

## MECHANISTIC STUDIES OF THE PHOTOREARRANGEMENT OF *o*-NITROBENZYL ESTERS

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(Received March 17, 1986)

### Summary

$\alpha$ -Methyl-*o*-nitrobenzyl isobutyrate and copolymers containing  $\alpha$ -methyl-*o*-nitrobenzyl acrylate were irradiated in dilute solution with 20 ns flashes of 347 nm light or with 60 ps flashes of 355 nm light. The formation of the absorption spectrum of a nitronic acid with  $\tau = 5$  ns was observed in each case. A transient absorption spectrum similar to that of the nitronic acid was formed with  $\tau \leq 0.5$  ns. This spectrum is assumed to belong either to the triplet biradical formed upon intramolecular triplet state hydrogen abstraction or to nitronic acid formed very rapidly by intramolecular singlet state hydrogen abstraction, the latter mechanism being operative in parallel with the triplet mechanism.

In 60vol.%EtOH-40vol.%H<sub>2</sub>O the nitronate anion was formed by dissociation of the nitronic acid with  $\tau = 3$   $\mu$ s as indicated by a build-up of a new absorption band with  $\lambda_{\text{max}} = 420$  nm and by an increase in electrical conductivity. The conversion into the end products (nitroso compound and carboxylic acid) occurred at a much faster rate from the nitronic acid than from the nitronate anion:  $\tau = 80$   $\mu$ s (CH<sub>2</sub>Cl<sub>2</sub>),  $\tau = 360$   $\mu$ s (60vol.%EtOH-40vol.%H<sub>2</sub>O, 10<sup>-4</sup> M H<sub>2</sub>SO<sub>4</sub>) and  $\tau = 10$  ms (60vol.%EtOH-40vol.%H<sub>2</sub>O, no H<sub>2</sub>SO<sub>4</sub>). Conversion of the nitronate anion into another transient was inferred from the partial decrease in the electrical conductivity ( $\tau \approx 15$   $\mu$ s)..

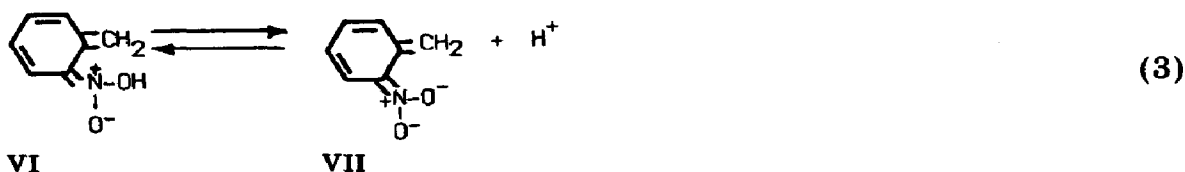
Irradiation of the copolymers gave the same results as for the low molecular weight model compound, indicating that there is no polymer effect with respect to the kinetics or the mechanism of the photorearrangement. This conclusion was substantiated by the quantum yields for acid formation (0.24 - 0.25) measured with both the model compound and the copolymers.

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### 1. Introduction

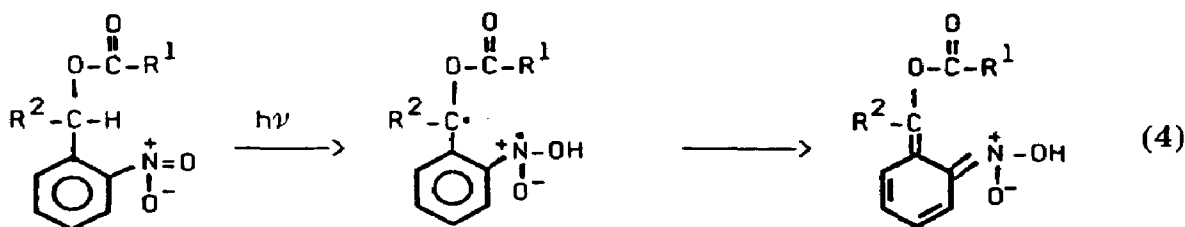
Recently, the photochemistry of *o*-nitrobenzyl compounds has attracted the attention of a number of researchers [1 - 9] because of their interes-



