Photolysis of 1-Bromo-2,2-bis(*p*-methoxyphenyl)ethene in solution

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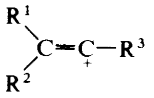
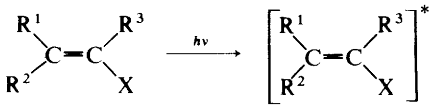
UV irradiation (λ_{inc} = 254 nm) of 1-bromo-2,2-bis(*p*-methoxyphenyl)ethene (AAHVB) in acetonitrile solution results in its decomposition: $\phi(-\text{AAHVB}) = 0.18$ both in the absence and presence of O_2. Apart from the isomers [(*E*)-1-bromo-1,2-bis(*p*-methoxyphenyl)ethene (HAAVB) and (*Z*)-1-bromo-1,2-bis(*p*-methoxyphenyl) ethene (AHAVB)] the main photoproducts are 1,2-bis(*p*-methoxyphenyl)ethine (P-2) and HBr ($\phi \approx 0.1$). Flash photolysis studies in acetonitrile, dichloromethane and *n*-hexane solution at 266 nm revealed that P-2 is formed with a halflife of less than a few ns *via* a singlet route involving vinyl cations which rapidly rearrange and split off protons. Part of the vinyl cations decay *via* a different route forming an ionic species with an optical absorption band at *ca*. 350 nm. The decay of the latter is not correlated with the formation of P-2. This ionic species probably results from an interaction of vinyl cations with solvent or AAHVB. AAHVB quenches triplet states of various compounds X (*e.g.* benzophenone, chrysene, benzil, pyrene) provided that $E_T(X) > 200$ kJ mol^{-1}. The energy transfer from these compounds to AAHVB does not result in the formation of P-2 or vinyl cations.

Recently, it has been shown that vinyl cations of the general structure



play an important role in initiating the cationic polymerization of appropriate compounds such as cyclohexene oxide or buyl vinyl ether.[1] Vinyl cations can be generated by chemical reactions[2,3] or by photolysis of vinyl halides.[4–8] According to Kitamura *et al.*[5] photolysis of vinyl halides involves in the primary step the homolysis of the carbon–halogen bond which leads to the formation of a radical pair. Subsequently, the radicals either escape from the solvent cage or undergo electron transfer. The two reactions yield free vinyl radicals or free vinyl cations, respectively:



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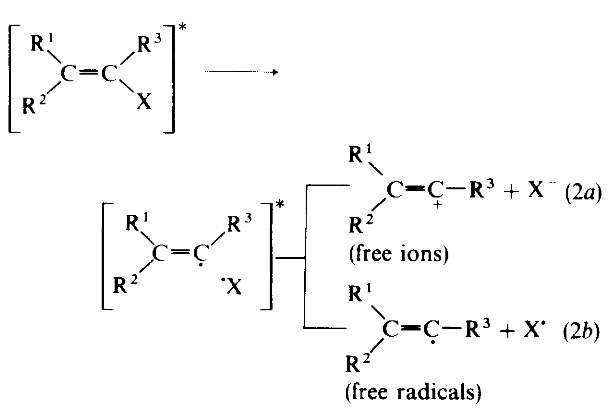
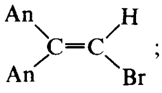


In former work[7] flash photolysis of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene showed that a photocurrent due to the formation of free ions (vinyl cation and bromide anion) was formed during the flash (*ca.* 20 ns). Similarly, van Ginkel *et al.*[9] reported the formation of a photocurrent within 5 ns upon irradiation of 1-bromo-1-*p*-methoxyphenyl-2,2-diphenylethene in acetonitrile solution. Obviously, in these cases vinyl cations are formed quite rapidly after excitation of the vinyl bromides.

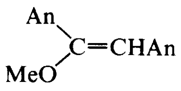
This paper reports on a study concerning the mechanism of the photolysis of 1-bromo-2,2-bis(*p*-methoxyphenyl)ethene, AAHVB, in solvents of different polarity.



