NITROXIDE AND NITRO-ANION RADICALS DERIVED FROM NITROPHENYL β-D-GLYCOSIDES

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ABSTRACT

Photolysis of *m*- and *p*-nitrophenyl β-D-glycopyranosides in methanol yields the corresponding nitroxide radical under neutral conditions and the nitro-anion radical in the presence of alkali. No stable radicals are produced from the *o*-isomer, due to facile hydrolysis of the glycosidic bond. From the e.s.r. spectra, it is clear that the glycosidic bond remains intact in these radicals, and *m*-proton couplings, not previously resolved, can be identified ($a_H = 1.0$ gauss). For the nitro-anion from the *p*-isomer, $a_N = 15.28$ gauss, which is larger than for other *p*-substituted ether nitro-anions. Radical anions from *o*-, *m*-, and *p*-isomers can be produced electrochemically in acetonitrile, and coupling to H-1 of the glycosyl group, not previously found, is evident ($a_H = 0.3$–0.4 gauss) in the nitro-anion from the *p*-isomers, but not from the *o*- and *m*-isomers. A Hammett-type correlation for *p*-substituents gives σ values of -0.15 for the galactoside and -0.13 for glucoside groups.

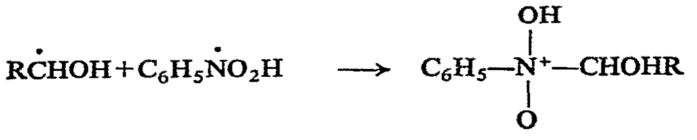
INTRODUCTION

Nitroxide radicals can be generated by photolysis of nitroaromatic compounds in alcohols[1]. Nitrobenzene, for example, gives first the hydrogen adduct which subsequently reacts with a radical derived from the alcohol to give an intermediate which disproportionates to a stable nitroxide radical and a hydroxyl radical, according to the reactions *1–4*.

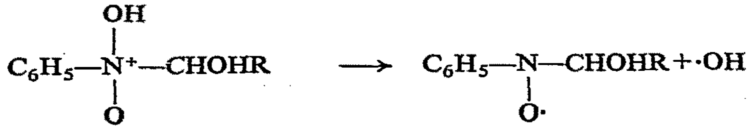
When nitrobenzene–methyltetrahydrofuran glasses are γ-irradiated at 77K, the

$$C_6H_5NO_2 \xrightarrow{h\nu} (C_6H_5NO_2)^* \qquad (1)$$

$$(C_6H_5NO_2)^* + RCH_2OH \longrightarrow C_6H_5\dot{N}O_2H + R\dot{C}HOH \qquad (2)$$



$$R\dot{C}HOH + C_6H_5\dot{N}O_2H \longrightarrow C_6H_5-\underset{\displaystyle O}{\overset{\displaystyle OH}{N^+}}-CHOHR \qquad (3)$$



$$C_6H_5-\underset{\displaystyle O}{\overset{\displaystyle OH}{N^+}}-CHOHR \longrightarrow C_6H_5-\underset{\displaystyle O\cdot}{N}-CHOHR + \cdot OH \qquad (4)$$

radical ion is observed[2a]. On warming the glass, the hydrogen adduct is formed and is then stable up to room temperature. Nitrobenzene–methanol glasses on γ-irradiation at 77K give the hydrogen adduct by reaction of the radical anion with the solvent with no prior warming (reaction *5*).

$$C_6H_5NO_2^{\overline{\cdot}} + CH_3OH \rightarrow C_6H_5\dot{N}O_2H + CH_3O^- \tag{5}$$

The nitrobenzene anion can also be stabilized by γ-irradiating an alkaline, ethanol solution containing nitrobenzene at room temperature for several hours, the main reaction being electron attachment [2b] to give $C_6H_5NO_2^{\overline{\cdot}}$.