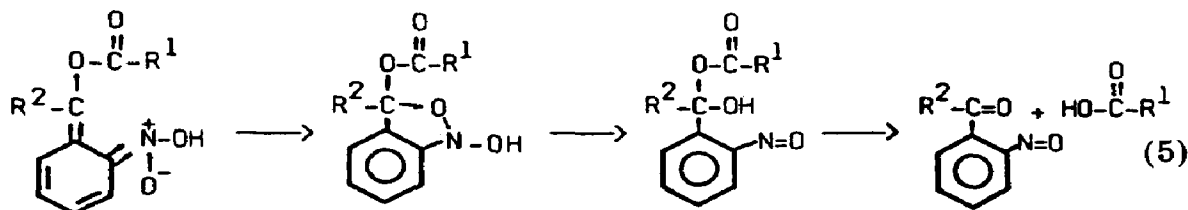


VI is a relatively strong acid with  $\text{p}K_a = 3.8$  [12].

In the photorearrangement of *o*-nitrobenzyl esters, which leads to irreversible bond cleavage (see reaction (1)), it is commonly assumed that the initial steps involve intramolecular hydrogen abstraction and the formation of the nitronic acid:

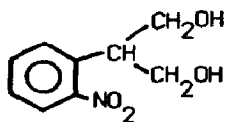


As it appeared improbable that the nitronic acid could be converted directly into the final products, one or two additional intermediates were postulated [6] as indicated in reaction (5):

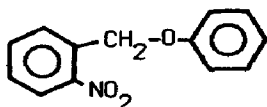


In picosecond flash photolysis studies with *o*-nitrotoluene Yip *et al.* [15] observed a transient absorption spectrum with a narrow band at 440 nm and a broad band at  $\lambda > 550$  nm, and this was assigned to triplets ( $\tau_T = 0.77$  ns). A very short singlet lifetime  $\tau_S \leq 5$  ps was estimated in this case. However, these researchers [15] did not report the formation of the transient absorption of the nitronic acid that had been recorded by microsecond flash photolysis [10]. In a more recent investigation, Yip *et al.* [16] obtained evidence for the formation of nitronic acid from singlet state intramolecular hydrogen abstraction. Apart from considering the possibility that a very short-lived triplet ( $\tau_T < 30$  ps) was involved, it was concluded that nitronic acid was formed directly from an electronically excited singlet state in compounds such as VIII. In this case, the formation of the transient absorption of the nitronic acid was observed immediately after irradiation with a 30 - 40 ps flash ( $\lambda = 355$  nm) whereas triplet absorption was not detected. With compounds containing polar substituents at the benzylic carbon, such as IX, triplet absorption was observed simultaneously with the absorption

of the nitronic acid. Since the rate of triplet decay was much slower than the rate of formation of the nitronic acid, the contribution to the latter process from a route involving triplets was considered to be negligible or nil.

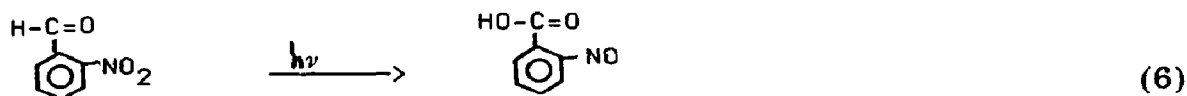


VIII



IX

In connection with the primary elementary steps in the photolysis of aromatic *o*-nitro compounds, work concerning *o*-nitrobenzaldehyde is noteworthy [17, 18]. This compound is converted into *o*-nitrosobenzoic acid upon absorption of light. [19].



It was concluded that triplet states, probably  $n\pi^*$  states, are involved in this rearrangement. Estimates of the triplet lifetime yielded the rather low value  $\tau_T \approx 0.3$  ns which is of the same order of magnitude as  $\tau_T = 0.77$  ns and  $\tau_T \approx 1$  ns reported for *o*-nitrotoluene [15] and for nitrobenzene [20] respectively.

## 2. Experimental details

### 2.1. Materials

#### 2.1.1. Synthesis of $\alpha$ -methyl-*o*-nitrobenzyl isobutyrate (I)

The synthesis of I was accomplished in two steps. First,  $\alpha$ -bromo-*o*-nitroethylbenzene ( $\alpha$ -BNB) was prepared by photobromination of *o*-nitroethylbenzene (NB). Then the  $\alpha$ -BNB was allowed to react with potassium isobutyrate, yielding I. In the first step, 22.7 g NB were dissolved in 250 ml Frigen 113, and this solution was irradiated at 36 - 40 °C with a mercury lamp, 23 g bromine being added in small portions. Subsequently, the solution was stirred for 1 h and then washed with solutions of NaHSO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and pure water. After drying with Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by distillation *in vacuo*. The yield of  $\alpha$ -BNB was 95%. In the second step, 23 g  $\alpha$ -BNB were added slowly to a dispersion of 12.6 g potassium isobutyrate in 50 ml dimethylformamide. The mixture was stirred for 3 h at 70 °C, cooled to room temperature and diluted with 150 ml toluene. This solution was then washed with water, a solution of Na<sub>2</sub>CO<sub>3</sub> and finally again with water. A yellow oil remained after removal of the solvent by distillation *in vacuo*. I was obtained by recrystallization from methanol at -20 °C. The yield was 85%.

