quantum yields of the photoreactions of 1cBr (R = H) are not influenced by the presence of extra 1cOCH<sub>3</sub>, 1cH, or 3 added to the irradiation mixture. Also the UV absorption spectra of 1X are completely insensitive to variation of the solvent from *n*-hexane to MeOH to MeCN. Finally, the compounds **10CH**<sub>3</sub> and 1H are photostable at both wavelengths of irradiation in deoxygenated MeOH; in oxygen-saturated MeOH 3 is photostable and, as discussed in the previous paragraph on the effect of oxygen, compounds 10CH<sub>3</sub> are slightly photolabile. Due to the relative extinction coefficients of 1X and 10CH<sub>3</sub> at 254 and 313 nm, however, the photolability will be more manifest at the shorter wavelength and lead to an apparent lower efficiency for the formation of vinyl cation-derived products at 254 nm, contrary to the effect of the wavelength of excitation observed. It is therefore concluded that the observed wavelength dependence is an intrinsic property of 1X.

The wavelength dependence possibly results from bond dissociation reactions from an upper excited state, populated at the lower wavelength of excitation, fast enough to compete with relaxation to the lowest excited state, which is not (or less) reactive. The following may be given as reasons for the different propensity of the lowest and higher excited states for bond cleavage: (a) the energy of the lowest excited state is too low for bond cleavage;<sup>28</sup> (b) cleavage from that state is impeded by an activation barrier which is overcome by excitation to a higher state;<sup>29</sup> (c) the electronic configuration of the lowest excited state is less suited for bond cleavage than that of a higher state; or (d) the different excited states populated at 254 and 313 nm may be the lowest excited states of different parts of a bichromophoric system.<sup>30</sup> Possibility d is certainly conceivable for 1X because due to steric hindrance the  $\alpha$ -aryl group is situated perpendicular to the 2,2'-biphenyldiyl group. Consequently the two moieties are not in conjugation and constitute separate chromophores. The various possibilities can only be distinguished after further study of the phenomenon of wavelength dependence for different types of vinyl halides. Such an investigation is in progress.

Previously, wavelength effects similar to the ones described here have been reported for radical formation in the reductive dehalogenation of 5-halouracils<sup>31,32</sup> and 2-bromo-4,4-dimethyl-2-cyclohexenone<sup>33</sup> and for the (heterolytic) photosolvolysis of certain types of benzoates.<sup>34</sup> In the former case the reactivity difference was ascribed to population of a reactive  $\pi - \pi^*$  state versus population of an unreactive  $n - \pi^*$  state, in the latter case to the occurrence of an intramolecular electron-transfer process.

Variation of the wavelength of excitation influences the quantum yields of formation of the ion and radical products to a different extent (Tables 1 and 2, see also laser results, section 2). The ratio of the radical to ionic processes is generally higher at 254 than at 313 nm.<sup>35</sup> This argues against the C-X bond cleavage mechanism being homolysis followed by electron transfer within the radical pair (eq 4), since in that case the partitioning to C<sup>•</sup> and C<sup>+</sup> occurs *after* the photoreaction and the ratio C<sup>•</sup>/C<sup>+</sup> should be independent of the wavelength of excitation.

$$\mathbf{RX} \xrightarrow{h\nu} \mathbf{RX^*} \to [\mathbf{R^*X^*}] \longrightarrow [\mathbf{R^*X^*}] \xrightarrow{(\mathbf{R^*X^-}] \to \mathbf{R^+} + \mathbf{X^-}}_{\mathbf{R^*} + \mathbf{X^*}}$$
(4)

Substituent Effect. The quantum yields of formation of the ion products  $10CH_3$  from the different para-substituted 1acBr and 1a-cCl increase in the order 1cX < 1bX < 1aX, i.e., they are proportional to the electron-donor properties of the para substituents:  $H < CH_3 < OCH_3$ . The thermally better stabilized cations are formed more efficiently in the photoreaction. However, the ratio of the quantum yields for ion product formation from 1cBr:1bBr:1aBr being 1:1.6:3.8 at 313 nm and 1:1.2:3.1 at 254 nm shows that there is no strong dependence on the nature of the para substituent. Probably the transition state in the bond heterolysis reaction is quite early. On the other hand, the quantum yields of formation of radical products 1H and 3 are rather independent of the substituent. Radical stabilization by the para substituent does not occur or is not important. The overall decrease in the ion/radical ratio (last column of Table 1) in going from  $OCH_3 \rightarrow CH_3 \rightarrow H$  is thus due to the decrease in the quantum yield for ion product formation in this direction. Unfortunately, a rigorous Hammett treatment of the quantum yields of ion product formation as a function of a substituent constant is not possible. This would require knowledge of the lifetimes of the excited states involved  $(\Phi_{\text{reaction}} = k_{\text{reaction}} \tau^{-1}).$ 

The increase in the amount of ion product with increasing electron donation of the para substituent not being accompanied by a decrease in the radical products argues against a mechanism of the photoreaction (eq 4) in which  $C^+$  and  $C^\bullet$  are formed from a common radical pair precursor. In that case the yields of ion and radical products should be complementary. However, the data are in line with a mechanism in which both homolysis and heterolysis occur in a parallel fashion starting from "the electronically excited state"<sup>36</sup> (eq 5).

$$RX \xrightarrow{h\nu} RX^* - \overbrace{[R^*X^*] \to R^* + X^*}^{\rightarrow R^* X^*}$$
(5)