; An: $p\text{-}H_3C\text{—}O\text{—}C_6H_4\text{—}$

(AAHVB)

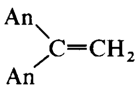
Of special interest was the question of the role of vinyl cations in product formation. A previous study[5] concerning the continuous UV irradiation of AAHVB in methanol solution revealed that various products are formed, the major ones being P-1 (39%), P-2 (12%) and P-3 (10%):



(P-1)

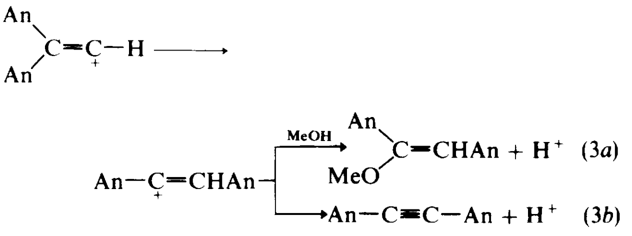
An—C≡C—An

(P-2)

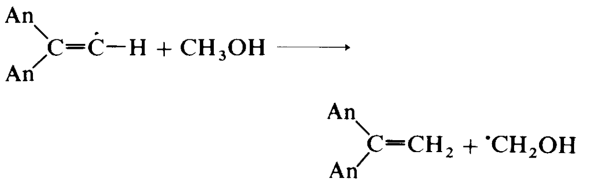


(P-3)

In methanol solution, products P-1 and P-2 were assumed to be formed *via* rearranged vinyl cations:



Free vinyl radicals formed according to reaction (2*b*) were assumed to react with methanol thus forming P-3:



(4)

As indicated by the rather low P-3 yields, reaction (4) contributes only to a minor extent to product formation in methanol solution. By contrast, in tetrahydrofuran solution the free-radical route dominates in product formation: P-3 was the major product and P-2 was not detected.[4] Interestingly, in benzene solution the photolysis of AAHVB yielded P-2 as the major product (53%) indicating the important role of vinyl cations in this case.[4]

By considering P-1 and P-2 as 'ionic' products and P-3 as a 'radical' product, it was concluded that in the photolysis of AAHVB in benzene and methanol, *i.e.* in solvents of quite different chemical nature, vinyl cations are formed in relatively high yields.

In the present work flash photolysis experiments on AAHVB dissolved in various solvents were performed to disclose details on the reaction mechanism.

Experimental

Materials

1-Bromo-2,2-bis(*p*-methoxyphenyl)ethene, AAHVB (m.p. 81.5 °C), (*E*)-1-bromo-1,2-bis(*p*-methoxyphenyl)ethene, HAAVB (m.p. 100.2 °C), (*Z*)-1-bromo-1,2-bis(-methoxyphenyl) ethene, AHAVB (m.p. 100.0 °C) and 1,1-bis(*p*-methoxyphenyl) ethene, AAHHE (m.p. 142.1 °C) were synthesized as described in the literature.[10] 1,2-Bis(*p*-methoxyphenyl)ethine, ACCA (m.p. 144.2 °C) was synthesized as described by Köbrich and Trapp.[11] Prior to use all compounds were twice recrystallized from ethanol solution.

The solvents were purified as follows: Acetonitrile (Baker or E. Merck) was refluxed over CaH_2 and fractionally distilled (b.p. 82 °C). Dichloromethane (E. Merck, Uvasol) was washed with concentrated H_2SO_4 and subsequently with aqueous $CaCO_3$ solution and water. After drying over $CaCl_2$ and CaH_2 it was distilled (b.p. 40 °C). *n*-Hexane (E. Merck, p.a.) was washed several times with concentrated aqueous HCl and H_2SO_4 solutions and subsequently with aqueous $NaHCO_3$ solution and water. After drying with $CaCl_2$ it was refluxed over sodium and distilled (b.p. 69 °C). Methanol was first distilled from CaH_2, then refluxed with sodium methanolate and again distilled (b.p. 64–65 °C). Triethylamine (Fluka) was distilled from CaH_2 (b.p. 88.5 °C).

Continuous Irradiations

A low-pressure mercury lamp (Heraeus Original Hanau, model TNN 15/32) emitting overwhelmingly light of $\lambda = 254$ nm (89%) was used. The solutions were irradiated under permanent stirring in rectangular quartz cuvettes. Prior to irradiation the solutions were flushed with either argon or oxygen. Actinometry was performed with Aberchrome 540 (Aberchromics Ltd) in toluene solution ($\lambda_{obs} = 494$ nm, $\varepsilon = 8.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}, $\phi = 0.15$).