### 2.1.2. Synthesis of copolymers

Copolymers of II with 2-hydroxypropyl acrylate (X), hydroxyethyl methacrylate (XI), methyl methacrylate (XII) and *n*-butyl methacrylate (XIII) were synthesized at 60 °C in solutions of ethyl acetate using AIBN as the initiator. The structures of these compounds are given in Table 1. The total monomer concentration was 50 vol.%. After the polymerization, the copolymers were precipitated with methanol and subsequently reprecipitated from acetone solution with methanol. The compositions and molecular weights of the copolymers are given in Table 2. All three polymers possessed unimodal relatively narrow molecular weight distributions as inferred from gel permeation chromatography measurements.

TABLE 1

Compounds for the synthesis of copolymers:  $R^2-\overset{\text{CH}_2}{\underset{\text{OR}^1}{\text{C}}}=\overset{\text{O}}{\text{C}}$

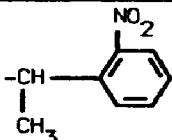
	$R^1$	$R^2$
II		H
X	$-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$	H
XI	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_3$
XII	$-\text{CH}_3$	$-\text{CH}_3$
XIII	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$-\text{CH}_3$

TABLE 2

Compositions and molecular weights of the copolymers

	Composition (wt.%)					$M_w$
	II	X	XI	XII	XIII	
CP-1	5	—	—	60	35	$8.5 \times 10^4$
CP-2	5	—	—	60	35	$7.5 \times 10^4$
CP-3	20	50	30	—	—	$6 \times 10^5$

### 2.2. Irradiation of samples

Dilute solutions of  $\alpha$ -methyl-*o*-nitrobenzyl derivatives, freed from oxygen by bubbling with argon, were irradiated in rectangular quartz cells either with 20 ns flashes of 347 nm light produced by a ruby laser with the aid of a second harmonic generator or by 60 ps flashes of 355 nm light produced by an actively mode-locked YAG laser (J. K. Lasers, model AML) using a third harmonic generator [21]. Actinometry was performed with solutions of benzophenone ( $1.15 \times 10^{-3}$  M) and naphthalene ( $1.03 \times 10^{-1}$  M)

in  $\text{CH}_2\text{Cl}_2$ . The absorbed dose per flash was calculated from the concentration of naphthalene triplets formed by energy transfer from benzophenone, with  $\epsilon_{T-T} = 1.51 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 425 nm and  $\phi(T) = 1.0$ .

### 2.3. Detection methods

Optical absorption and electrical conductivity methods were employed. In the latter case a quartz cell containing a pair of parallel platinum electrodes was used. The cell was attached to a flow system. Both a d.c. and an a.c. set-up were used to follow changes in the electrical conductivity of the irradiated solutions [22]. In the case of the picosecond flash photolysis, the time resolution of the optical absorption changes was about 500 ps.

### 2.4. Determination of quantum yields

Measurements of quantum yields were performed with a conventional high pressure mercury lamp equipped with an interference filter transparent to light of wavelength 365 nm. Acetonitrile solutions (solute concentration, 5 wt.%) were irradiated in quartz cells. The potassium ferrioxalate actinometer was used for the determination of the absorbed dose rate. The photo-product yield was determined by titration of the resulting carboxylic acid with an ethanolic solution of KOH (0.01 M).

