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IONIC INTERMEDIATES IN THE PHOTOLYSIS OF 1,2,2-TRIS(p-METHOXYPHENYL)VINYL BROMIDE

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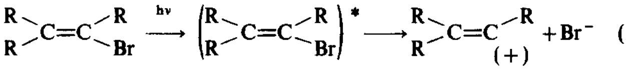
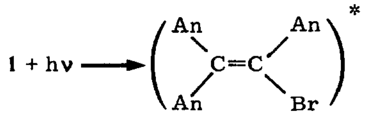
Abstract—1,2,2-Tris(p-methoxyphenyl)vinylbromide was irradiated in dilute, oxygen-free, acetonitrile with 25 ns flashes of 347.1 nm light. From transient photocurrent measurements it was inferred that ionic intermediates are formed.

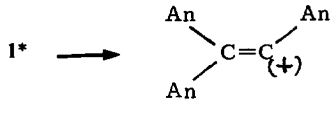
The photolysis of substituted vinyl bromides has been postulated to occur in solvents of relatively high polarity via ionic intermediates:


(1)

Evidence for the occurrence of process (1) was obtained from stationary irradiations.[1–3] It should be pointed out that according to the extensive work of the groups of Hanack[4] and Rappoport,[5] vinyl cations are formed as intermediates during the solvolysis of many vinyl compounds in their ground states.

Recently it was reported[1] that upon irradiation of 1,2,2-tris(p-methoxyphenyl)vinyl bromide (**1**) in tetrabutylammonium azide containing acetonitrile solution 1,1,3,4,6,6-hexakis(p-methoxyphenyl)-2,5-diazahexa-1,3,5-triene (**2**) was formed.


(2)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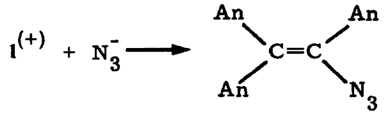
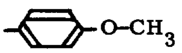

(4)

An: 

For the generation of **2** two further photochemical steps (involving the absorption of two additional photons) have been assumed.[1]

This paper reports on flash photolysis experiments carried out at the Hahn–Meitner–Institut Berlin, where the electrical conductivity detection method was applied in order to detect the formation of ionic intermediates. It was possible, this way, to obtain direct evidence for the occurrence of reaction (3).

1,2,2-Tris(p-methoxyphenyl)vinyl bromide (**1**), synthesized at Kyushu University, Fukuoka, was irradiated at a concentration of 2.9×10^{-5} mol/l in acetonitrile solution with 25 ns flashes of 347.1 nm light produced by a ruby laser (Korad model K1QS2) with the aid of a frequency doubler. The photocurrent measurements were performed as described earlier.[6]

A quartz cell containing platinum electrodes spaced about 4 mm apart was connected to a flow system. The platinum plates were placed parallel to the photolyzing light beam which irradiated the solution between them. Battery voltages up to 600 V were applied. The load resistor was 50 Ω. The total capacity of the system amounted to about 60 pF. This corresponds to a rise time $t_{10\rightarrow 90} \approx 7$ ns. For the purpose of actinometry anthracene was irradiated in cyclohexane as described earlier.[7]

Figure 1 shows typical oscilloscope traces demonstrating the rise of a photocurrent after the flash. It is seen to decrease after passing a maximum value. The decay of the current occurs via two clearly distinct modes. No photocurrent was detected within the noise limit (*ca* 0.3 mV) upon irradiating pure acetonitrile under the conditions, the traces shown in Fig. 1 were obtained. The maximum photocurrent was found to increase linearly with the absorbed dose per pulse indicating that the photo-current is not due to

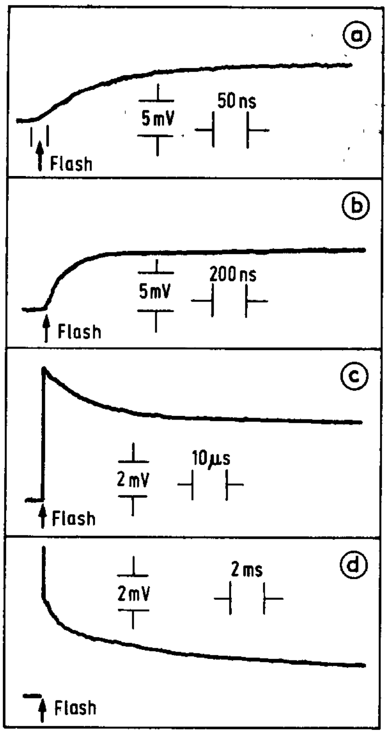


Fig. 1. Oscilloscope traces depicting the rise and the decay of the photocurrent after irradiation of compound 1 in Ar-saturated acetonitrile solution (2.9 × 10^{-5} mol/l). The absorbed dose per flash varied from 2.7 × 10^{-5} to 3.2 × 10^{-5} einstein/l during these experiments.