Flash Photolysis Experiments

A neodymium YAG system (J.K. Lasers) operated in conjunction with two frequency doublers was used. The intensity of the light ($\lambda_{inc} = 266$ nm) incident to the sample was *ca.* 10^{-7} einstein cm^{-2} flash^{-1}. The flash duration was 15 ns. The absorbed dose was determined with the $K_4Fe(CN)_6$ actinometer: Ar-saturated aqueous solutions ($[K_4Fe(CN)_6] = 1.4 \times 10^{-5}$ mol dm^{-3}) were irradiated with single flashes and the concentration of hydrated electrons was measured at the end of the flash at $\lambda = 600$ nm ($\varepsilon = 1.32 \times 10^4$ dm^3 mol^{-1} cm^{-1},[12] $\phi(e_{aq}^-) = 0.51$,[13]).

For experiments with HAAVB a ruby laser (Korad, model K1 QS2) operated in conjunction with a frequency doubler was used ($\lambda_{inc} = 347$ nm, flash duration: *ca.* 25 ns).

Product Analysis

A gas chromatograph (Perkin Elmer, model 8500) was used in conjunction with a flame ionization detector and a quartz capillary column (Permaphase PVMS/54, 25 m long, i.d. = 0.3 μm). Absorption spectra were recorded with a UV–VIS spectrophotometer (Perkin Elmer, model 550 S). The quantum yield ϕ(P-2) was obtained by measuring the absorbance at 310 or 315 nm ($\varepsilon_{310} = 2.92 \times 10^4$ and $\varepsilon_{315} = 1.81 \times 10^4$ dm^3 mol^{-1} cm^{-1}, in acetonitrile).

Results

Continuous Irradiation

Optical Absorption Spectra

Figure 1(*a*1) shows optical absorption spectra of an acetonitrile solution of AAHVB recorded before and after 4 and 14 h UV irradiation at $\lambda_{inc} = 254$ nm in the absence of O_2. It can be seen that upon irradiation the spectrum of P-2 with

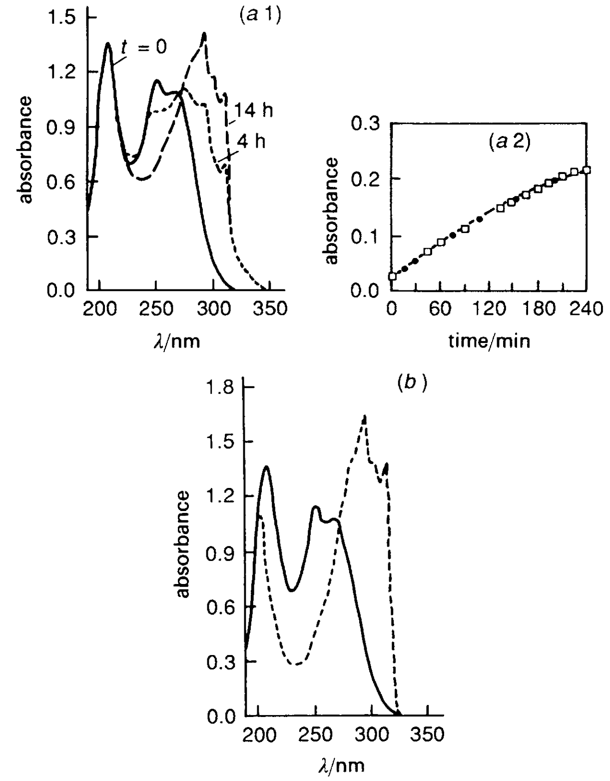
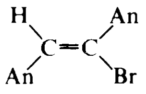


Fig. 1 Continuous irradiation of AAHVB in Ar-saturated acetonitrile solution, [AAHVB] = 5.85×10^{-5} mol dm^{-3}. (*a*1) Ground-state optical absorption spectra recorded before (——) and after irradiation [4 (- - -) and 14 h (— —)] at $\lambda_{inc} = 254$ nm and $D_{abs} = 1.6 \times 10^{-7}$ Einstein dm^{-3} s^{-1}. (*a*2) Increase in the absorbance at 315 nm as a function of irradiation time. (□) Ar, (●) air. (*b*) Ground-state optical absorption spectra of P-2 (— — —) and AAHVB (——) in acetonitrile solution ($c = 4.26 \times 10^{-5}$ mol dm^{-3}; $d = 1$ cm)

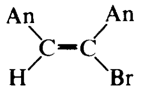
maxima at *ca.* 290 and 310 nm is formed. The authentic spectrum of P-2 is shown in Fig. 1(*b*). In the presence of O_2 the same spectral changes were observed as in its absence. These results demonstrate that also in acetonitrile solution P-2 is a major photoproduct.