## 3. Results and discussion

### 3.1. Experiments with $\alpha$ -methyl-*o*-nitrobenzyl isobutyrate in dichloromethane

Irradiation of I with a 20 ns flash of 347 nm light yielded the transient spectrum (1) in Fig. 1(a) with  $\lambda_{\text{max}} \approx 395$  nm. This spectrum is attributed to the nitronic acid as in the case of *o*-nitrotoluene, where a very similar transient absorption spectrum was observed [10]. The formation of spectrum (1) is depicted in Figs. 2(a) and 2(b), which present kinetic traces obtained upon irradiating a solution of I with a 60 ps flash of 355 nm light. It can be seen that the transient absorption was formed in two steps:

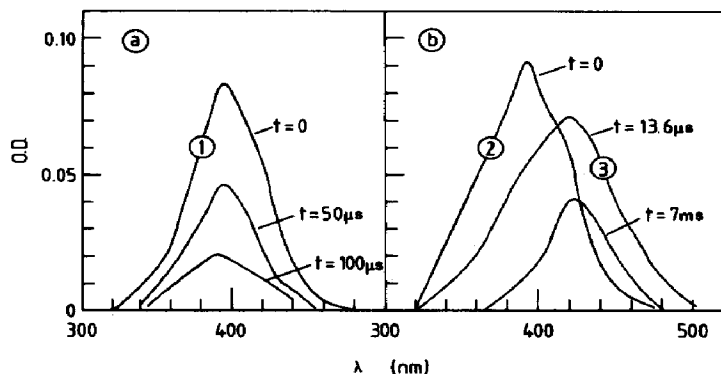


Fig. 1. Transient spectra recorded with I at various times after the flash ( $\lambda_{\text{inc}} = 347$  nm;  $D_{\text{abs}} = 2 \times 10^{-5}$  einsteins  $\text{l}^{-1} \text{ flash}^{-1}$ ). (a) Argon-saturated  $\text{CH}_2\text{Cl}_2$  solution,  $[\text{I}] = 5.5 \times 10^{-4}$  M; (b) argon-saturated 60vol.%ethanol-40vol.%water,  $[\text{I}] = 6.7 \times 10^{-4}$  M.

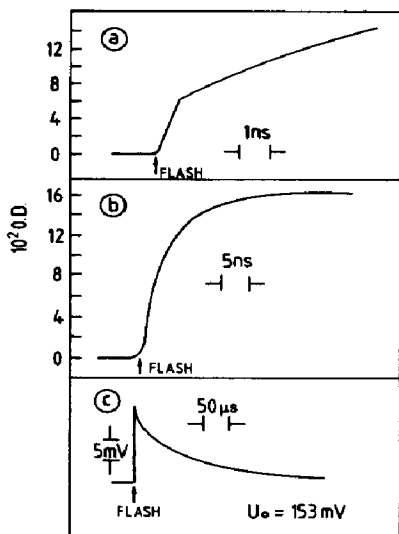


Fig. 2. Formation and decay of the optical absorption at  $\lambda = 380$  nm in argon-saturated  $\text{CH}_2\text{Cl}_2$  solution: (a) and (b),  $\lambda_{\text{inc}} = 355$  nm,  $[\text{I}] = 3.3 \times 10^{-4}$  M and  $D_{\text{abs}} \approx 5 \times 10^{-6}$  einsteins  $\text{l}^{-1} \text{flash}^{-1}$ ; (c)  $\lambda_{\text{inc}} = 347$  nm,  $[\text{I}] = 5.5 \times 10^{-4}$  M and  $D_{\text{abs}} = 1.7 \times 10^{-5}$  einsteins  $\text{l}^{-1} \text{flash}^{-1}$ .

a very rapid step with a rate corresponding to the time constant of the set-up (500 ps) and a slower step with a lifetime of about 5 ns. The spectrum recorded 500 ps after the flash was very similar to that of spectrum (1) in Fig. 1(a). The fraction of the total absorption recorded at  $t = 500$  ps was significantly higher (by a factor of about 2.5) than expected on the basis of the build-up lifetime of 5 ns (see Fig. 2(b)). Therefore, the possibility that we were dealing with a single process which was artificially separated into two modes by the time resolution of the set-up can be ruled out. Consequently, two possible mechanisms must be discussed.

(1) A precursor of the nitronic acid, probably a biradical, is formed at times shorter than 500 ps. It is converted into nitronic acid with  $\tau = 5$  ns and its spectrum was recorded at  $t = 500$  ps. In this case, exclusively triplets are involved in the formation of nitronic acid.

(2) Nitronic acid is formed via two different routes, *i.e.* from excited singlets as well as from triplets. The former process is very rapid, so that the spectrum of nitronic acid (formed from singlets) was recorded at  $t = 500$  ps. The latter process is relatively slow and corresponds to the formation of the additional absorption of the nitronic acid with  $\tau = 5$  ns.

