FORMATION AND DECAY OF NITRONIC ACID IN THE PHOTOREARRANGEMENT OF *o*-NITROBENZYL ESTERS

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Summary

o-Nitrobenzyl benzoate (oNBB), α-methyl-*o*-nitrobenzyl benzoate (αMoNBB), α-phenyl-*o*-nitrobenzyl benzoate (αPoNBB) and copolymers of methyl methacrylate and of *o*-nitrobenzyl, methyl-*o*-nitrobenzyl and phenyl-*o*-nitrobenzyl acrylates were flash photolysed or continuously irradiated with UV light in dilute solution. The quantum yield $\phi(PR)$ of bond cleavage in the photorearrangement of the *o*-nitrobenzyl esters does not depend on the chemical nature of the ester group but is significantly influenced by the substituent in the α position: $\phi(PR) = 0.22 \pm 0.03$ (αMoNBB, αPoNBB) and $\phi = 0.10 \pm 0.02$ (oNBB). This was revealed from the yields of carboxylic acid and *o*-nitrosobenzyl groups. The differences in $\phi(PR)$ correspond to the differences in the yields of nitronic acid formed as an intermediate. In aqueous systems the kinetics of the decay of the nitronic acid were found to be determined by the formation of rather stable nitronate ions according to the equilibrium

$$\text{Nitronic acid} \rightleftharpoons \text{nitronate ion} + H^+$$
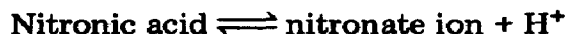
The relatively long lifetime of the nitronate ion formed in the case of oNBB (longer than 100 ms) is assumed to be caused by a rather strong intramolecular interaction of the hydrogen at the α-carbon with the nitronate group and the carbonyl group. In acetonitrile solution, where nitronate ions were not formed, the non-substituted compound (oNBB) also behaved differently from the substituted compounds (αMoNBB and αPoNBB): two transients differing in lifetime (6×10^{-4} and 5.8×10^{-3} s) were observed with oNBB which were ascribed to different isomers of the nitronic acid. Addition of H_2SO_4 to acetonitrile solutions accelerated the rearrangement of the nitronic acid. The acceleration is assumed to be caused by protonation of the oxygen of the carbonyl group. The carbocation formed this way strongly interacts intramolecularly with oxygens of the nitronic acid group, thus inducing the rearrangement.

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1. Introduction

α-substituted o-nitrobenzyl esters undergo a rearrangement upon irradiation with UV light. The rearrangement results in the formation of the corresponding α-substituted o-nitrosobenzaldehyde and a carboxylic acid [1 - 3]:

$$\text{(structure: } R^1, CH\text{-}O\text{-}C(=O)\text{-}R^2, NO_2 \text{ on benzene)} \xrightarrow{h\nu} \text{(structure: } R^1, C{=}O, NO \text{ on benzene)} + HO\text{-}C(=O)\text{-}R^2 \tag{1}$$

In this process an intermediate possessing a strong optical absorption band ($\lambda \approx 400$ nm) is formed, as was recently demonstrated for the case of α-methyl-o-nitrobenzyl isobutyrate ($R^1 \equiv CH_3$, $R^2 \equiv CH(CH_3)_2$) [4]. This intermediate was assigned to a nitronic acid formed with a lifetime of about 5 ns both in polar and in non-polar solvents. The decay of the nitronic acid depended markedly on the polarity of the solvent. In a polar medium (60vol.%EtOH−40vol.%H$_2$O) the nitronic acid dissociated with a lifetime of 3 μs as indicated by a build-up of a new absorption band and an increase in the electrical conductivity.

$$\text{(structure with } CH_3, C\text{-}O\text{-}C(=O)\text{-}CH(CH_3)CH_3, H, NO_2\text{)} \xrightarrow{h\nu} \text{(nitronic acid structure, } {}^+N\text{-}OH, {}^-O\text{)} \rightleftharpoons \text{(nitronate anion structure, } {}^+N\text{-}O^-, {}^-O\text{)} + H^+ \tag{2}$$

<div align="center">nitronic acid   nitronate anion</div>

The present work deals with substituent effects on the formation and the decay of the nitronic acid. The acceleration of the decay of the nitronic acid by sulphuric acid was also studied.

As will be shown below, the chemical nature of the substituent R^2 (aliphatic or aromatic) has no influence on the rearrangement. With respect to R^1 it was found that the unsubstituted compound ($R^1 \equiv H$) exhibited behaviour quite different from that of methyl- or phenyl-substituted compounds.

2. Experimental details

2.1. Materials

Both low molecular weight o-nitrobenzyl derivatives and copolymers possessing, in one of the comonomers, repeating units with pendant o-nitrobenzyl groups were used in this work. Tables 1 and 2 present information concerning the structure of the compounds and the composition of the copolymers.