Substituent effects similar to the one described here have also been observed for the ratio of homolytic to heterolytic cleavage of the carbon-halogen bond in the photolysis of triarylvinyl halides in acetic acid,  $^{6,37}$  and also for benzhydryl halides in MeCN, for which a mechanism as in eq 5 was proposed.<sup>9</sup>

Leaving Group Effect. The quantum yields for formation of the ion products  $10CH_3$  follow the order -1cI > 1cBr > 1cCl $\gg$  1cF, i.e., that of the leaving group abilities of the halides observed for thermal  $S_N1$  reactions in protic solvents:  $I^- >$  $Br^- > Cl^- > F^{-.38}$  The quantum yields of formation of the radical product 1cH decrease in the order Br > Cl > F (Table 1), those for formation of the radical product 3 (in oxygenated solution) follow the order I > Br > Cl (Table 2), as expected on the basis of the C-X bond dissociation energies.<sup>39</sup> However, in *deoxygenated* MeOH 1cI is an exception, the order I < Brnot reflecting bond strength. The reason for this discontinuity in leaving group effects on radical formation in the absence of O<sub>2</sub> is not clear.<sup>40</sup> As the quantum yields of radical product formation vary less with the nature of the halogen than the quantum yields of ion product formation, the ratio ion:radical decreases in going from  $I \rightarrow Br \rightarrow Cl$ . The fluoro compound 1cF is barely photoreactive. C-F bond cleavage is energetically not feasible. The C-F bond dissociation energy is considerably higher (119 kcal/mol)<sup>41</sup> than the energy of the exciting radiation (254 nm = 112 kcal/mol). The leaving group orders Br > Cl are also found for the p-methoxy and p-methyl substituted compounds 1aBr-1aCl and 1bBr-1bCl.

The quantum yields of ion formation and also the ratio of the ion products to radical products as function of the halide correlate with the  $pK_a$  values of the corresponding conjugate acids HX ( $pK_a(HX)$  {X = I, Br, Cl, F} = -8, -8, -7, and 3.45)<sup>42</sup> and not with the electron affinities of the halogen atoms X<sup>•</sup> (EA(X<sup>•</sup>) = 3.06, 3.36, 3.61, and 3.40 eV)<sup>43</sup> or the reduction potentials in MeCN of X<sup>•</sup> (0.7, 1.2, 1.6, and 2.4 V/NHE).<sup>44,45</sup> This indicates once more that the photoreactions under study occur via direct heterolysis, in competition with homolysis, from the electronically excited state (eq 5) and not via homolysis followed by electron transfer (eq 4).

Analogous leaving group effects as described here have been reported by Kropp for 1-bromo- and 1-iodocyclohexene<sup>46</sup> and for (halomethylene)cycloalkanes.<sup>47</sup> The iodides afforded higher ratios of ionic to radical products than the corresponding bromides, and the chlorides yielded only radical products. Similar phenomena were observed in the photolysis of benzhydryl halides and explained in terms of homolysis and heterolysis occurring *in parallel.*<sup>9</sup> Interestingly, Sket and Zupan<sup>48</sup> and Kitamura et al.<sup>49</sup> observed a completely opposite leaving group effect in the photolysis of 1,1-diphenyl-2-haloethenes and 1,1diaryl-2-halopropenes, respectively. With these compounds the ratio ion:radical products decreases in the order Cl > Br > I, in parallel with the electron affinity of X<sup>•</sup>. Other researchers<sup>46–49</sup> propose homolysis followed by electron transfer (eq 4) as mechanism.

b. Acetonitrile as Solvent. Compounds 1aBr and 1cBr were also irradiated at both 254 nm and 313 nm in aerated MeCN containing 10 mM [82Br]-labeled tetraethylammonium bromide and 1 M MeOH. Under these reaction conditions isotopically exchanged 1-82Br is formed next to compounds 10CH<sub>3</sub> and 3. The sum of the quantum yields of exchange (= formation of labeled 1X) and of formation of 10CH<sub>3</sub> represents the quantum yields of formation of ionic product ( $\Phi_{ion} = \Phi_{ex} + \Phi_{OCH3}$ ) (Table 2). The overall photoreactivity is somewhat lower in MeCN than in MeOH, solvents of comparable polarity. The presence of the heavy atom containing Et<sub>4</sub>NBr salt may have to do with this, due to conversion of (reactive) excited singlet into (unreactive) triplet. However, the laser photolysis results (section 2), which are obtained without Et<sub>4</sub>NBr, also show MeOH to be the superior solvent with respect to supporting the photocleavage of the C-Br bond (see Figure 4 parts a and b). The conclusion is thus that the difference between MeCN and MeOH with respect to the efficiency of photocleavage is due to a solvent effect. A further support is the behavior in mixtures of MeCN and MeOH (Figure 4).

With regard to the variation of  $\Phi_{ion}$  and of the ratio ion: radical product with variation of the wavelength of excitation and of the para substituent the same trends are observed as in MeOH. At the shorter wavelength both  $\Phi_{ion}$  and  $\Phi_{H}$  are larger and relatively more radical product is formed. Also upon changing R = H to  $R = OCH_3$  more ionic product is produced.

From the ratio of the quantum yields of formation of labeled **1X** and of **1OCH**<sub>3</sub>, the selectivity ( $\alpha$ ) of the photogenerated vinyl cation toward the nucleophiles bromide ion and MeOH can be calculated:  $\alpha = (\Phi_{ex}/\Phi_{OCH3})$  ([MeOH]/[Et<sub>4</sub>NBr]). The  $\alpha$ -values for **1a**<sup>+</sup> (R = OCH<sub>3</sub>) (1.1 × 10<sup>3</sup> at  $\lambda$  = 313 nm, 1.5 × 10<sup>3</sup> at  $\lambda$  = 254 nm) are larger than those for **1c**<sup>+</sup> (R = H) (50 at  $\lambda$  = 313 nm, 70 at  $\lambda$  = 254 nm) in accordance with the reactivity selectivity principle: the better stabilized ion displays the higher selectivity.