A mechanism in accord with case (1), covering the whole process from the absorption of the photon up to the formation of end products, is proposed in the scheme in Fig. 3. It is assumed that the biradical is formed by intramolecular triplet state hydrogen abstraction and that I behaves similarly to *o*-nitrotoluene [10], *i.e.* that the singlet lifetime is less than 5 ps and the triplet lifetime is less than 0.5 ns.

In case (2) the spectrum observed at  $t = 500$  ps is due to nitronic acid generated by intramolecular singlet state hydrogen abstraction whereas the





slow process with  $\tau \approx 5$  ns. It is therefore concluded that nitronic acid is formed by the same mechanism both in  $\text{CH}_2\text{Cl}_2$  and in ethanol-water. However, differences in the decay mechanism were observed: in ethanol-water, transient absorption spectrum (2) decayed relatively quickly with a lifetime of about  $3 \mu\text{s}$  and, simultaneously, spectrum (3) with a maximum at about  $420$  nm was formed, as can be seen from Fig. 1(b) and Figs. 4(a) and 4(b). Spectrum (3) is assigned to the nitronate anion, again by analogy with the assignment in the case of *o*-nitrotoluene [10] where a similar spectrum was observed as outlined in Section 1. It seems that an equilibrium was established between acid and anion, in analogy with eqn. (3), with a lifetime of  $3 \mu\text{s}$ , and that the nitronic acid was dissociated to a great extent. This was corroborated by irradiating I in 60vol.%ethanol-40vol.%water containing  $10^{-4}$  M  $\text{H}_2\text{SO}_4$ . In this case also the spectrum of the nitronic acid (spectrum (2) in Fig. 1(b)) but not the spectrum of the anion (spectrum (3) in Fig. 1(b)) was formed. Obviously, the dissociation of the nitronic acid was suppressed in the acidic medium. It is interesting to note that the decay of the nitronic acid in the acidic medium was a first-order process with a lifetime of about  $360 \mu\text{s}$  (in  $\text{CH}_2\text{Cl}_2$ ,  $\tau \approx 80 \mu\text{s}$ ). In contrast, the anion decayed with a much lower rate ( $\tau \approx 10$  ms), as is shown in Fig. 4(c).

Additional information concerning the decay of the anion was obtained from time-resolved electrical conductivity measurements. As can be seen from Fig. 5, the conductivity increased with a lifetime of  $3 \mu\text{s}$ , corresponding exactly to the lifetime of the build-up of the absorption band of the anion with the peak at  $420$  nm. Subsequently, the conductivity decreased again with a lifetime of about  $15 \mu\text{s}$  and approached a limiting value definitely

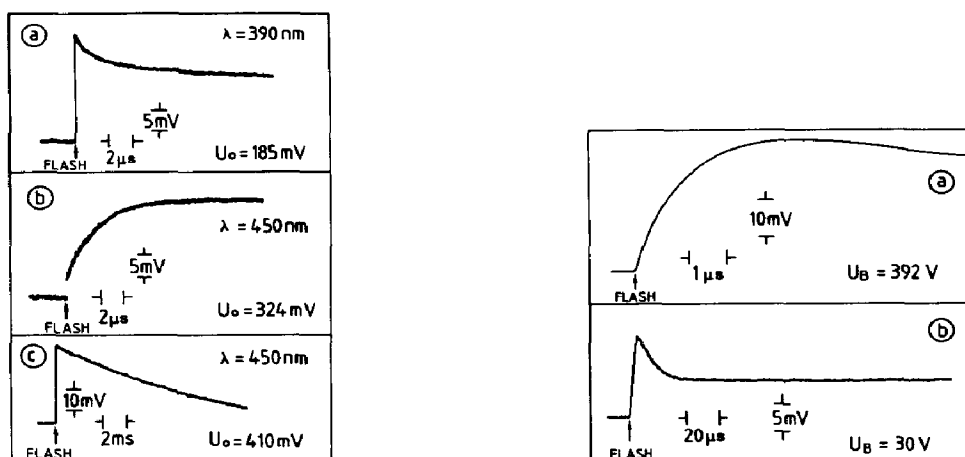


Fig. 4. Rise and decay of the optical absorption at (a)  $\lambda = 390$  nm and (b) and (c)  $450$  nm upon irradiation of I in argon-saturated 60vol.%ethanol-40vol.%water ( $\lambda_{\text{inc}} = 347$  nm;  $[\text{I}] = 5.5 \times 10^{-4}$  M;  $D_{\text{abs}} = 1.6 \times 10^{-5}$  einsteins  $\text{l}^{-1}$  flash $^{-1}$ ).