GC Analysis of the Products formed in the Photolysis of AAHVB in Acetonitrile Solution

Gas chromatography analyses revealed apart from the decomposition of AAHVB the formation of four products. Two of the products were identified with the aid of authentic compounds P-2 and an isomer of AAHVB: AHAVB and/or HAAVB.



(AHAVB)



(HAAVB)

The two other products appeared only after prolonged irradiation and, therefore, are probably attributable to secondary products (stemming from the photolysis of primary products). Although these products have not yet been identified with certainty they are tentatively assigned to AnCH=CHAn and a phenanthrene derivative. The formation of phenanthrene derivatives has been previously evidenced in the case of other substituted vinyl bromides.[4,5] Notably, P-3 was not formed in detectable amounts in the present case. Very similar results were obtained upon irradiating AAHVB in *n*-hexane solution.

Quantum Yields

For the determination of quantum yields an AAHVB solution in acetonitrile (6.4×10^{-4} mol dm^{-3}) was irradiated at $\lambda_{inc} = 254$ nm both in the presence and absence of O_2 at an absorbed dose rate $D_{abs} = 1.6 \times 10^{-7}$ einstein dm^{-3} s^{-1}. Typical results are shown in Fig. 1(*a*2), where the absorbance at 315 nm (due to P-2) is plotted *vs.* the irradiation time. From the slope of the initial linear portion of the curve the quantum yield ϕ(P-2) = 0.11 was obtained. The conversion of AAHVB was determined by gas chromatography: $\phi(-$AAHVB) = 0.18. Molecular oxygen did not influence the conversion of AAHVB and the formation of P-2. The formation of protons was evidenced with the aid of sodium *p*-nitrophenolate (PNP, $\lambda_{obs} = 430$ nm, $\varepsilon = 2.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}). The absorption of PNP in acetonitrile was bleached upon addition of irradiated AAHVB solution. $\phi(H^+) = 0.09$ was obtained which is roughly equal to ϕ(P-2) = 0.11.

Sensitization Experiments

Attempts to sensitize the photolysis of AAHVB with the aid of a triplet sensitizer failed. P-2 was not formed when a solution of AAHVB (3.2×10^{-4} mol dm^{-3}) containing benzophenone (1×10^{-3} mol dm^{-3}) was irradiated at $\lambda_{inc} = 355$ nm.

Flash Photolysis

Transient Absorption Spectra and Quantum Yields

Fig. 2 shows transient optical absorption spectra of Ar-saturated solutions of AAHVB recorded after irradiation with a 15 ns flash ($\lambda_{inc} = 266$ nm). The spectrum recorded in acetonitrile solution [Fig. 2(*a*)] at the end of the flash has a shoulder at *ca.* 290 nm and peaks at *ca.* 310, 350 and 450 nm. The absorptions at 290 and 310 nm were assigned to P-2 which is formed during the flash so rapidly that it absorbs a significant portion of the light of the generating flash.