TABLE 1

Chemical structures and extinction coefficients (solvent, CH_3CN) at 347 nm of o-nitrobenzyl derivatives

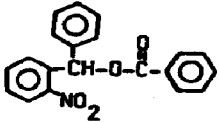| Compound	Formula	$\epsilon_{347\,nm}$ $(1\ mol^{-1}\ cm^{-1})$
o-Nitrobenzyl benzoate (oNBB)	structure	290 ± 10
α-Methyl-o-nitrobenzyl benzoate (αMoNBB)	structure	375 ± 10
α-Methyl-o-nitrobenzyl isobutyrate (αMoNBI)	structure	375 ± 10
α-Phenyl-o-nitrobenzyl benzoate (αPoNBB)	structure	346 ± 6
o-Nitrobenzyl alcohol (oNBAL)	structure	346 ± 6

TABLE 2

Chemical structures and extinction coefficients (solvent, CH_3CN) at 347 nm of copolymers of o-nitrobenzyl acrylates (oNBA) and methyl methacrylate (MMA)

Copolymer	Structure of oNBA	Content of oNBA (mol.%)	$\epsilon_{347\,nm}$ $(1\ mol^{-1}\ cm^{-1})$
CP-oNBA–MMA	structure	31.3	290 ± 10
CP-αMoNBA–MMA	structure	32.9	375 ± 10
CP-αPoNBA–MMA	structure	22.9	346 ± 10

2.1.1. Synthesis of the o-nitrobenzyl compounds

2.1.1.1. o-Nitrobenzyl benzoate.
o-Nitrobenzyl alcohol (38.3 g, 0.25 mol) and triethylamine (37.9 g, 0.375 mol) were dissolved in 300 ml toluene at room temperature. Benzoyl chloride (38.7 g, 0.275 mol) dissolved in 50 ml toluene was added dropwise with stirring and the mixture was allowed to react for 3 h at 60 °C. The solution was then diluted with 1 l toluene and washed with water, an aqueous solution saturated with sodium hydrogen carbonate and again with water. After the organic phase had been dried over sodium sulphate, the solvent was evaporated, leaving 51.4 g of a crystalline solid. After recrystallization from ethanol the melting point was 101 - 102 °C.

The following elemental analysis was obtained. Calculated: C, 65.4%; H, 4.3%; O, 24.9%; N, 5.4%. Found: C, 66.0%; H, 4.3%; O, 24.7%; N, 5.5%.

2.1.1.2. o-Nitro-α-methylbenzyl benzoate.
To a solution of 24.72 g (0.44 mol) potassium hydroxide in 120 ml methanol a mixture of 56.68 g (0.44 mol) benzoic acid and 150 ml methanol was added with vigorous stirring at a temperature below 10 °C. 60 ml dimethylformamide (DMF) were added and the methanol was evaporated *in vacuo*. A solution of 54 g (0.23 mol) α-bromoethylbenzene in 100 g DMF was added dropwise for 30 min. After additional stirring at 60 °C for 3 h the mixture was diluted with toluene to 1.5 l, washed with water, sodium hydrogen carbonate solution and again with water and then dried over anhydrous sodium sulphate. The solvent was evaporated *in vacuo* and the remaining solid was recrystallized from ethanol.

The yield of o-nitro-α-methylbenzyl benzoate was 32.7 g, and its melting point was 64 - 65 °C. The following elemental analysis was obtained. Calculated: C, 66.4%; H, 4.83%; O, 23.6%; N, 5.2%. Found: C, 66.6%; H, 4.6%; O, 23.6%; N, 5.4%.

2.1.1.3. o-Nitro-α-phenylbenzyl benzoate: (a) o-nitro-α-phenylbenzyl alcohol.
A Grignard reagent was prepared from 24.3 g (1 mol) Mg and 157 g (1 mol) bromobenzene in 200 ml anhydrous tetrahydrofuran. o-Nitrobenzaldehyde was dissolved in 300 ml toluene and cooled to −30 °C. The Grignard reagent was added dropwise at −30 °C and afterwards allowed to react for an additional 60 min. After the solution had been warmed to −10 °C, 20 ml ethanol were added. Then 100 g ice were added and the mixture was acidified with HCl. The organic phase was separated and the aqueous phase extracted twice with toluene. The combined organic solutions were washed with water, sodium hydrogen carbonate solution and again with water and were then dried over sodium sulphate. After evaporation of the solvent, 200 g of a viscous oil remained, which was distilled *in vacuo* at 160 °C and 30 Pa.

2.1.1.3. o-Nitro-α-phenylbenzyl benzoate: (b) preparation of the benzoic acid ester. The esterification was carried out in the same manner as with o-nitrobenzyl alcohol. The yield of o-nitro-α-phenylbenzyl benzoate was 82%, and its melting point was 92 °C. The following elemental analysis was obtained. Calculated: C, 72.07%; H, 4.5%; O, 19.22%; N, 4.2%. Found: C, 72.0%; H, 4.7%; O, 19.0%; N, 4.2%.

2.1.2. Synthesis of copolymers

The o-nitrobenzyl acrylates listed in Table 2 were synthesized by esterification of o-nitrobenzyl alcohols with acrylic acid. The monomers were copolymerized with methyl methacrylate (MMA) in ethyl acetate solution at 60 °C using azobis(isobutyronitrile) (AIBN) as the initiator. 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 copolymers possessed unimodal molecular weight distributions as inferred from gel permeation chromatography measurements.