The  $\approx$ 30% higher selectivities at the shorter wavelength are most probably an artifact. As already discussed in the paragraph on the effect of oxygen, compounds **10CH**<sub>3</sub> are somewhat photolabile in aerated solution. Due to the relative extinction coefficients of **1X** and **10CH**<sub>3</sub> at 254 and 313 nm, products **10CH**<sub>3</sub> are more susceptible to this secondary photoreaction at the shorter wavelength. This leads to underestimation of  $\Phi_{\text{OCH}3}$  and thus overestimation of  $\alpha$ . In flash photolysis experiments this problem with secondary photoreactions does not occur. The selectivity toward Br<sup>-</sup> and MeOH of the vinyl cation **1a**<sup>+</sup> is independent of whether it is produced by 248- or by 308-nm light (see section 2). It is very interesting that the ratio of the rate constants for reaction of **1a**<sup>+</sup> with Br<sup>-</sup> and

TABLE 3: Rate Constants k for Reaction of the Vinyl Cations  $1a^+$  (R = MeO) and  $1b^+$  (R = Me) with Nucleophiles Nu in Acetonitrile at  $20 \pm 1$  °C<sup>a</sup>

	<i>k</i> /M <sup>-1</sup> s <sup>-1</sup>			
Nu	R = MeO	R = Me		
solvent MeOH	$5.0 \times 10^{7 b}$	$> 1 \times 10^{8 b}$		
solvent MeCN	$1.4  imes 10^{5 \ b}$	$1.5 \times 10^{7 b}$		
$H_2O$	$2.5 \times 10^{5}$	$2.9 \times 10^{7}$		
MeOH	$1.5  imes 10^{6}$	$1.3 \times 10^{8}$ c		
EtOH	$1.2 \times 10^{6}$	$9.7  imes 10^{7}$ c		
i-PrOH	$6.5 \times 10^{5}$	$7.1 \times 10^{7}$		
t-BuOH	$7.7 \times 10^{4 d}$	$1.4 \times 10^{7}$		
THF	$2.5 \times 10^{6}$	$1.4 \times 10^{8}$		
1,4-dioxane	$6.2 \times 10^{5}$	$6.0 \times 10^{7}$		
Cl-	$1.4  imes 10^{10}$	$1.7 \times 10^{10}$		
Br <sup>-</sup>	$1.7 \times 10^{10}$	$3.2 \times 10^{10}$		
	$7.9 \times 10^{9} e$			
NO <sub>3</sub> -	$5.8 \times 10^{9}$	$1.4 \times 10^{10}$		
MeCO <sub>2</sub> H	$1.5 \times 10^{4 f}$	$5.9 \times 10^{6}$		

<sup>*a*</sup> The rate constants are the average from determinations with  $\lambda_{exc}$  = 248 and 308 nm. Error limits ±10%. <sup>*b*</sup> Rate constant for decay in the solvent. Unit, s<sup>-1</sup>. <sup>*c*</sup>  $\lambda_{exc}$  = 248 nm. <sup>*d*</sup> Error limits ±20%. <sup>*e*</sup> In MeCN containing 1 M MeOH. <sup>*f*</sup> From the slope of the linear part of the  $k_{obsd}$  vs [CH<sub>3</sub>CO<sub>2</sub>H] plot (see Figure 3d) in the range 1–4.5 M CH<sub>3</sub>CO<sub>2</sub>H.

MeOH thus determined is  $10^4$  (see Table 3), whereas that measured by product analysis, which refers to MeCN containing 1 M MeOH ( $\approx$ 5 vol %) and 10 mM Br<sup>-</sup>, is only 1.1 × 10<sup>3</sup> (see above). In order to resolve this discrepancy, the rate constant for reaction of 1a<sup>+</sup> with Br<sup>-</sup> was measured in MeCN containing 1 M MeOH. The number obtained from  $k_{obsd}$  versus  $[Br^-]$  plots at  $[Br^-] \le 3 \text{ mM}$  is  $7.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , i.e., only half the value in pure MeCN,  $1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (Table 3). The reason for the difference in reactivity may be specific solvation of the ions,  $1a^+$  and  $Br^-$ . Above  $\approx 3$  mM, an ionic strength effect on the reaction rate between  $1a^+$  and  $Br^-$  is clearly visible by "leveling" in the  $k_{obsd}$  versus [Br<sup>-</sup>] plots. As a result, the "effective" rate constant for reaction between  $1a^+$ and Br<sup>-</sup> in MeCN containing 1 M MeOH and 10 mM Br<sup>-</sup> is lowered: it was determined to be  $5.3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. In contrast, the rate constant for reaction of  $1a^+$  with MeOH, k = $1.5 \, \times \, 10^{6} \; M^{-1} \; s^{-1}$  , is essentially independent of [MeOH] in the range 0-20 vol %, see Figure 5. With these numbers, the selectivity,  $\alpha$ , results from the rate constants as  $k(Br^{-})/k(MeOH)$ =  $3.5 \times 10^3$ , which is 3 times larger than the value from product analysis  $(1.1 \times 10^3)$ , see above). At present, the reason for this difference is not clear.