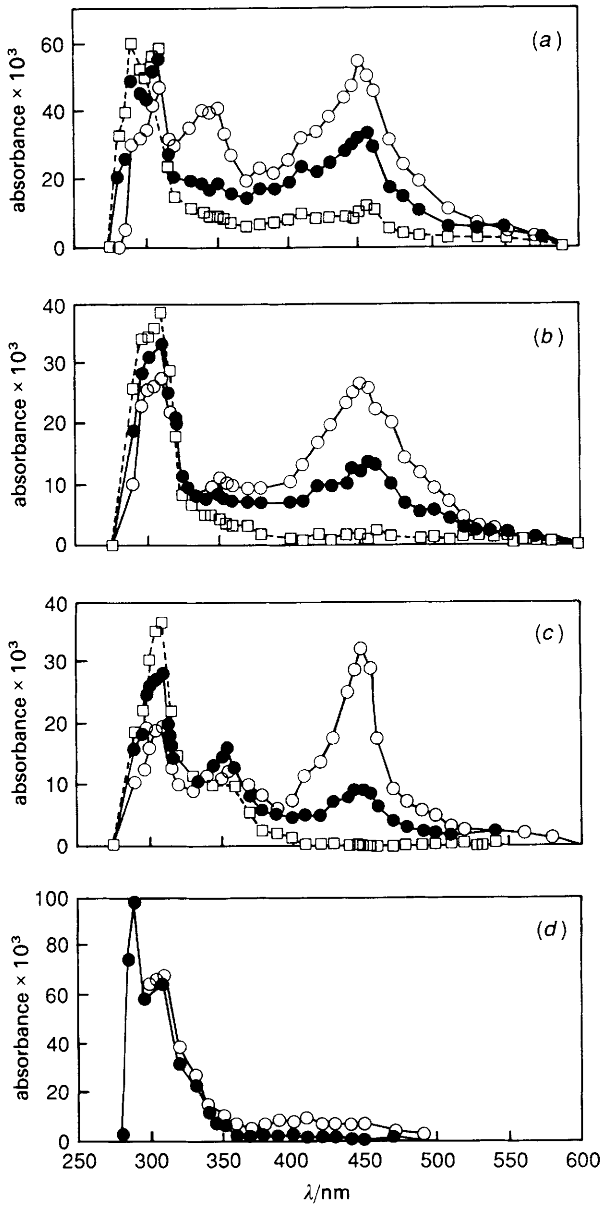


Fig. 2 Transient optical absorption spectra recorded with Ar-saturated AAHVB solutions at different times after the flash. Flash duration *ca.* 15 ns, $\lambda_{inc} = 266$ nm, $I_{inc} = 1.25 \times 10^{-7}$ einstein cm^{-2} flash^{-1}, [AAHVB] = 3.1×10^{-5} mol dm^{-3}; solvent; (*a*) acetonitrile, *t* = 0 (○), 4 (●), 16 μs (□); (*b*) dichloromethane, *t* = 0 (○), 10 (●), 70 μs (□); (*c*) *n*-hexane, *t* = 0 (○), 5 (●), 35 μs (□), (*d*) methanol, *t* = 0 (○), 7 μs (●)

Actually, triplet-excited P-2 molecules give rise to the absorption band located at $\lambda_{max} = 450$ nm. This was confirmed by flash excitation of authentic P-2, which yielded the same absorption band, and moreover, by flash photolysis of HAAVB at $\lambda_{inc} = 347$ nm, where the ethine derivatives are transparent. In this case, only the transient absorption band at 350 nm, but not the T–T absorption band at 450 nm, was formed during the flash. Kinetic traces depicting formation and decay of the transient absorption in acetonitrile solution are shown in Fig. 3. Notably, the slow mode of absorption build-up around 310 nm after the flash is not due to the formation of additional P-2, but to the relaxation of excited ethine (P-2) molecules to the ground state, as was concluded from the identical decay and formation rates at 450 and 310 nm, respectively. Notably, the amplitude of the absorption band at 450 nm decreased non-linearly when the absorbed dose per flash was lowered. From the total transient absorption at 310 nm in both the absence and presence of O_2 the quantum yield ϕ(P-2) ≈ 0.08 was estimated. This value is of the same magnitude as that determined during continuous irradiation (see above). In O_2-saturated solutions P-2 triplets (absorbing at 450 nm) were quenched. Therefore, the total absorption at 310 nm occurred very rapidly [see Fig. 3(*d*)]. Similar observations were made in dichloromethane and *n*-hexane solution as can be seen from the transient spectra shown in Fig. 2(*b*) and (*c*) and the kinetic traces presented in Fig. 4. In methanol solution only very weak transient absorptions at 350 and 450 nm were formed. This is in accordance with earlier findings that vinyl cations react effectively with methanol forming P-1.[5] The low wavelength portion of the spectrum generated during the flash [see Fig. 2(*d*)] with peaks at 290 and 310 nm is permanent and, therefore, reflects the fast formation of stable products, probably, mostly P-1 and to some extent P-2.