2.2. Flash photolysis studies

2.2.1. Irradiation of samples

Dilute solutions of o-nitrobenzyl compounds, freed from oxygen by bubbling with argon, were irradiated in rectangular quartz cells with 20 ns flashes of 347 nm light produced by a ruby laser with the aid of a second harmonic generator. Actinometry was performed using cells of path length 1 cm with solutions of benzophenone (1.15×10^{-3} mol l^{-1}) and naphthalene (1.03×10^{-1} mol l^{-1}) in CH_2Cl_2. The absorbed dose per flash was calculated from the concentration of naphthalene triplets formed by energy transfer from benzophenone, with $\epsilon = 1.51 \times 10^4$ l mol^{-1} cm^{-1} at 425 nm and $\phi(T) = 1.0$.

2.2.2. Detection methods

Optical absorption and electrical conductivity methods were employed. In the latter case a quartz cell containing a pair of platinum electrodes was used. The cell was attached to a flow system. Both a d.c. set-up and an a.c. set-up were used to follow changes in the electrical conductivity of the irradiated solutions [5].

2.3. Determination of quantum yields

For quantum yield determination dilute solutions of o-nitrobenzyl compounds were continuously irradiated either with the light of a high pressure mercury lamp equipped with an interference filter transparent to light of wavelength 365 nm or with the light of a xenon lamp using a monochromator (Polytech, model 6M 252) for selecting light of wavelength 336 nm. In some experiments the solutions were irradiated with 254 nm light produced by a low pressure mercury lamp (TNN 15/32, Heraeus, Original Hanau). The quantum yield of the photorearrangement was determined from the yield of carboxylic acid and of o-nitrosobenzyl groups.

2.3.1. Determination of carboxylic acid groups

Carboxylic acid groups were determined in the irradiated solution by titration with an ethanolic solution of KOH (0.01 M). Benzoic acid was also determined with the aid of thin-layer chromatography. For this purpose an apparatus of Iatron Laboratories Inc. (Iatroscan TH-10) was used together with rods (Chromarod S II). 15 μl of the irradiated solution was applied to each rod. A mixture of benzene, methanol, acetonitrile and aqueous ammonia solution (25 wt.% NH$_3$) in the volume ratio of 3:2.5: 1:0.3 was employed as the developer. After development the rods were dried at 50 °C in a vacuum oven at about 150 Pa.

2.3.2. Determination of o-nitrosobenzyl groups

At wavelengths between 300 and 340 nm, the absorptivities of o-nitrosobenzyl and o-nitrobenzyl groups differ markedly. For example, the extinction coefficients of o-nitrosobenzene and o-nitrobenzene at 330 nm, in acetonitrile solution, are $\epsilon_{nitroso}$ = 2300 l mol^{-1} cm^{-1} and ϵ_{nitro} = 227 l mol^{-1} cm^{-1}. The increase Δ(OD) in the optical density resulting from the formation of o-nitrosobenzyl groups and the simultaneous decay of o-nitrobenzyl groups is given by the equation

$$\Delta(OD) = \Delta(OD)_{nitroso} - \Delta(OD)_{nitro} \tag{3}$$

Accordingly, the concentration $c_{nitroso}$ (mol l^{-1}) of o-nitrosobenzyl groups was obtained from the equation

$$c_{nitroso} = \frac{\Delta(OD)}{(\epsilon_{nitroso} - \epsilon_{nitro})d} \tag{4}$$

$\epsilon_{nitroso}$ and ϵ_{nitro} denote the extinction coefficients, in litres per mole per centimetre, of the o-nitrosobenzyl group and the o-nitrobenzyl group respectively. d is the optical path length in centimetres.

3. Results

3.1. Transient absorption spectra

Irradiation of oNBB, αMoNBB and αPoNBB in 60vol.%ethanol–40vol.%water or acetonitrile with 20 ns flashes of 347 nm light led to the appearance of the absorption spectrum of nitronic acid during the flash. Typical results are presented in Figs. 1 and 2.

