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# The matrix-isolation IR spectrum of the *o*-quinonoid intermediate in the photolysis of 2-nitrobenzyl methyl ether

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## Abstract

Photolysis of 2-nitrobenzyl methyl ether in Ar and N<sub>2</sub> matrices at 12 K generated an intermediate with  $\lambda_{max}$  at 430 nm, and which was itself photolabile at 430–460 nm. Matrix IR spectra, as well as the UV-visible absorption, were obtained for this species. An analogous intermediate had previously been observed in flash-photolysis studies of 2-nitrobenzyl 4-cyanophenyl ether, and had been assigned an *o*-quinonoid structure on the basis of its kinetic behaviour and the position of its UV-visible absorption. In the matrix studies with 2-nitrobenzyl methyl ether, the IR spectra confirmed the *o*-quinonoid structure. © 1997 Elsevier Science B.V.

Keywords: Matrix IR spectra; Photolysis; UV-visible absorption

# 1. Introduction

The 2-nitrobenzyl group is well known to provide photocleavable protection for hydroxy compounds, such as alcohols, phenols and carboxylic acids [1,2], and has also been applied to thiols [3] and aldehydes [4]. The majority of organic photocleavages eliminate a small molecule, such as  $N_2$  or CO<sub>2</sub>, as one of the fragments. The photolysis of 2-nitrobenzyl derivatives is one of the relatively rare photocleavage reactions in which two substantial fragments are produced, both capable of bearing functionality. As a result, compounds and materials containing 2-nitrobenzyl groups have been developed as photocleavable polymers (for use as resists) [5], cryptands [6] and DNA building blocks [7,8], and for the photocleavage of oligonucleotides from solid-phase supports [9]. Other interesting applications can be envisaged.

The mechanism of the photocleavage of 2nitrobenzyl ethers and some analogues has been studied by flash photolysis [10,11], and reaction pathways such as those shown in Scheme 1 are understood to operate. Flash photolysis of 2-nitrobenzyl 4-cyanophenyl ether in acetonitrile led to the observation of three transient species: the first, with a lifetime of about 50 ps and with  $\lambda_{max}$ at 650 nm, was identified as the triplet excited

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state of the starting material, the second, with a lifetime of about 1 ns and  $\lambda_{max}$  at 460 nm, was identified as a triplet biradical (see 3), while the third, which persisted beyond 10 ns, had  $\lambda_{max}$  at about 420 nm and was assigned an *o*-quinonoid structure (see 2) [11].

Despite the interest in this reaction and its potential importance for novel 'photochemical effect' materials, there appears to have been no previous study of the reactive intermediates by IR spectroscopy. In this paper we report matrixisolation studies of the photolysis of 2-nitrobenzyl methyl ether 1 and the IR spectrum of the o-quinonoid intermediate 2.

# 2. Experimental

2-Nitrobenzyl methyl ether **1** was prepared by treatment of 2-nitrobenzyl alcohol (Aldrich) with dimethyl sulphate under phase transfer catalysis [12]. At room temperature in acetonitrile **1** had  $\lambda_{\text{max}} = 261 \text{ nm}$  ( $\epsilon = 5400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). Research grade argon (min. 99.9994%) and nitrogen (min. 99.995%) were obtained from BOC.

The matrix-isolation cold cell and its method of use have been described in detail previously [13,14]. Ar and N<sub>2</sub> matrices containing 1 were prepared by evaporation of 1 onto a spectroscopic window cooled to 12 K, with simultaneous deposition of an excess of the host gas. For UV-visible spectra, the cell was fitted with quartz external windows and matrices were deposited on a CaF<sub>2</sub> cold window, while for IR spectra, a KBr cold window and KBr external windows were used.

UV-visible spectra were recorded on a Shimadzu UV-250 instrument, with a double monochromator. IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. Photolyses at 254 nm were carried out with unfiltered low pressure Hg arcs (Vilber Lourmat,  $2 \times 4$  W or  $2 \times 8$  W), and at  $430 \pm 10$  and  $460 \pm 10$  nm with a high pressure Hg arc (Oriel, 200 W) via a high radiance grating monochromator (Applied Photophysics, f/3.4).