Fig. 5. Rise and decay of the photocurrent after the flash measured (a) with a d.c. set-up ( $D_{\text{abs}} = 2.3 \times 10^{-5}$  einsteins  $\text{l}^{-1}$  flash $^{-1}$ ) and (b) with an a.c. set-up ( $D_{\text{abs}} = 3.3 \times 10^{-5}$  einsteins  $\text{l}^{-1}$  flash $^{-1}$ ). ( $[\text{I}] = 3.3 \times 10^{-4}$  M; solvent, argon-saturated 60vol.%ethanol-40vol.%water;  $\lambda_{\text{inc}} = 347$  nm.)

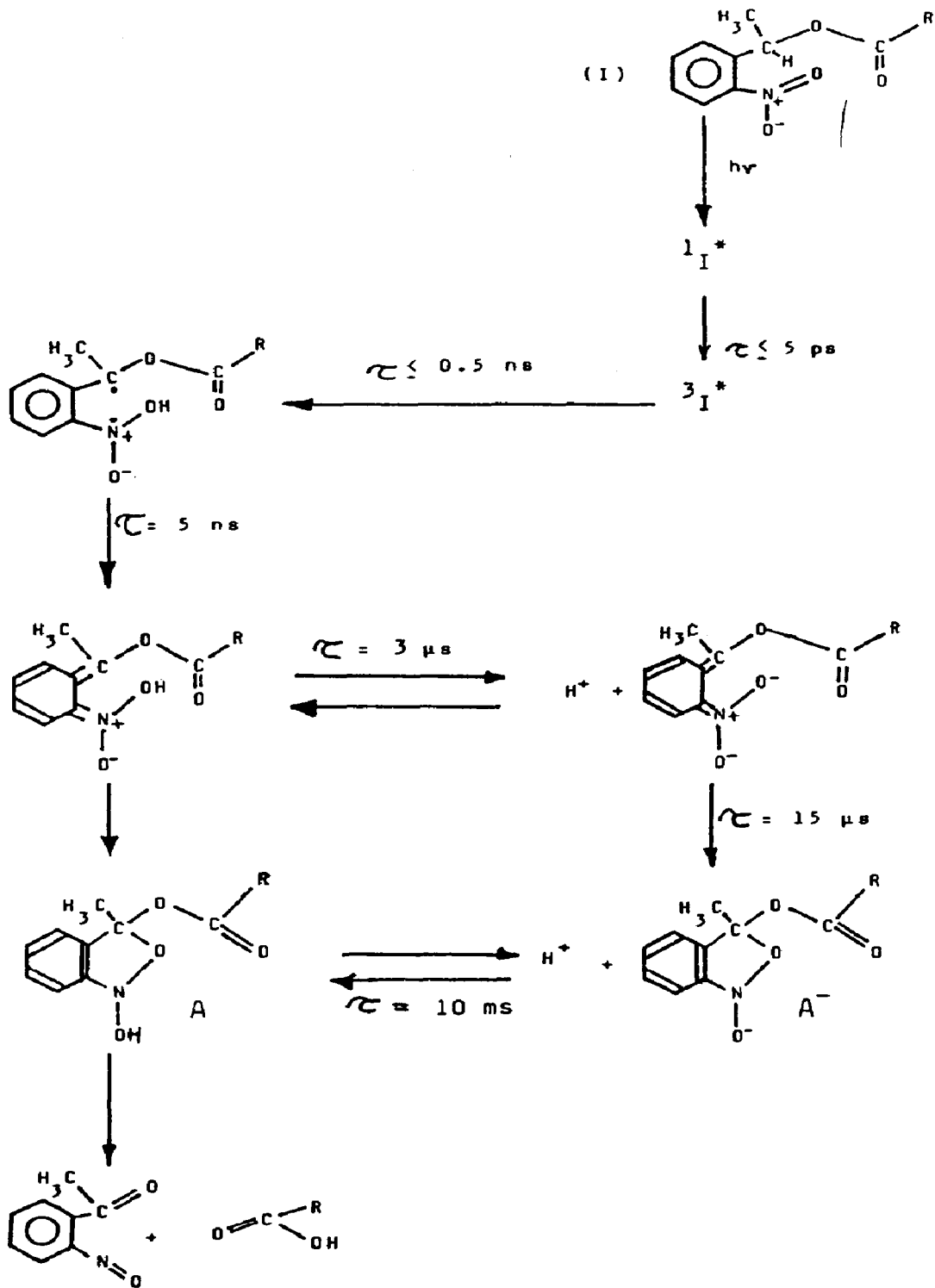


Fig. 6. Mechanism of the photorearrangement of I in 60vol.%ethanol-40vol.%water according to case (1) ( $R \equiv -CH(CH_3)_2$ ).