The spectra recorded at the end of the flash ($t = 0$) possess maxima between 390 and 430 nm depending on the chemical nature of the substituent in the α position. This can be seen from Table 3, which also shows results obtained with the copolymers. Obviously, there is no polymer effect: the corresponding pairs of compounds, namely oNBB and CP-oNBA–MMA, αMoNBB and CP-αMoNBA–MMA and αPoNBB and CP-αPoNBA–MMA exhibit maxima at the same wavelengths. Moreover, the optical density measured at constant absorbed dose (6×10^{-5} einsteins l^{-1}) is the same for
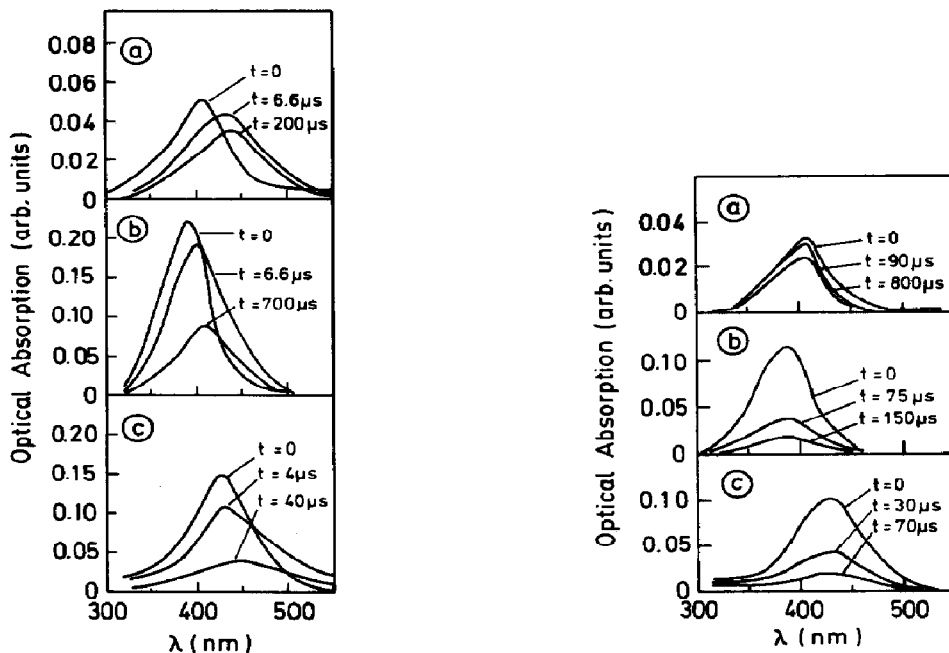
Fig. 1. Transient absorption spectra recorded with argon-saturated dilute solutions of (a) oNBB (7.7×10^{-4} mol l^{-1}), (b) αMoNBB (5.6×10^{-4} mol l^{-1}) and (c) αPoNBB (5.8×10^{-4} mol l^{-1}) in 60vol.%ethanol–40vol.%water. $\lambda_{inc} = 347$ nm; duration of flash, about 20 ns; $D_{abs} = 7 \times 10^{-5}$ einsteins l^{-1}.

Fig. 2. Transient absorption spectra recorded with argon-saturated dilute solutions of (a) oNBB (7.5×10^{-4} mol l^{-1}), (b) αMoNBB (6.1×10^{-4} mol l^{-1}) and (c) αPoNBB (5.8×10^{-4} mol l^{-1}) in acetonitrile. $\lambda_{inc} = 347$ nm; duration of flash, about 20 ns; $D_{abs} = 7 \times 10^{-5}$ einsteins l^{-1}.

TABLE 3

Absorption maxima and quantum yields of bond cleavage for various o-nitrobenzyl compounds

Compound	λ_{max} [a]	$(OD)_{max}$ [b]	ϕ_{AC} [c]	$\phi_{nitroso}$ [d]
oNBB	410	0.025	0.08	
αMoNBB	390	0.104	0.19	0.19
αPoNBB	430	0.077	0.20	0.23
oNBAL	390	0.091		0.35
CP-oNBA–MMA	410	0.029	0.11	
CP-αMoNBA–MMA	390	0.107	0.24	
CP-αPoNBA–MMA	430	0.074	0.24	

[a] Wavelength of maximum absorption of nitronic acid.

[b] Optical density of nitronic acid at λ_{max} at $D_{abs} = 6 \times 10^{-5}$ einsteins l^{-1}.

[c] Quantum yield of carboxylic acid determined by titration with KOH in ethanolic solution.

[d] Quantum yield of nitrosobenzene groups determined from the increase in the optical density at 330 nm with the aid of the extinction coefficients of nitrosobenzene and nitrobenzene (see Section 2.3.2).

each couple. It is interesting to note that $(OD)_{max}$ increases significantly upon substituting a hydrogen in the α position by a methyl or a phenyl, the increase being most pronounced in the case of methyl substitution. Notably, the same trend was observed with respect to the variation in the quantum yields of bond cleavage as can be seen from a comparison of columns 3 and 4 of Table 3.

The non-substituted compounds exhibit quantum yields about half as high as those of the phenyl- or methyl-substituted compounds. A quantitative correlation between the $(OD)_{max}$ and the ϕ is not possible since the extinction coefficients of the nitronic acids are unknown.

3.2. Decay of transient absorption spectra

In ethanol—water the decay of the optical absorption band formed during the flash was accompanied by the build-up of a new absorption band with a maximum shifted to the red with respect to the initial spectrum.

The similar behaviour observed previously [4] upon irradiation of α-methyl-o-nitrobenzyl isobutyrate in ethanol—water was assumed to reflect the dissociation of the nitronic acid according to reaction (2). It appears that analogously the formation of the new red-shifted absorption band also reflects the formation of nitronate ions. Within the error limit, the half-life of formation of the new band was the same for all three compounds ($\tau_{1/2} = 1.0 \pm 0.1$ μs). Evidence for the assignment of the new band to nitronate ions formed by dissociation of the nitronic acids came from electrical conductivity measurements (*vide infra*).

Whereas the rate of formation of nitronate ions was the same for the three compounds, the rates of decay were quite different as is shown in Table 4.

In the case of the phenyl-substituted compound $\tau_{1/2}$ was 36 μs. A value about one order of magnitude higher was found for the methyl-substituted compound and in the case of the non-substituted compound $\tau_{1/2}$ was so long that it could not be measured with our set-up. A value greater than 100 ms was estimated for the half-life.

Kinetic data obtained in acetonitrile solution with the three benzoates are compiled in Table 5. With acetonitrile solutions of αMoNBB and αPoNBB, the spectra formed during the flash decayed steadily according to first-order kinetics with half-lives of 65 ± 5 μs and 30 ± 5 μs respectively.