### 3. Results and discussion

Fig. 1 shows UV-visible spectra of 1 in an Ar matrix, before and after photolysis. A weak broad absorption  $\lambda_{max} = 430$  nm was observed to arise during the initial photolysis at 254 nm, and this was bleached by subsequent photolysis at 460 nm. Similar results were obtained with  $N_2$  matrices. Allowing for differences in temperature, medium and starting material, this observation agrees closely with the absorption ( $\lambda_{max} = 421$  nm) of the relatively long lived intermediate observed after flash photolysis of the 4-cyanophenyl analogue of **1** [11]. This intermediate was previously assigned an *o*-quinonoid structure (see 2). Not surprisingly, in our matrix experiments we saw no absorption at longer wavelengths that could be attributed to the triplet biradical 3.

Table 1 lists the observed IR absorptions of **1** isolated in Ar and  $N_2$  matrices. There is good agreement between the spectra for the two different matrix hosts, small differences in band positions and intensities being attributed to matrix site effects. Assignments have been made by reference to standard tabulations of data [15]. All these bands diminished in intensity when the matrices were irradiated with 254 nm light, while a large number of new bands arose. Amongst the latter were absorptions which could be attributed to the



Scheme 1.



Fig. 1. UV-visible spectra of 1 in an Ar matrix at 12 K: (a) before photolysis; (b) after 6.5 min photolysis at 254 nm; (c) after a further 30 min photolysis at  $460 \pm 10$  nm. The spectra all have the background subtracted.

expected final products, 2-nitrosobenzaldehyde 5 (v(C=O) at 1724 (Ar) or 1719 (N<sub>2</sub>), v(NO) at 1527 (Ar) or 1528 cm<sup>-1</sup> (N<sub>2</sub>)) [16] and methanol (v(OH) 3340 and 3230 (Ar), or 3362 and 3222  $cm^{-1}$  (N<sub>2</sub>)). The overall reaction thus followed the normal course, but clearly more than one product species was present. Amongst the IR bands which arose on initial photolysis at 254 nm, were a group which diminished in intensity on subsequent long wavelength photolysis (430 + 10)or 460 + 10 nm). These latter IR bands behaved in exactly the same way as the broad electronic absorption at 430 nm, and can therefore be assigned, reasonably confidently, to the same intermediate species. Fig. 2 shows a portion of an IR difference spectrum showing the IR bands which diminish on 460 nm photolysis and which are assigned to the intermediate with the 430 nm electronic absorption. Table 2 lists all the IR

bands assigned to this intermediate in both Ar and  $N_2$  matrices. There is excellent agreement between the two matrix hosts. In most experiments, irradiation at 460 nm (rather than 430 nm) was chosen so as to minimize further photolysis of the starting material. Even so, a very small amount of photolysis of 1 occurred, as shown by the appearance of the strongest two bands of 1 as weak bands in the difference spectrum (Fig. 2), but this caused no ambiguity in assigning bands to the intermediate.

Apart from an OH group, the functionality in 2 would be expected to give rise to IR bands only in the skeletal region of the spectrum, where assignments are difficult to make with certainty. For this reason, the observed IR spectra of the inter-

Table 1

IR absorptions (cm<sup>-1</sup>) of 2-nitrobenzyl methyl ether 1 isolated in Ar and N<sub>2</sub> matrices at 12 K<sup>a</sup>

Ar matrices	N <sub>2</sub> matrices	Assignment
3093 vw <sup>b</sup>	3093 vw	v(C–H) (aromatic)
2998	3002	
2935	2938	
2911	2915	v(C-H) (CH <sub>3</sub> , CH <sub>2</sub> )
2890	2896	
2830	2830	
2090 vw	2090 vw	Combination band
1870 vw	1874 vw	Combination band
1618	1617	v(C=C) (aromatic)
	1598	
1581 vw	1581 vw	v(C=C) (aromatic)
1535 vs	1536 vs	$v_{a}(NO_{2})$
1469	1481	v(C=C) (aromatic)
1452	1454	
1378 m	1382	
1344 s	1351 s	$v_{s}(NO_{2})$
1309	1303 vw	5, 2,
1203 m	1204 w	
1120 s	1116 s	$v_{a}(C-O-C)$
1078	1079	
983 m	981 m	
933 vw	932 vw	
860	859	
792	796	
728 m	734 m	$\gamma$ (C–H) (aromatic)
684	684	

<sup>a</sup> IR spectra were recorded on a Bomem MB-100 FT instrument with MCT detector.