2. Laser Flash Photolysis Results. a. Compound laBr (R = OMe). The time-resolved absorption spectra recorded on 248-nm photolysis of **1aBr** in deoxygenated MeCN are shown in Figure 3. At 0.2 µs after the pulse, there is a strong band with  $\lambda_{\rm max}$  at 355 nm, which decays rapidly (lifetime  $\approx 7 \ \mu s$ ) in a predominantly but not purely exponential fashion (see inset b),<sup>50</sup> and a weak band at  $\approx$ 305 nm, whose intensity is not much reduced at 33 µs, at which time the band at 355 nm has almost completely disappeared. In addition, there is negative  $\Delta OD$  at 260 nm, where the parent absorbs, and a very narrow positive band at 250 nm. The rate of decay of the latter is the same as that of the 355-nm band ( $k = 1.5 \times 10^5 \text{ s}^{-1}$ ). Below 240 nm, there was insufficient analyzing light intensity to see signals. The amplitudes of the laser pulse induced OD changes (formation and depletion) were found to be proportional to the laser dose in the range 3-40 mJ/pulse,<sup>51</sup> which means that the processes responsible are monophotonic.

On introduction of oxygen into the solution  $([O_2]_{\text{saturation}} = 8.2 \text{ mM})$ , the 305-nm band was completely gone starting at 0.2  $\mu$ s after the pulse, whereas the other bands, including the negative band showing the depletion of parent, were essentially



Figure 3. Absorption spectra observed on 248-nm photolysis of 1aBr (30  $\mu$ M) in Ar-saturted MeCN. In inset a is shown the situation in the presence of 8.2 mM O<sub>2</sub>, and in b the decay of the absorption at 355 nm, due to the cation 1a<sup>+</sup> (the decay rate is not influenced by O<sub>2</sub>). Inset c displays the rate enhancement of decay of cation (measured in the presence of O<sub>2</sub>) due to reaction with Cl<sup>-</sup>, and inset d shows the rate change due to the presence of acetic acid (solution containing O<sub>2</sub>).

unaffected (see Figure 3, inset a). Also uninfluenced by O<sub>2</sub> were the lifetimes of the 250- and 355-nm bands. Several conclusions can be drawn from these observations: (a) since the photochemical decomposition of **1aBr** is not influenced by  $O_2$  (this is in agreement with the product analysis data, section 1), the excited state leading to the transients is probably not a triplet. (b) The 250- and 355-nm bands cannot be due to a radical, since there is no reaction with  $O_2$ . (c) In contrast, based on its reactivity with  $O_2$ , the 300-nm species is likely to be a radical. The rate constant for reaction of this radical with O<sub>2</sub> is  $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , as determined by the O<sub>2</sub>-induced decay  $(k = 1.85 \times 10^7 \text{ s}^{-1})$ . In O<sub>2</sub>-saturated solution, after complete decay of the 355-nm species and of the radical, a weak absorption with a center at  $\approx$ 390 nm remains (see inset a, 33  $\mu$ s). This is assigned to the peroxyl radical formed by addition of O<sub>2</sub> to the vinyl radical (see also later). That a peroxyl radical should have an absorption band at such a long wavelength is rather exceptional, since the band positions of simple peroxyl radicals<sup>52</sup> such as alkO<sub>2</sub>• are typically at  $\approx 250$  nm.<sup>53</sup>

The species responsible for the 250- and 355-nm bands was found to react rapidly with nucleophiles (Nu) such as alcohols, ethers, and halides and is therefore identified as a cation. As an example for the reactivity, in inset c is shown the acceleration of the (pseudo-first-order) rate  $k_{obsd}$  of decay of the cation (measured at 355 nm) observed on introducing increasing concentrations of Cl<sup>-</sup>. The dependence of  $k_{obsd}$  for cation decay on [Nu] follows the equation

$$k_{\rm obsd} = k_0 + k_{\rm Nu} [\rm Nu] \tag{6}$$

where  $k_0$  is the rate in the absence of Nu (in the case of nucleophilic solvents,  $k_0$  is identical to the pseudo-first-order rate constant  $k_s$  for reaction with solvent, see later) and  $k_{Nu}$  the second-order rate constant for reaction of the transient with Nu. The rate constants determined for reaction of a series of nucleophiles, obtained from linear  $k_{obsd}$  vs [Nu] plots, were found to be independent of the wavelength of excitation. The kinetic data are presented in Table 3.

In inset d is shown the effect of acetic acid on the exponential decay of the cation. It is evident that small concentrations of acetic acid *increase* the lifetime of the cation (decrease the decay rate) by  $\approx 10\%$ , whereas at concentrations  $\geq 1.5$  M the lifetime



decreases. A similar effect has previously been seen with other vinyl cations.<sup>54</sup>

The results so far described are explained in terms of photohomolysis and -heterolysis of the vinyl bromide to yield the vinyl radical  $1^{\circ}$  (absorpting at 305 nm) and the vinyl cation  $1^{+}$  (absorbing at 250 and 355 nm) (Scheme 2, eq 7).

Deoxygenated solutions of **1aBr** in MeCN were also photolyzed with 308-nm light. The spectrum observed did not contain any evidence for radical; it was identical to that on 248nm photolysis in the presence of  $O_2$  which scavenges the radical **1a**° produced in this circumstance (see Figure 3, inset b).<sup>55</sup> Thus, in terms of the behavior of the photochemically responsible state, excitation with 308-nm light leads to more selectivity than in the case of the higher energy 248-nm light, in agreement with the product analysis data, see section 1, Table 2. In comparison, in MeOH as solvent, there was also radical on excitation with 308 nm (see Figure 4a), but the relative amount was less than that on photolysis with 248-nm light (see below).