TABLE 4

Half-lives of formation and decay of the absorption band[a] formed after the flash in ethanol—water solutions (error limit, ±10%)

	oNBB	αMoNBB	αPoNBB
$\tau_{1/2}$(formation)	1.0 μs	1.0 μs	1.0 μs
$\tau_{1/2}$(decay)	>100 ms	550 μs	36 μs

[a]At λ_{max} (see Table 3).

TABLE 5

Half-lives of decay of the absorption of nitronic acids in argon- and O_2-saturated aceto-nitrile solution[a] ($\lambda_{inc} = 347$ nm; $D_{abs} = 5 \times 10^{-5}$ einsteins l^{-1})

Compound	Concentration (mol l^{-1})	$\tau_{1/2}(Ar)$ (s)	$\tau_{1/2}(O_2)$ (s)
oNBB[b]	7.7×10^{-4}	Rapid mode (30%): $(4 \pm 2) \times 10^{-4}$	Rapid mode (30%): $(4 \pm 2) \times 10^{-4}$
		Slow mode (70%): 4×10^{-3}	Slow mode (70%): 3×10^{-3}
αMoNBB	6.1×10^{-4}	6.3×10^{-5}	6.6×10^{-5}
αPoNBB	5.8×10^{-4}	3.0×10^{-5}	3.3×10^{-5}

[a]Measured at λ_{max} (see Table 3).
[b]Almost identical results were obtained with o-nitrobenzyl isobutyrate (oNBI).

The non-substituted compound, oNBB, in contrast, exhibited quite different behaviour: the transient absorption was much longer lived than that of the other two compounds. Moreover, two transient species could be discriminated. As can be seen in Fig. 3, subtraction of the spectra shown in Fig. 2(a) yields two absorption spectra: a rapidly decaying absorption band ($\tau_{1/2} = 500$ μs) with a maximum at about 440 nm and a more slowly decaying band ($\tau_{1/2} = 4$ ms) with a maximum at about 410 nm.

Table 5 also gives the half-lives of the transient optical absorption measured with oxygen-saturated acetonitrile solutions. Within the error limits, these values do not differ from those obtained in the absence of oxygen, and this is in accordance with the assignment of the transient absorption to nitronic acid. If the transient absorption were due to a free radical, oxygen should affect its lifetime.
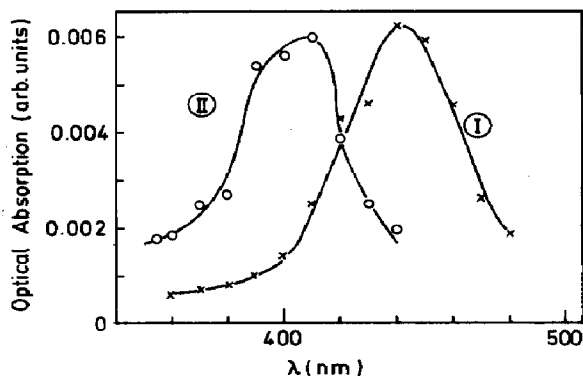

Fig. 3. Flash photolysis of oNBB in argon-saturated acetonitrile solution: difference spectra obtained by subtraction of spectra presented in Fig. 2(a). I, spectrum ($t = 0$) — spectrum ($t = 90$ μs). II, spectrum ($t = 90$ μs) — spectrum ($t = 800$ μs).

3.3. Experiments concerning the ionic dissociation of nitronic acids

It was found previously [4] that the electrical conductivity increased after the flash when αMoNBI was irradiated in 60vol.%ethanol–40vol.%-water. The rate of increase corresponded exactly to the rate of formation of the new absorption band. These findings were interpreted on the basis of the ionic dissociation of the nitronic acid according to reaction (2). In the present work analogous results were obtained on irradiating the three benzoates oNBB, αMoNBB and αPoNBB in ethanol–water solution. In each case the electrical conductivity increased after the flash with a half-life of 0.8 ± 0.2 μs, corresponding very well to the half-life of the build-up of the absorption band of the nitronate ions. A typical result is presented in Fig. 4 which shows the increase in the electrical conductivity after the flash observed in the case of αMoNBB.
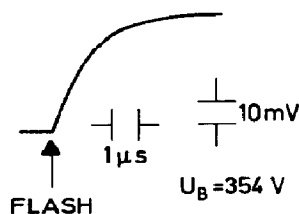
Fig. 4. Flash photolysis of αMoNBB in argon-saturated 60vol.%ethanol–40vol.%water: increase in the electrical conductivity. [αMoNBB] = 5.6×10^{-4} mol l^{-1}; D_{abs} = 7×10^{-5} einsteins l^{-1}. λ_{inc} = 347 nm.

Contrary to these findings, no change in the electrical conductivity was detectable when the three benzoates were irradiated in acetonitrile solution. Thus, it was concluded that, in acetonitrile solution, the nitronic acids of the three benzoates do not undergo ionic dissociation.