<sup>b</sup> Bands were weak unless denoted: vs, very strong; s, strong; m, medium; vw, very weak.



Fig. 2. An IR difference spectrum in the region  $1800-500 \text{ cm}^{-1}$  obtained after 1.5 h photolysis of 1 with 254 nm light in Ar at 12 K, followed by 3 h photolysis at  $460 \pm 10$  nm. The spectrum shows bands which diminished (downwards) and arose (upwards) on 460 nm photolysis. The former are assigned to the *o*-quinonoid species 2. The two strongest bands of 1 (marked with an asterisk) appear weakly in the spectrum, indicating a very small amount of further photolysis of 1 at 460 nm.

mediate do not allow its unequivocal identification as the *o*-quinonoid species 2. Nevertheless, the observed spectrum accords with structure 2 very well. Firstly, the spectrum is dominated by a small number of strong bands, especially that at 1244 cm<sup>-1</sup> (Ar matrix), which are much stronger than those arising from photolysis of the intermediate (positive-going bands in Fig. 2), and this suggests a highly polar structure. Secondly, the spectrum contains the expected v(OH) absorption. Thirdly, the C=N(O)OH moiety is very similar to a nitrone, differing from the latter by replacement of N-alkyl or -aryl by N-OH; and the observed very strong band at 1244 and strong band at 1556 cm<sup>-1</sup> (Ar matrix) agree well with the expected  $v(N^+-O^-)$  and v(C=N) absorptions, respectively [15,17,18]. Finally, the strong bands at 1124 and 950 cm<sup>-1</sup> (Ar matrix) can reasonably be attributed to  $v_a(C-O-C)$  and v(N-OH) (by comparison with oximes), respectively [15]. Thus all the expected features for 2 are present in the matrix IR spectra. The stereochemistry shown for 2 in Scheme 1 cannot, of course, be deduced from the spectroscopic data, but is expected on stereoelectronic grounds. The possibility that more than one stereoisomer of 2 was present cannot be ruled out, but the IR spectra show few splittings that would suggest that this was the case.

Additional support for the identification of the intermediate as 2 comes from the observation that on photolysis it gives a new species (possibly more than one) with prominent IR bands at 1637, 1091 and 756 cm<sup>-1</sup>, but no carbonyl band in the region of 1700 cm<sup>-1</sup>. This is consistent with the formation of the bicyclic intermediate 4, in which the aromatic ring is regained. Significant further photolysis of 4 would not be expected to occur at 460 nm.

Finally, it should be noted that evidence for the *o*-quinonoid ketene **6** was previously obtained in Ar-matrix studies of the photolysis of 2-nitrobenzaldehyde [19]. This species had  $\lambda_{max}$  at 435 nm, very close to that of **2**, but proved to be very photosensitive; so, despite careful selection of photolysis wavelengths, only ketene bands at 2118 and 2107 cm<sup>-1</sup> could be observed in the IR, and these only weakly.

Table 2

IR bands (cm<sup>-1</sup>) arising after 254 nm photolysis of **1** and diminishing upon subsequent long wavelength photolysis (460 ± 10 nm) in Ar and N<sub>2</sub> matrices at 12 K

Ar matrices	N <sub>2</sub> matrices	Assignment
3533ª	3519	<i>v</i> (OH)
2943	2946	v(CH)
2115	2115	
	1587	
1556 s	1552 s	v(C=N)
1384 m	1384 m	
1267 m	1270 s	
1244 vs	1243 vs	$v(N^+ - O^-)$
1205 m	1203 m	
1147 s	1149 s	
1124 s	1124 s	$v_{a}(C-O-C)$
1101	1098 m	
993	991	
950 s	956 s	v(N-OH)
842	844	
740	746	

<sup>a</sup> The relative intensities of bands were weak unless denoted: vs, very strong; s, strong; m, medium.

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