The extinction coefficients of  $1a^+$  and  $1a^\cdot$  were measured in MeCN containing 1 M MeOH by comparing the initial optical densities at the  $\lambda_{max}$  values of the species (350 and 298 nm), after excitation with 248-nm light, with the  $\Delta$ OD values at 600 nm for  $e_{aq}^-$  production ( $\phi = 0.29$ )<sup>56</sup> from a deoxygenated aqueous KI solution. Assuming that the quantum yields for formation of  $1a^+$  and  $1a^\bullet$  are the same as those for formation of the corresponding stable products (0.023 and 0.0066, see, Table 2) and using  $\epsilon(e_{aq}^-)_{600 \text{ nm}} = 1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,<sup>57</sup> the extinction coefficients of  $1a^+$  and  $1a^\bullet$  are calculated to be 1.3  $\times 10^5$  and  $1.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. A pronounced similarity in the extinction coefficients of radicals and the corresponding cations has previously been found<sup>9</sup> for benzhydryl systems.<sup>58</sup>

Compound **1aBr** was also photolyzed in MeOH as solvent, using 248- or 308-nm light. Under both conditions, the radical and the cation were clearly present. In MeOH, the effect of wavelength of excitation on the cation:radical ratio is similar to that in MeCN: on excitation with the less energetic 308-nm light, there is less homolysis of the C-Br bond compared to its heterolysis (by the factor 2.3), i.e., the selectivity of the bond cleavage is increased compared to the situation with  $\lambda$ (excitation) = 248 nm. While the lifetime of the radical is similar in MeOH, that of the cation is much reduced compared to the situation in MeCN, k(decay of cation) being 5.0 × 10<sup>7</sup> s<sup>-1</sup>, compared to 1.4 × 10<sup>5</sup> s<sup>-1</sup>. The radical reacts with O<sub>2</sub> with  $k = 1 × 10^9$ M<sup>-1</sup> s<sup>-1</sup>, giving rise to an absorption at ≈390 nm (as in MeCN, see above), which is assigned to the vinylperoxyl radical **1aO<sub>2</sub>**• (see later).<sup>59</sup>

In the solvent MeOH, as the cation decays, a species is formed

with  $\lambda_{max}$  at 335 nm and another (weaker) maximum at 298 nm, with a rate similar to the decay of the cation. This species has *no* reactivity with O<sub>2</sub> or nucleophiles, and it does not at all decay (observed up to the millisecond time scale). Since the spectrum of this permanent species is identical to that of **1aOCH<sub>3</sub>**, as measured with a recording spectrophotometer, it is obvious that the 335- and 298-nm absorptions are due to this enol ether, whose formation as a stable product has been described in section 1.

The effect of solvent composition (MeOH:MeCN) was tested on (a) the amount of heterolysis and homolysis, as measured right after the pulse, and (b) on the rate of decay of the cation. The results are shown in Figures 4 and 5, respectively.

Concerning yields, it is evident from Figure 4a and b that, starting with pure MeCN, at *low* MeOH contents the yields of both radical *and* cation increase with increasing [MeOH], whereas at *high* MeOH concentrations the yields decrease. The optimum for radical production is at 50-70% MeOH, that for cation production at 20-40%. It is interesting that the cation: radical *ratio* decreases with increasing [MeOH], see Figure 4c. At low [MeOH], the decrease is very drastic (Figure 4c), and it is the increase in *radical* yield which contributes strongly to this (Figure 4b). In pure MeCN, the cation:radical ratio shown in Figure 4c is probably a lower limit since the  $\Delta$ OD measured at  $\lambda_{max}$ (radical) is likely to contain contributions due to cation.

Concerning *reaction rate*, it is clear from Figure 5 that the rate constant for decay of cation increases with increasing MeOH content, with initially a linear dependence from which a rate constant for reaction of  $1a^+$  with MeOH in MeCN can be obtained (see Table 3). As the solvent approaches pure MeOH, the rate of cation decay increases *more* than linearly. In pure MeOH, the lifetime of  $1a^+$  is shorter than that in MeCN by the factor 360, see Table 3.

Quite different is the effect of *water* on the lifetime of the cation (Figure 6). At low concentrations of water ( $\leq 0.8$  M),  $k_{obsd}$  for cation decay increases linearly with [H<sub>2</sub>O]. Above 0.8 M, however, the increase levels off and at higher water contents ( $\geq 25\%$ ) there is a pronounced plateau in the  $k_{obsd}$  versus concentration dependence, i.e., the lifetime of the cation becomes independent of [H<sub>2</sub>O]. This is quite interesting since the nucleophilicity of water—MeCN mixtures is expected to *increase* with water content. Analogous phenomena have been previously seen with other cations: in the case of the  $\alpha, \alpha$ -dimethoxybenzyl cation there is even an *increase* of cation lifetime on increasing the concentration of water as a nucleophilic cosolvent.<sup>60</sup> Observations of this kind are an example of how dangerous it may be to predict the lifetime of a cation



Figure 4. The effect of solvent composition (MeCN/MeOH) on (a) the yield of radical, (b) the yield of cation, measured immediately after the pulse, and (c) the [cation]:[radical] ratio (inset: 5-100% MeOH), calculated using the  $\epsilon$  values given in the text. Photolysis with 308-nm light ( $\approx$ 10 mJ/pulse), [1aBr] = 0.12 mM. The  $\Delta$ ODs are per cm and have been normalized to a 100 mJ pulse.