3.4. Quantum yields of photorearrangement

In order to determine the quantum yields of photorearrangement the o-nitrobenzene compounds were continuously irradiated. After irradiation the concentration of nitrosobenzyl and/or carboxylic acid groups was measured. In columns 4 and 5 of Table 3, the quantum yields of carboxylic acid groups, ϕ_{CA}, and of nitrosobenzyl groups, $\phi_{nitroso}$, are compiled. These groups are formed in equal parts by the photorearrangement and, therefore, the yields should be equal. It can be seen that the $\phi_{nitroso}$ values obtained with the aid of the extinction coefficients of nitrobenzene and nitroso-benzene are in fair agreement with the ϕ_{CA} values obtained by titration. It is notable that the lowest values were found in the case of the non-substituted esters, although o-nitrobenzyl alcohol undergoes the photorearrangement with the highest yield. The value obtained in the latter case is about three times lower than that reported previously [1].

3.5. Influence of sulphuric acid on the photorearrangement
3.5.1. Formation and decay of nitronic acid

In aqueous solution, nitronic acids of phenylmethanes with an o-nitro group have been reported to undergo an acid-catalyzed isomerization to the nitro form [6 - 8]. In the photoisomerization of 2,4-dinitrotoluene to the corresponding nitronic acids, Wettermark and Ricci [8] found half-lives for the first-order fading of the nitronic acid absorption varying from 20 μs to 1 s in the pH range 2 - 13. In this case, the back reaction, i.e. the formation of 2,4-dinitrotoluene, was accelerated by Brønsted acids. It appears that protons strongly influence the equilibrium (pK = 2.2)

$$\text{Nitronic acid} \rightleftharpoons H^+ + \text{nitronate ion} \qquad (5)$$

and that the accelerating effect of protonic acids is a consequence of a shift of this equilibrium to the left-hand side. It should be taken into account that direct isomerization of the nitronate to the nitro form is not possible.

In the present work, we thought it would be interesting to study the influence of a protonic acid, H_2SO_4, on the behaviour of undissociated nitronic acids dissolved in an aprotic solvent. For this purpose, flash photolysis experiments with acetonitrile solutions of αMoNBI and αMoNBB were carried out. In these studies it was found that the formation of nitronic acid was not influenced by sulphuric acid. The same transient absorption spectrum was formed both in the absence and in the presence of sulphuric acid, as can be seen in Fig. 5, which shows transient absorption spectra recorded at the end of the flash and at various times after the flash. Moreover, the yield of nitronic acid was not influenced by sulphuric acid; this was concluded from the fact that at constant absorbed dose the optical density measured at the end of the flash was the same whether or not sulphuric acid was present in the solution.
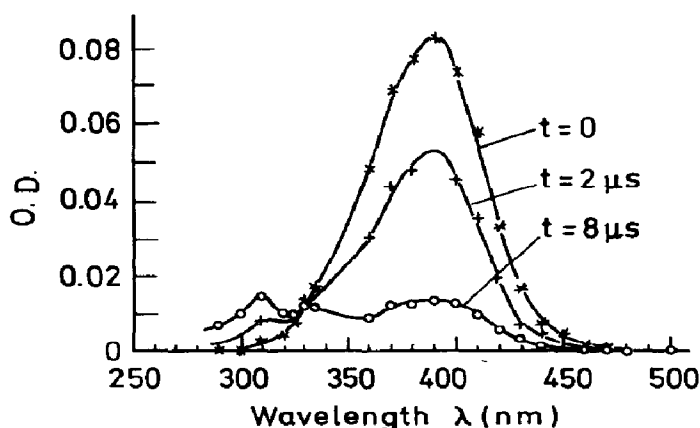

Fig. 5. Flash photolysis of αMoNBI in argon-saturated acetonitrile solution containing sulphuric acid: transient absorption spectra recorded at the end of the flash (t = 0) and 2 and 8 μs after the flash. [αMoNBI] = 3.3 $\times$ 10^{-4} mol l^{-1}; [H_2SO_4] = 3.7 $\times$ 10^{-4} mol l^{-1}; D_{abs} = 2.7 $\times$ 10^{-5} einsteins l^{-1}. λ_{inc} = 347 nm.

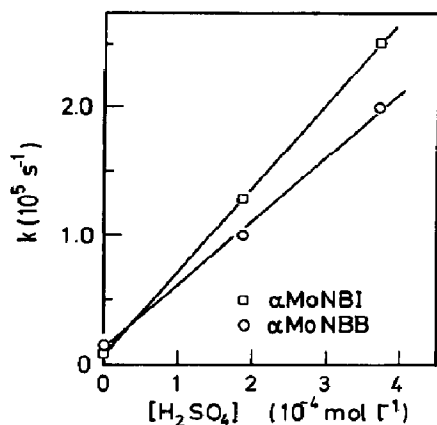Fig. 6. Flash photolysis of αMoNBB and αMoNBI in argon-saturated acetonitrile solution: first-order rate constants of the decay of the optical absorption at λ = 390 nm *vs.* the concentration of sulphuric acid.

With respect to the decay rate of the absorption of the nitronic acid, sulphuric acid was observed to have a marked influence: the decay rate of the transient absorption was strongly accelerated, as is demonstrated in Fig. 6, where the first-order rate constant of the decay of the transient absorption is plotted *vs.* the concentration of the sulphuric acid. The shape of the spectrum did not change during its decay. Thus, the measured decay rate reflects the disappearance of the nitronic acid.