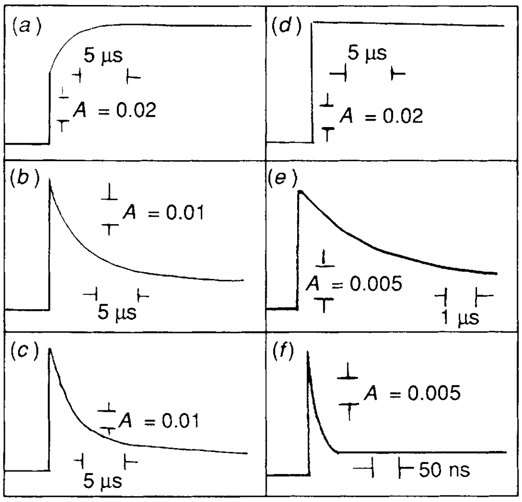


Fig. 3 Flash photolysis of AAHVB in acetonitrile solution. [AAHVB] = 3×10^{-5} mol dm^{-3}. Kinetic traces depicting formation and decay of the optical absorption during and after a 15 ns flash, λ_{inc} = 266 nm, $I_{inc} = 1.25 \times 10^{-7}$ einstein cm^{-2} flash^{-1}. (*a*)–(*c*) Ar, (*d*)–(*f*) O_2. λ/nm = 310 (*a*), (*d*); 350 (*b*), (*e*); 450 (*c*), (*f*).

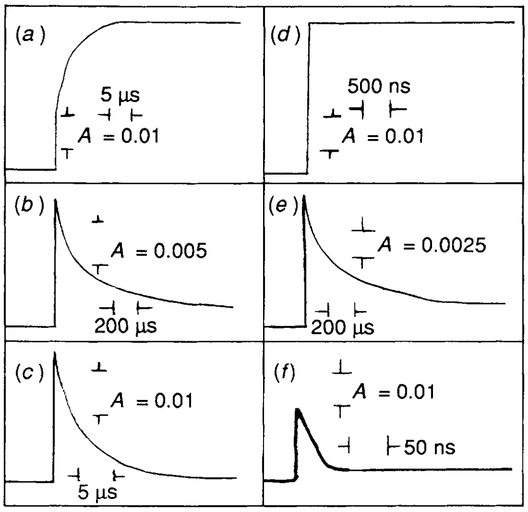


Fig. 4 Flash photolysis of AAHVB in *n*-hexane solution. [AAHVB] = 2.8×10^{-5} mol dm^{-3}. Kinetic traces depicting formation and decay of the optical absorption during and after a 15 ns flash, λ_{inc} = 266 nm, $I_{inc} = 1.25 \times 10^{-7}$ einstein cm^{-2} flash^{-1}. (*a*)–(*f*) see Fig. 3 caption

The transient absorption band at 350 nm is assigned to an ionic species. Its decay was strongly accelerated by triethylamine, the quenching rate constant (in acetonitrile solution) being $k_q = 1 \times 10^9$ dm^3 mol^{-1} s^{-1}. Notably, O_2 did not affect the decay at 350 nm.

Experiments involving AAHVB Triplets

In order to elucidate whether AAHVB triplets play a role in product formation various compounds which readily form excited triplet states were irradiated in the presence of AAHVB at λ_{inc} = 355 nm, where AAHVB is transparent. It turned out that AAHVB acts as a triplet quencher according to reaction (5)

$$^3\text{sens}^* + {}^1\text{AAHVB} \rightarrow {}^1\text{sens} + {}^3\text{AAHVB}^* \qquad (5)$$

provided the triplet energy of the sensitizer (sens) is larger than *ca.* 200 kJ mol^{-1}. Quenching rate constants are given in Table 1. Note that triplet quenching was never accompanied by build-up of an absorption at 310 nm, *i.e.* P-2 is not formed from the triplet state of AAHVB, the latter being deactivated by non-chemical routes.

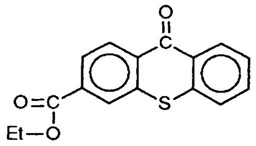
Discussion

The outstanding feature of this work is the very rapid formation of P-2. Actually, P-2 is formed so quickly that at the absorbed doses per flash applied in most experiments a large fraction (*ca.* 50%) of it is excited in the singlet manifold and subsequently converted by intersystem crossing to the triplet state during the generating 15 ns flash. Triplet-excited P-2 molecules were detected upon irradiation of AAHVB at the end of the flash by the characteristic T–T absorption band at λ_{max} = 450 nm. Its deactivation to the ground state was accompanied by an increase in the absorption at 310 nm. Also, at the end of the flash the absorption of an ionic species at λ_{max} = 350 nm was detected. The nature of this species has not yet been disclosed. As compared with the rapid formation of P-2 within a few ns its decay is rather slow ($\tau \approx 4$ µs) and, therefore, is not correlated to the formation of P-2. In terms of the mechanism discussed in the Introduction [reactions (1)–(3)] these results are interpretable on the basis of the very rapid formation of vinyl cations, $An_2C{=}C^+H$. These ions rearrange very quickly forming $(An)HC{=}C^+(An)$. In the absence of scavengers $(An)HC{=}C^+(An)$ ions deprotonate rapidly according to reaction (3*b*). All these processes occur with lifetimes shorter than a few ns. Vinyl cations can also decay by other reaction routes. In methanol solution, *e.g.*, the reaction with the solvent leading to product P-1 is important.