higher than the initial value before irradiation. From these results the existence of another intermediate, with a conductivity lower than that of the anion, is inferred. Notably, the decrease in electrical conductivity in the microsecond range was not accompanied by a significant change in the transient optical absorption spectrum, which decayed in the millisecond range. Therefore, there is no basis for speculation on the chemical structure of the new species except for the fact that its acidity is weaker than that of the nitronic acid. Thus, the species is assumed to have a structure with an oxygen bridge between the  $\alpha$ -benzyl carbon and the nitrogen, as indicated in the scheme in Fig. 6 by the structures A and A<sup>-</sup>. Compound A is a weak acid of the same strength as isobutyric acid, which is one of the final products. Therefore, the electrical conductivity remains constant in the course of the process in which A (or A<sup>-</sup>) is converted into the final products.

The mechanism of the photoreactions proceeding in ethanol-water, derived from these studies, is depicted in Fig. 6.

### 3.3. Experiments with copolymers

The copolymers CP-1 and CP-2 were irradiated in argon-saturated dichloromethane and copolymer CP-3 was irradiated in a 60vol.%ethanol-40vol.%water mixture. Actually, the results obtained did not differ from those found with I, the low molecular weight model. The transient absorption spectra recorded with the copolymers and with the model were quite similar, and the rates of formation and decay of the transient absorption spectra were the same within the error limits, as can be seen from Tables 3 and 4. The electrical conductivity measurements also yielded quite similar results as is shown in Table 5. Therefore, it can be concluded that there is no polymer effect with respect to the photorearrangement of *o*-nitrobenzyl esters. This result was substantiated by the quantum yields  $\phi(\text{RCOOH})$  for acid formation. Within the error limits, equal values were obtained for I ( $\phi(\text{RCOOH}) = 0.25$ ) and for copolymer 3 ( $\phi(\text{RCOOH}) = 0.24$ ).

TABLE 3

Irradiation of the copolymers and the model compound in argon-saturated CH<sub>2</sub>Cl<sub>2</sub>: half-lives of formation and decay of the transient absorption at  $\lambda = 400$  nm

Compound	Concentration (g l <sup>-1</sup> )	Formation of absorption (s)	Decay of absorption (s)
I	0.08 <sup>a</sup>	$(4.0 \pm 0.3) \times 10^{-9}$	$(6.0 \pm 0.5) \times 10^{-5}$
CP-1	1.5	$(4.4 \pm 0.3) \times 10^{-9}$	$(6.0 \pm 0.5) \times 10^{-5}$
CP-2	1.5	$(4.0 \pm 0.3) \times 10^{-9}$	$(6.0 \pm 0.5) \times 10^{-5}$

<sup>a</sup> $3.2 \times 10^{-4}$  M.

TABLE 4

Irradiation of copolymer CP-3 and the model compound in 60vol.%ethanol-40vol.%water: half-lives of the formation and the decay of transient absorption spectra

Compound	Concentration (g l <sup>-1</sup> )	Formation at $\lambda = 380 \text{ nm}$ (s)	Decay at $\lambda = 380 \text{ nm}$ (s)	Formation at $\lambda = 450 \text{ nm}$ (s)	Decay at $\lambda = 450 \text{ nm}$ (s)
I	0.08	$(4.0 \pm 0.3) \times 10^{-9}$	$(1.8 \pm 0.1) \times 10^{-6}$	$(1.8 \pm 0.1) \times 10^{-6}$	$(4 \pm 3) \times 10^{-3}$
CP-3	0.3	$(4.0 \pm 0.3) \times 10^{-9}$	$(1.8 \pm 0.1) \times 10^{-6}$	$(1.8 \pm 0.1) \times 10^{-6}$	$(4 \pm 3) \times 10^{-3}$

TABLE 5

Irradiation of copolymer CP-3 and the model compound in 60vol.%ethanol-40vol.%water: half-lives of formation and decay of the photocurrent

Compound	Concentration (g l <sup>-1</sup> )	Formation (s)	Decay (s)
I	0.08 <sup>a</sup>	$(1.5 \pm 0.3) \times 10^{-6}$	$(1.0 \pm 0.2) \times 10^{-5}$
CP-3	0.4	$(1.5 \pm 0.3) \times 10^{-6}$	$(1.0 \pm 0.2) \times 10^{-5}$

<sup>a</sup> $3.2 \times 10^{-4} \text{ M}$ .