Numerous e.s.r. studies on nitro-anion radicals produced from nitro-aromatic compounds in solution have been reported, and the coupling constants found have been compiled by Bowers[3]. The anions in certain substances have been generated by electrolysis[4,5], photolysis[6], and chemical reduction [6,7]. In alkaline, alcoholic solution, the hydrogen adduct, primarily formed during photolysis, ionises to give the anion radical (reaction *6*).

$$C_6H_5\dot{N}O_2H + {}^-OH \rightleftharpoons C_6H_5NO_2^{\overline{\cdot}} \tag{6}$$

In this study, nitroxide and nitro-anion radicals generated photolytically from *o*-, *m*-, and *p*-nitrophenyl β-D-glycopyranosides in neutral and alkaline alcoholic solution have been investigated by e.s.r. We shall seek to demonstrate that the radicals are of the nitroxide or nitro-anion type, where the D-glucose or D-galactose moiety remains attached to the aglycone. The nitro-anion radicals can be more readily generated electrochemically, and in this way more information can be obtained about the electronic effects of the glycoside groups.

EXPERIMENTAL

Materials. — The nitrophenyl β-D-gluco- and galacto-pyranosides were "Analar" grade chemicals obtained from Koch–Light, and were recrystallised from ethanol before use. Methanol, ethanol, and isopropyl alcohol were distilled before use. Acetonitrile was purified by a method previously described[8].

Tetra-*tert*-butylammonium perchlorate was prepared by neutralizing a solution of tetra-*tert*-butylammonium hydroxide in methanol–toluene with 60% perchloric acid (60% w/v), and the aqueous phase was collected. Water was added to precipitate the tetra-*tert*-butylammonium perchlorate which was filtered, recrystallised from aqueous acetonitrile (20% v/v), and finally dried *in vacuo* over phosphorus pentaoxide.

Nitroxide radical formation. — Neutral, alcoholic solutions of the nitrophenyl β-D-glycopyranosides (10 mM) were efficiently equilibrated with nitrogen and either photolysed directly in the cavity in a flat e.s.r. cell or outside in an e.s.r. quartz dewar vessel tip, when long irradiations were necessary.

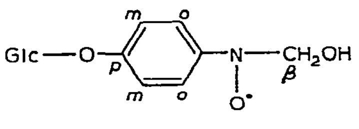
Nitro-anion formation. — (*a*) *Photochemical.* Neutral, alcoholic solutions of nitrophenyl β-D-glycopyranosides (10 mM) were made alkaline with potassium hydroxide (25 mM) before photolysis, and equilibration with nitrogen was unnecessary The light source used was a Hanovia 100-watt Hg high-pressure point-arc housed in a Wild Heerbrugg, Universal lamp-holder. The full spectrum was utilised.

(*b*) *Electrochemical.* For electrolytic generation of nitro-anion radicals, the Varian V-4556 electrolytic cell assembly was used, coupled to a simple potentiometer circuit with a microammeter. The potential adopted for electrolysis was normally *ca.* 100 mV more negative than the half-wave potential ($E_{\frac{1}{2}}$), which was measured with respect to a saturated calomel electrode. Under these conditions, the only reaction taking place is one of reversible electron transfer[4]. The solutions used for electrolysis consisted of the parent compound, nitrobenzene, or nitrophenyl glycoside (mM) with supporting electrolyte, tetra-*tert*-butylammonium perchlorate (0.1 M) dissolved in the solvent, acetonitrile.

E.s.r. spectra were recorded on a Varian V-4502 spectrometer, using 100 KHz field modulation. Hyperfine splittings were measured by using an AEG gaussmeter and proton-resonance probe coupled to a Hewlett–Packard frequency counter. Errors were estimated to be ±0.05 gauss.