Table 1 Triplet quenching by AAHVB in acetonitrile solution at room temperature: quenching rate constants

compound	E_T/kJ mol^{-1}	k_q/dm^3 mol^{-1} s^{-1}
benzophenone	289	6.0×10^9
ETX[a]	260	5.0×10^9
Michler's ketone	256	3.0×10^9
chrysene	239	6.2×10^8
benzil	226	1.0×10^7
pyrene	205	5.7×10^6
eosin yellow	180	no reaction

[a] ETX:



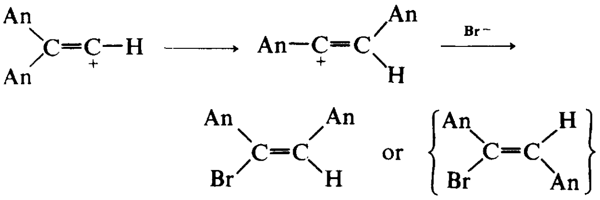
In acetonitrile, and to a smaller extent, in dichloromethane and *n*-hexane solution some of the $(An)HC{=}C^+(An)$ ions are assumed to interact with AAHVB or solvent molecules forming the complexes $(C\text{-}1)^+$ and $(C\text{-}2)^+$, respectively:

$$\underset{(C\text{-}1)^+}{An_2C{=}CHBR\cdots(An)HC{=}\overset{+}{C}An} \qquad \underset{(C\text{-}2)^+}{CH_3CN\cdots(An)HC{=}\overset{+}{C}An}$$

This assumption is based on the fact that the absorption spectrum of the ionic species resembles the spectra of the vinyl cations $An_2C{=}C^+(An)$, $An(Ph)C{=}C^+(An)$ and $An(Me)C{=}C^+(An)$.[8] In the case of $(C\text{-}2)^+$ the formation of a new chemical bond is feasible:

$$(C\text{-}2)^+ \rightarrow (An)HC = C(An){-}N = \underset{+}{C}{-}CH_3 \qquad (6)$$

Interestingly, by product analysis, AAHVB was shown to isomerize to a remarkable extent. A feasible mechanism for this process involves the combination of rearranged vinyl cations with Br^- ions, as is illustrated by reaction (6):



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References

1 Y. Yağci, C. H. Fischer and W. Schnabel, *Makromol. Chem., Rapid Commun.*, 1989, **10**, 137.
2 P. J. Stang, Z. Rappoport, M. Hanack and C. R. Subramanian, *Vinyl Cations*, Academic Press, New York, 1980.
3 M. Hanack, *Pure Appl. Chem.*, 1984, **56**, 1819.
4 T. Suzuki, T. Sonoda, S. Kobayashi and T. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1976, 180.
5 T. Kitamura, S. Kobayashi and H. Taniguchi, *J. Am. Chem. Soc.*, 1986, **108**, 2641.
6 W. Schnabel, I. Naito, T. Kitamura, S. Kobayashi and H. Taniguchi, *Tetrahedron*, 1980, **36**, 3229.
7 S. Kobayashi, T. Kitamura, H. Taniguchi and W. Schnabel, *Chem. Lett. Chem. Soc. Jpn.*, 1983, 1117
8 S. Kobayashi, T. Kitamura, H. Taniguchi and W. Schnabel, *Chem. Lett. Chem. Soc. Jpn.*, 1984, 2101.
9 F. I. M. van Ginkel, R. J. Visser, C. A. G. O. Varma and G. Lodder, *J. Photochem.*, 1985, **30**, 453.
10 W. Tadroz and G. Azia, *J. Chem. Soc.*, 1951, 2553.
11 G. Köbrich and H. Trapp, *Chem. Ber.*, 1966, **99**, 680.
12 E. Hart and M. Anbar, *The Hydrated Electron*, Wiley-Interscience, New York, 1970, p. 42.
13 G. Stein, *Adv. Chem. Ser.*, 1965, **50**, 230.

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