#### 4. Conclusions

The photorearrangement of I and of copolymers containing II in solution involves nitronic acids as relatively long-lived species. The formation of the nitronic acid following the excitation of I and the copolymers with UV light is a rather fast process with a lifetime of 5 ns which is independent of the polarity of the solvent. On the contrary, the rate of conversion of the nitronic acid is strongly influenced by the solvent: under conditions favouring the dissociation of the nitronic acid, its decomposition is significantly retarded. Typically, a lifetime of 10 ms was found for solutions of the *o*-nitrobenzyl compounds in mixtures of ethanol and water. In CH<sub>2</sub>Cl<sub>2</sub>, however, the lifetime was 80  $\mu$ s. In ethanol-water evidence for the existence of an intermediate formed during the decomposition of nitronate anions was obtained from electrical conductivity measurements.

#### Acknowledgments

The authors are grateful to Dr. G. Beck for maintaining the flash photolysis set-ups and to Dr. J. Lilie who assisted in the computer evaluation of the data.

## References

- 1 H. Barzynski and D. Sanger, *Makromol. Chem.*, **93** (1981) 131.
- 2 E. Reichmanis, R. Gooden, C. W. Wilkins and H. Schonhorn, *J. Polym. Sci., Polym. Chem. Ed.*, **21** (1983) 1075.
- 3 E. Reichmanis, B. C. Smith and R. Gooden, *J. Polym. Sci., Polym. Chem. Ed.*, **23** (1985) 1.
- 4 B. Amit, U. Zehari and A. Patchornik, *Isr. J. Chem.*, **12** (1974) 103.
- 5 W. N. R. Pillay, *Synthesis*, (1980) 1.
- 6 D. Gravel, J. Hebert and D. Thoraval, *Can. J. Chem.*, **61** (1982) 400.
- 7 H. Barzynski, M. J. Jun, D. Sanger and O. Volkert, *Ger. Offen. 2150691* (1973).  
H. Barzynski, M. Marx, D. Sanger and G. Storck, *Ger. Offen. 2242394* (1974).
- 8 C. C. Petropoulos, *J. Polym. Sci., Polym. Chem. Ed.*, **15** (1977) 1637.
- 9 E. Reichmanis, C. W. Wilkins and E. A. Chandross, *J. Vac. Sci. Technol.*, **19** (1981) 1338.
- 10 G. Wettermark, *Nature*, **194** (1962) 677; *J. Phys. Chem.*, **66** (1962) 2560.
- 11 G. Wettermark and R. Ricci, *J. Chem. Phys.*, **39** (1963) 1218.
- 12 G. Wettermark, E. D. Black and L. Dogliotti, *Photochem. Photobiol.*, **4** (1965) 229.
- 13 M. E. Langmuir, L. Dogliotti, E. D. Black and G. Wettermark, *J. Am. Chem. Soc.*, **91** (1969) 2204.
- 14 K. Suryanarayanan and C. Capellos, *Int. J. Chem. Kinet.*, **6** (1974) 89.
- 15 R. W. Yip, D. K. Sharma, R. Giasson and D. Gravel, *J. Phys. Chem.*, **88** (1984) 5770.
- 16 R. W. Yip, D. K. Sharma, R. Giasson and D. Gravel, *J. Phys. Chem.*, **89** (1985) 5328.
- 17 W. G. Filby and K. Gunther, *Z. Phys. Chem. N. F.*, **95** (1975) 289.
- 18 M. V. George and J. C. Scaiano, *J. Phys. Chem.*, **84** (1980) 492.
- 19 G. Ciamician and P. Silber, *Ber. dtsh. chem. Ges.*, **34** (1901) 2040; **35** (1902) 1992.
- 20 R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **90** (1968) 1949.
- 21 G. Beck, *J. Radioanal. Nucl. Chem.*, **101** (1986) 151.
- 22 R. Kuhlmann and W. Schnabel, *J. Photochem.*, **7** (1977) 287.