Figure 5. The effect of solvent composition on the rate of decay of  $1a^+$  (measured at 340–350 nm) in MeCN–MeOH mixtures. [1aBr] = 0.1 mM.  $\lambda_{exc} = 308$  nm.



Figure 6. Effect of water content on the rate of decay of  $1a^+$  in MeCN. [1aBr] = 55  $\mu$ M,  $\lambda_{exc}$  = 248 nm. Inset: at low water content, the relation between  $k_{obsd}$  and [H<sub>2</sub>O] is linear.

in a particular solvent from bimolecular reactivity data in a different solvent.

When **1aBr** was photolyzed in the less polar solvent CH<sub>2</sub>-Cl<sub>2</sub>, only the radical (**1a**<sup>•</sup>;  $\lambda_{max} = 300$  nm) was seen (at  $\ge 20$  ns after the pulse), from which it might be concluded that in this circumstance photodecomposition of the vinyl bromide proceeds exclusively by homolysis. However, the nondetectibility of cation may also be due to its lifetime being  $\le 20$  ns, due to very rapid combination with the anion. From the decay of **1a**<sup>•</sup> at 300 nm or the buildup of **1aO<sub>2</sub>**<sup>•</sup> at 390 nm ( $k = 1.1 \times 10^7$  s<sup>-1</sup>),  $k(\mathbf{1a}^{\bullet} + O_2) = 1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>61</sup>

b. Compounds 1bBr and 1bCl (R = Me). Upon 248-nm photolysis of 1bBr in MeCN in the absence of O<sub>2</sub>, two transients



Figure 7. Absorption spectra of transients produced on 248-nm photolysis of a 0.05 mM solution of **1bBr** in MeCN saturated with Ar (triangles, recorded 75 ns after the pulse; squares, 16  $\mu$ s) or O<sub>2</sub> (circles, 375 ns). Insets: decay of **1b**<sup>•</sup> (a) in the absence of O<sub>2</sub> and (b) with O<sub>2</sub> present (saturated). In inset c the concomitant buildup of **1bO<sub>2</sub><sup>•</sup>** is shown. In inset d, the decay of **1b**<sup>+</sup> is exhibited (O<sub>2</sub> saturated).

were observed (see Figure 7). One transient, which is quite long lived in the absence of  $O_2$  (see inset a) but not in its presence (see inset b), has  $\lambda_{max}$  at 275 nm. This transient is identified as the radical, 1b, produced by photohomolysis from 1bBr. Synchronous with the decay of the vinyl radical, 1b, by reaction with  $O_2$  (see inset b), a species absorbing at  $\approx 380$ nm was produced (see inset c). On the basis of this kinetic behavior, the 380-nm species is identified as the vinylperoxyl radical, formed by addition of O<sub>2</sub> to 1b<sup>•</sup> ( $k = 2 \times 10^9 \text{ M}^{-1}$ s<sup>-1</sup>). The other species has a band with  $\lambda_{max}$  at 340 nm and is very short lived, decaying exponentially (see inset d) with k = $1.5 \times 10^7$  s<sup>-1</sup>, and it does not react with O<sub>2</sub>. The 340-nm transient does, however, show pronounced reactivity with nucleophiles such as halides and alcohols (for the rate constants, see Table 3). It is thus evident that this species is a cation, obviously the vinyl cation  $1b^+$ , produced by photoheterolysis from 1bBr. In agreement with this assignment is the fact that the 340-nm species is not observable in (the nucleophilic) MeOH as solvent. If it is assumed that the rate enhancement for decay of  $1b^+$  in going from MeCN to MeOH is the same as that (360) for  $1a^+$ , the lifetime of  $1b^+$  in MeOH is calculated to be 0.2 ns, i.e., only 1% of the 20-ns pulse width of the laser apparatus. In MeCN solvent, the signal intensity ratio  $1b^+:1b^-$  was  $\approx 0.6$ , as measured immediately after the pulse.

On photolysis of **1bBr** with 308-nm light, **1b**<sup>+</sup> and **1b**<sup>•</sup> were also formed, however, the ratio **1b**<sup>+</sup>:**1b**<sup>•</sup> was 0.8, i.e., larger than with  $\lambda_{exc} = 248$  nm, which shows that the longer wavelength leads to comparatively more heterolysis, in agreement with the product analysis data (see Tables 1 and 2).

The cation,  $1b^+$ , and the radical,  $1b^{\bullet}$ , were also observed on photolysis of the vinyl *chloride*, 1bCl, with 248-nm light, but not with light at 308 nm. In this case the ratio of the band intensities of the cation and of the radical, as measured immediately after the pulse, was 0.6, somewhat smaller than on 308-nm photolysis of the bromide (see above). On addition of O<sub>2</sub> to the solution, the 380-nm band of  $1bO_2^{\bullet}$  was seen, with exactly the same shape as in the case of 1bBr as precursor.

c. Compounds 1cCl, -Br, and -I (R = H). On photolysis of these compounds in MeCN with 248-nm light, a species characterized by a band with  $\lambda_{max}$  at 275 nm and a shoulder at  $\approx$ 300 nm was observed. The 275-nm species was found to react rapidly with O<sub>2</sub> and is thus identified in terms of the radical 1c<sup>•</sup>, produced by photohomolysis of the precursors. In the  $O_2$ containing solutions ( $[O_2] = 8.2 \text{ mM}$ ), as the radical decayed, a species characterized by a broad band between 340 and 430 nm with  $\lambda_{\rm max} \approx 380$  nm developed with the same rate, k = 2.0 $\times 10^7$  s<sup>-1</sup>, from which the rate constant from reaction of O<sub>2</sub> with 1c<sup>•</sup> is calculated to be  $2.4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. With the bromide and the iodide, exactly the same observations were made on photolysis with 308-nm light. In contrast, with the chloride, only a very weak signal was seen on photolysis with this wavelength, indicating that there is essentially no photoreaction.