multiphotonic ionization. In the latter case the conductivity should be generated during the pulse without delay. The maximum photocurrent was, furthermore, found to be directly proportional to the battery voltage indicating that Ohm's law holds for this system.

The kinetic treatment of the data yielded the following: the formation of the photocurrent follows a 1st order law (see typical plot in Fig. 2(a)).

The 1st order rate constant was determined as 1.4 × 10^7 s^{-1} ± 10%. The short-lived mode of the decay of the photocurrent also follows 1st order kinetics (see Fig. 2b), rate constant (6 ± 0.3)10^4 s^{-1}. The long-lived mode decays according to a second order law in the ms-range as can be seen from the typical plot in Fig. 3. From these results the following conclusions can be drawn. (i) Ionic intermediates are formed upon irradiating compound **1** in acetonitrile; (ii) ions are formed relatively slowly, i.e. excited molecules of **1** are relatively stable and dissociate primarily into radicals

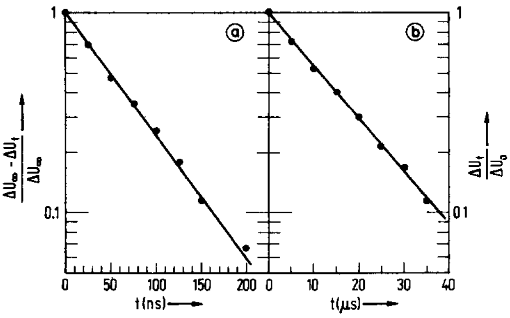


Fig. 2. Typical 1st order plots of the formation of the photocurrent after the flash (a) and of the decay of the short-lived mode (b). For experimental conditions see caption of Fig. 1.

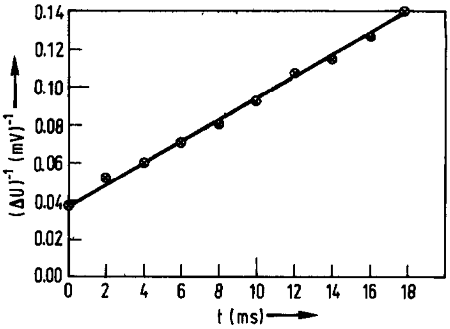
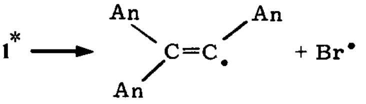
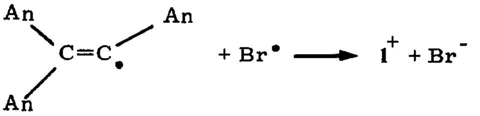


Fig. 3. 2nd order plot of the decay of the long-lived mode of photocurrent. For experimental conditions see caption of Fig. 1.



(5)

The radicals undergo electron transfer in the radical cage according to eqn (6)



(6)

This mechanism has been discussed previously.[1] Reaction (6) might indeed become feasible in relatively highly polar solvents. Alternatively, the relatively long lifetime of the excited state might be an intrinsic property of **1**, i.e. reaction (3) might occur without involving intermediate steps such as (5) and (6). (iii) From the existence of a rapid mode of conductivity decrease, which 1st order or pseudo 1st order kinetics hold for, it is inferred that the ions or one of the ions (probably the cation) react with the solvent, thus forming more stable positive ions of lower mobility. An alternative explanation would be based on the assumption that a certain fraction of ion pairs reacts before escaping the solvent cage. However, it is rather uncertain whether radical pairs in this case have a lifetime of about 10 μs. (iv) Rather stable ions are created decaying in the ms-range (see Fig. 3). These ions are certainly distributed homogeneously in the system.

A more precise assignment of the effects observed during these studies (involving solely electrical conductivity measurements) is hoped to be achieved with the aid of absorption and emission measurement, and further studies are under way.

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