It is notable that in these experiments the decay rate of the nitronic acid was not affected by adding water (up to 5.6 mol l⁻¹) or NaOH (up to 3×10^{-3} mol l⁻¹) to acetonitrile solutions of αMoNBB. This can be seen from Table 6 which shows that, except for the case of sulphuric acid, the same half-life was found ($\tau_{1/2}$ = 77 ± 7 μs).

TABLE 6

Irradiation of αMoNBB in argon-saturated acetonitrile solution containing various additives: half-lives of the decay of the transient absorption at λ = 390 nm ([αMoNBB] = 2.9×10^{-4} mol l⁻¹; D_{abs} = 7×10^{-5} einsteins l⁻¹)

Additive	Concentration of additive (mol l⁻¹)	$\tau_{1/2}$ (μs)
—	—	75
H_2O	5.6×10^{-2}	70
H_2O	5.6	84
NaOH	2.0×10^{-3}	70
H_2SO_4	3.7×10^{-4}	3.5

3.5.2. Quantum yields of the photorearrangement

The quantum yield of the photorearrangement was not influenced by sulphuric acid. This was evidenced by continuously irradiating αMoNBB in
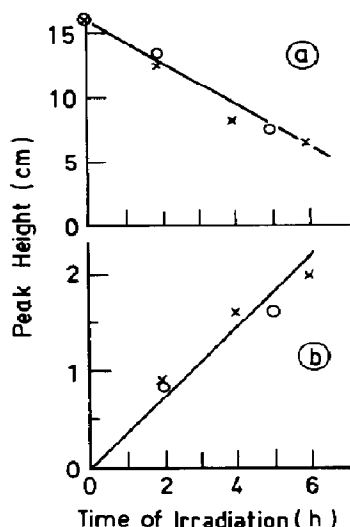
Fig. 7. Continuous irradiation of αMoNBB (6.0×10^{-4} mol l^{-1}) in argon-saturated acetonitrile solution at λ_{inc} = 254 nm in the absence (O) and the presence ($\times$) of sulphuric acid (3.7×10^{-4} mol l^{-1}). Absorbed dose rate Dr_{abs} = 3.6×10^{-4} einsteins l^{-1} h^{-1}. Decrease in (a) [αMoNBB] and increase in (b) [benzoic acid] as determined by thin-layer chromatography vs. the irradiation time.

acetonitrile solution containing sulphuric acid up to 3.7×10^{-4} mol l^{-1} with 336 nm light. After the irradiation, the increase in the optical density at λ = 330 nm owing to the formation of nitrosobenzyl groups was measured. The results yielded $\phi_{nitroso}$ = 0.19 ± 0.2, i.e. the same value as that obtained in the absence of sulphuric acid. Moreover, the yield of benzoic acid was determined by thin-layer chromatography. As can be seen from Fig. 7, where the peak heights of the chromatograms are plotted vs. the irradiation time, neither the increase in the concentration of benzoic acid nor the consumption of αMoNBB were affected by sulphuric acid. It is therefore concluded that sulphuric acid only accelerates the rate of decay of nitronic acid, and does not influence the chemistry of this process.

4. Discussion

The results clearly show that the quantum yield of the photorearrangement of the o-nitrobenzyl esters studied in this work does not depend on the chemical nature of the ester group: the same yield was obtained whether R^2 was a phenyl group or an aliphatic group. Moreover, a polymer effect was not detectable. The quantum yield, however, increased by a factor of about 2 on substitution of an α-hydrogen by a methyl group or a phenyl group. This difference between the quantum yields is due to differences between the extents to which precursors of the nitronic acids are formed. These processes occur on the nanosecond and sub-nanosecond range and their study was not the objective of this work, which is concerned primarily

with the fate of nitronic acids that exist at the end of the 20 ns flash and can be conveniently detected by their characteristic absorption spectra.

Actually, the decay of the nitronic acid was found to be strongly solvent dependent. In aqueous systems the decay rate was determined by the fact that the nitronic acid–nitronate equilibrium was overwhelmingly shifted to the side of the nitronate. Interestingly, the longest lifetime was observed for the nitronate without a hydrogen substituent in the α position, i.e. the nitronate of oNBB. In this case, the lifetime is at least three orders of magnitude longer than that of αMoNBB and four orders of magnitude longer than that of αPoNBB. This large difference must be due to a very stable structure which is formed in the case of oNBB and which cannot be formed in the two other cases. This structure might be of the form
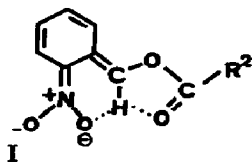

Here, the hydrogen remaining at the α-carbon after the first step of the rearrangement is supposed to interact markedly with the negatively charged oxygen of the nitro group.