In order to see whether there was any spectroscopic evidence for the cation  $1c^+$ , the cation scavenger MeOH (1 M) was added to a solution of 1cBr in MeCN. The spectrum observed on photolysis with 248- or 308-nm light was exactly the same as that in the *absence* of MeOH. Since, on the basis of the product analysis data (Tables 1 and 2), heterolysis does occur, the failure to see  $1c^+$  means that its lifetime in MeCN is smaller than the 20-ns pulse width. This lifetime can be estimated from the data of Table 3 using a Hammett consideration, albeit with only two points (with  $\sigma^+$  for MeO and Me), to be 3 ns.

d. Reactions of Cations  $1a^+$  and  $1b^+$  with Nucleophiles. The second-order rate constants for reaction of the vinyl cations  $1^+$ (R = MeO, Me) with nucleophiles Nu, as obtained from the slopes of the linear  $k_{obsd}$  versus [Nu] plots, are collected in Table 3. Within experimental error  $(\pm 10\%)$ , the rate constants obtained were independent of the wavelength of excitation (248 and 308 nm). Concerning the cation  $1a^+$  (R = MeO), its lifetime in MeCN is 7 µs, which corresponds to a pseudo-firstorder rate constant for decay of  $\approx 1.4 \times 10^5 \text{ s}^{-1}$ . The rate constants for reaction with the halide anions are  $\approx 2 \times 10^{10}$  $M^{-1}$  s<sup>-1</sup>, a value which represents the diffusion-controlled limit in MeCN.<sup>62,63</sup> Diffusion-controlled reaction with halides was also observed for 4-substituted benzhydryl cations.<sup>64</sup> The value for NO<sub>3</sub><sup>-</sup> (5.7  $\times$  10<sup>9</sup>) is less than diffusion control but it is still very high, whereas the values of 10<sup>5</sup> to 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> for water, the simple alcohols, and ethers show that these reactions are activation controlled. The number for THF is higher than that for dioxane. This finding is in agreement with previous observations relating to other cations.<sup>10b,65</sup> The reason for the lower reactivity of dioxane is that this ether is a weaker base and nucleophile, as compared to THF, due to the -I effect of the second oxygen in the ring. Concerning the alcohols, there is a systematic decrease of reactivity in going from MeOH to t-BuOH, the difference between MeOH and t-BuOH corresponding to a factor of 20, very similar to that<sup>10b</sup> observed with triarylvinyl cations. Since the basicity of the alcohols increases in this direction, the reduction in reactivity must be due to increasing steric crowding in the encounter complex. It is interesting that the reactivity of THF (2.5  $\times$  10<sup>6</sup>) is larger than that of ethanol  $(1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$ . This may indicate that in the case of the reaction with the alcohol, as the  $C^+-O-H$ 



Figure 8. Time resolved absorption spectra observed on 248-nm photolysis of 0.16 mM 2aBr in deoxygenated MeCN. Insets: a, decay of  $2a^+$  measured at 355 nm; b, dependence of  $k_{obsd}$  for decay of  $2a^+$  on added [MeOH].

TABLE 4: Rate Constants k for Reaction of  $Me_2C=C^+-C_6H_4-p-OCH_3$  (2a<sup>+</sup>) with Nucleophiles Nu in Acetonitrile at 20 ± 1 °C

Nu	$k/M^{-1} s^{-1}$	Nu	$k/M^{-1} s^{-1}$
CH <sub>3</sub> CN	$1.3 \times 10^{6 a}$	t-BuOH	$7.7 \times 10^{5}$
MeOH	$1.3 \times 10^{7}$	THF	$1.7 \times 10^{7}$
EtOH	$8.8  imes 10^{6}$	Cl-	$1.6 \times 10^{10}$
2-PrOH	$5.4 \times 10^{6}$	$NO_3^-$	$9.3 \times 10^{9}$

<sup>*a*</sup> Unit  $s^{-1}$ .

bond is formed, there is little deprotonation from O-H in the transition state. If there were deprotonation (with "instantaneous" solvation of the proton), this would probably lower the energy of the transition state and thus increase the reaction rate for the alcohol.

Concerning  $\mathbf{1b}^+$  (R = Me), from the data in Table 3 it is obvious that this cation is much more reactive than  $\mathbf{1a}^+$  (R = MeO). The rate constant for reaction with solvent,  $k_S$ , is 100 times larger, and the same factor applies, on the average, to the difference in reactivity with added nucleophiles such as the alcohols and ethers. As expected for diffusion-controlled reactions, the values for the halides are not increased on increasing the electron deficiency of the cationic center, i.e., in going from R = MeO to R = Me.

e. Compounds 2Br. Since these compounds have essentially no absorption at 308 nm, the irradiations of solutions of 2Br in MeCN were performed with 248-nm light. In Figure 8 are shown the time-dependent absorption spectra observed in the case of 2aBr (R = MeO) in the absence of oxygen. There is only one band ( $\lambda_{max} = 338$  nm), which decays exponentially with  $k (=k_s) = 1.3 \times 10^6 \text{ s}^{-1.66}$  Introduction of oxygen (8.2 mM) to the solution had absolutely no effect on the shape of the absorption spectrum or the lifetime of the species, from which it is concluded that the species is not a radical, i.e., that 2aBr does not undergo photohomolysis. Small concentrations of nucleophiles such as Cl<sup>-</sup> or alcohols lead to appreciable acceleration of the decay of the 338-nm band, from which it is concluded that it is a cation. Obviously, it is  $2a^+$ , produced by photoheterolysis from **2aBr**. From the slopes of the linear  $k_{obsd}$ -(cation decay) versus [Nu] plots the bimolecular rate constants presented in Table 4 were obtained.<sup>67</sup> The reactivity of  $2a^+$ with the alcohols, which decreases in going from MeOH to t-BuOH as in the case of  $1a^+$  and  $1b^+$ , is in between that of  $1a^+$  and  $1b^+$ . With a value of  $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , the rate constant for reaction with Cl<sup>-</sup> is limited by diffusion, whereas that for reaction with  $NO_3^-$  is slightly below the diffusion limit. The compounds 2bBr (R = Me) and 2cBr (R = H) were also photolyzed. In these cases, rather similar transients were observed which reacted with O<sub>2</sub> but had *no* reactivity with MeOH or EtOH (0.1-1 M). This is in sharp contrast to the case of 2aBr (R = MeO). From this observation it is concluded that the observed species are not the cations  $2b^+$  or  $2c^+$ . Thus, 2bBr and 2cBr seem to react by photohomolysis. If photoheterolysis does occur, the resulting cations have a lifetime less than the laser pulse width (20 ns). The lifetime of  $2b^+$  can be estimated, using the effect of MeO and Me on  $1^+$  as a model system (reactivity difference  $1a^+/1b^+ = 1/100$ , see Table 3), to be 8 ns.

f. Other Vinyl Halides. The compound PhCH=CCl<sub>2</sub> was studied in MeCN, with 248-nm light for excitation. A transient with  $\lambda_{max} = 370$  nm was formed, which decayed exponentially with  $k = 1.0 \times 10^6 \text{ s}^{-1}$ . This decay was *not* influenced by O<sub>2</sub>, and the species can therefore not be a triplet or radical. However, there was an acceleration of the rate of decay on addition of nucleophiles such as chloride ( $k_{Cl} = 2.8 \times 10^9 \text{ M}^{-1}$  $s^{-1}$ , which is a high value but clearly below the diffusion limit of 2 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>), bromide ( $k_{Br} = 2.7 \times 10^7 M^{-1} s^{-1}$ ),<sup>68</sup> or MeOH ( $k_{MeOH} = 3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), and on the basis of this behavior the 370-nm species is identified as a cation, name PhCH=CCl<sup>+</sup>. Since on addition of  $O_2$  there were some weak changes in the spectral appearance in the 300-nm region, it is concluded that C-Cl homolysis is an additional, albeit probably only minor path in the 248-nm photolysis of  $PhCH=CCl_2$  in MeCN.

### 3. Summary and Conclusions

It has been shown that photolysis of the vinyl halides 1X in MeOH or MeCN results in heterolysis and homolysis of the C-X bond to give vinyl cations and vinyl radicals, which were identified (a) by their stable products from the reaction with MeOH and (b) directly, using time-resolved laser photolysis, via their characteristic absorptions and reactivities. It was found that the cationic leaving group property of the moiety 1 increases with increasing electron donor strength of the substituent on 1, a behavior which is analogous to that in thermal solvolysis reactions. Concerning the anionic leaving group properties of the halides X, they are more related to the acidities of the conjugate acids HX than to the electron affinities or reduction potentials of the halogen atoms, X\*. From these observations it is concluded that the cleavage of the C-X bond to give C<sup>+</sup> and  $X^-$  occurs by heterolysis and not by homolysis followed by electron transfer in a radical pair. The details of the process-(es) leading to closed-shell (cation, anion) or open-shell (radical) products and the influence of the solvent on these are still unknown.<sup>36</sup> It was found that there is an effect of wavelength of excitation on the ratio of heterolysis to homolysis, the longer wavelengths increasing the heterolysis:homolysis ratio. A further aspect is that there are interesting, "nonlinear" solvent effects on the absolute and the relative yields of photoheterolysis and -homolysis as well as on the lifetimes of the vinyl cations (see Figures 3d and 4-6). These solvent effects require further study in order to obtain a better understanding. There is very good agreement between and mutual support of the product analysis and the time-resolved spectroscopic data.

The vinyl radicals formed by C-X homolysis have a high reactivity with O<sub>2</sub> ( $k = (1-2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ); however, it is interesting that these rate constants are *below* the diffusion-controlled limit in the solvents MeCN or CH<sub>2</sub>Cl<sub>2</sub> by more than an order of magnitude. The vinylperoxyl radicals exhibit absorption bands at 360-390 nm, which is a region shifted to longer wavelengths by  $\geq 100 \text{ nm}$ , compared to alkylperoxyl

radicals. This is indicative conjugation of the oxygen  $\pi$ -orbitals with the vinylic C-C double bond.

The compound **2aBr** ( $\mathbf{R} = MeO$ ) also undergoes photoheterolysis and -homolysis, whereas in the systems containing less strongly electron donating substituents than MeO, the lifetimes of potentially formed cations are  $\leq 20$  ns. The styrene derivative PhCH=CCl<sub>2</sub> reacts in MeCN predominantly by photoheterolysis.

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