In acetonitrile solution, oNBB exhibited kinetic behaviour quite different from that observed with αMoNBB and αPoNBB. As described above, two decay modes of the transient optical absorption were found with oNBB, indicating the transient existence of two species possessing different absorption spectra. With respect to the assignment of the two transients, it could be assumed that the rapid mode is due to a precursor of the nitronic acid. However, this possibility is not very probable since additional picosecond flash photolysis studies revealed [9] that the processes involving the formation of nitronic acids are completed in less than 10 ns. Therefore, alternatively, the two transient absorption bands with different lifetimes may be assigned to two isomers of the nitronic acid. With respect to the chemical structure of the nitronic acid of oNBB, four isomers can be discriminated:
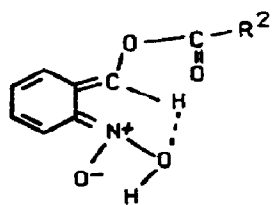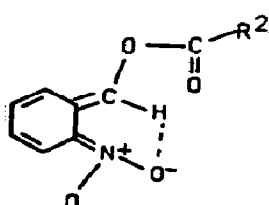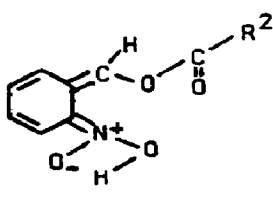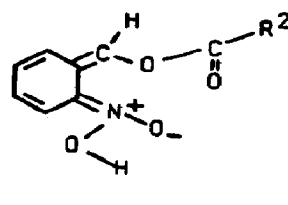

II - 1   II - 2   III - 1   III - 2

It seems that the isomers II-1 and II-2 could be amenable to temporary stabilization based on an interaction of the α-hydrogen with an oxygen of the nitronic acid group. In the case of the isomers III-1 and III-2 such an interaction is sterically precluded and, therefore, the rearrangement can
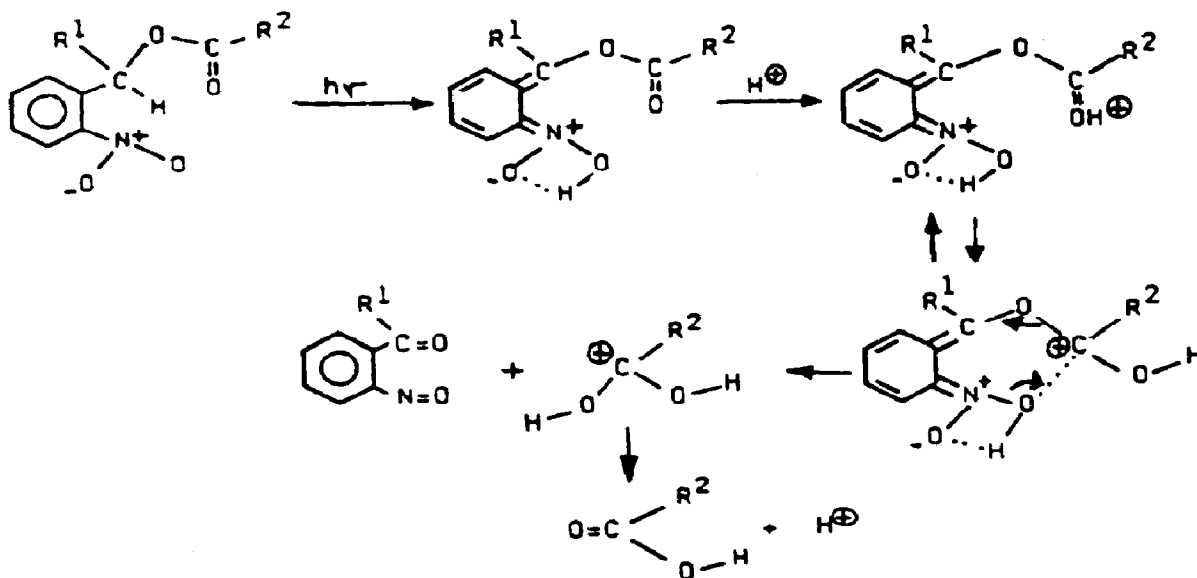
Fig. 8. Scheme for the proton-catalysed rearrangement of nitronic acids derived from o-nitrobenzyl esters.

proceed much more rapidly than with the isomers of structure II. With respect to the interaction of the α-hydrogen with the nitronic acid group, the position of the hydrogen at the nitronic acid group might be of minor importance, which would explain the fact that only two rather than four kinds of transients were kinetically and spectroscopically detectable.

Regarding αMoNBB and αPoNBB, there is no α-hydrogen to improve the stability of the nitronic acid.

Another interesting aspect of this work concerns the mode of action of sulphuric acid in the photorearrangement of o-nitrobenzyl compounds in acetonitrile solution, where nitronic acids do not undergo ionic dissociation. Experiments with the α-methyl-substituted compounds αMoNBI and αMoNBB revealed that both the yield of nitronic acid and the quantum yield of the photorearrangement are not affected by sulphuric acid. The rate of decay of the nitronic acid, however, was strongly accelerated. This effect can be interpreted in terms of a protonation at the carbonyl oxygen, a process leading to the formation of carbocations which are capable of interacting intramolecularly with oxygens of the nitronic acid group. Thus, the decomposition of the molecule is induced. The whole mechanism is illustrated in Fig. 8.

On the basis of this mechanism (which probably pertains specifically to systems containing protons) a bicyclic intermediate such as
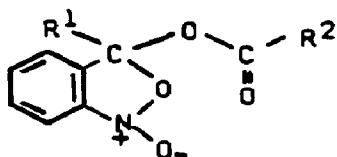
must not be postulated in trying to understand the formation of o-nitroso-benzyl compounds and carboxylic acids in the photorearrangement of o-nitrobenzyl esters.

Acknowledgments

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