RESULTS AND DISCUSSION

Nitroxide radicals. — Although nitro-anions and hydrogen adducts of nitrophenyl β-D-glycosides can be stabilised by γ-irradiation of methyltetrahydrofuran and methanol glasses at 77K, no stable hydrogen adduct was observed on warming to room temperature[9], a method which was successful for nitrobenzene. We have, there-



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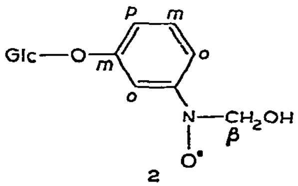

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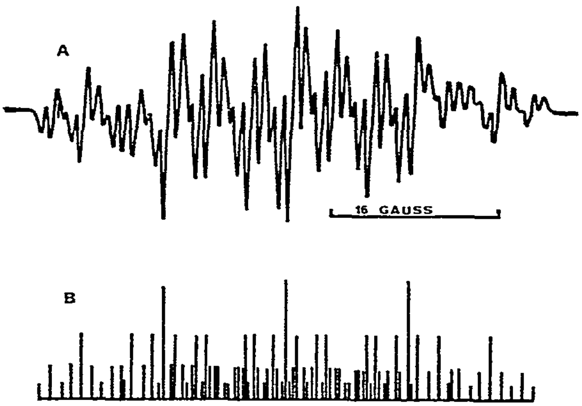


Fig. 1. E.s.r. spectrum of the nitroxide radical photolytically generated from *p*-nitrophenyl β-D-glucopyranoside in neutral methanol solution. A, observed spectrum; B, reconstructed line diagram.

fore, used direct photolysis of the glycosides in neutral, alcoholic solution as a method for stabilising radicals. Even by this procedure, the rate of formation was extremely slow, and with the *o*-nitrophenyl *β*-D-glucopyranoside no nitroxide radical could be observed, because of the extremely facile hydrolysis of the glycosidic bond in this isomer[10].

p-*Nitrophenyl β*-D-*glucopyranoside*. — After prolonged photolysis in neutral methanol, a well-resolved e.s.r. spectrum of the nitroxide radical could be observed (Fig. 1A). Analysis of this spectrum indicated that the structure of the radical is **1**.

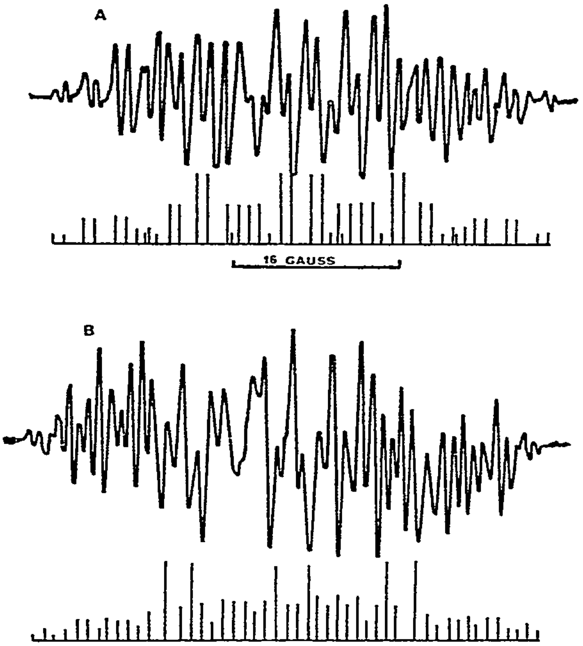


Fig. 2. E.s.r. spectra of nitroxide radicals photolytically generated in neutral methanol solution. A, *m*-nitrophenyl *β*-D-glucopyranoside; B, nitrobenzene.

Due to the absence of the aromatic *p*-proton coupling which is evident in the parent molecule, nitrobenzene[1], it can be deduced that the glucopyranoside moiety is present. The coupling constants derived from the spectra are $a_N = 11.8$, $a_H\beta(2) = 7.9$; $a_H ortho(2) = 3.0$, compared with $a_N = 11.1$, $a_H\beta(2) = 8.0$, $a_H ortho,para(3) = 3.0$ gauss for the nitroxide radical from nitrobenzene (see Fig. 2B for spectrum). The higher a_N value for the *p*-glucoside is indicative of its electron-donating power with respect to *p*-H. These coupling constants are in exact agreement with those reported by Chachaty and Forchioni[1]. In addition to the coupling constants observed by these workers, we have also observed the *m*-proton couplings, $a_H meta(2) = 1.0$ gauss in the nitroxides derived from both nitrobenzene and *p*-nitrophenyl *β*-D-glucopyranoside, because of our better resolved spectra. A reconstructed line diagram based on these coupling

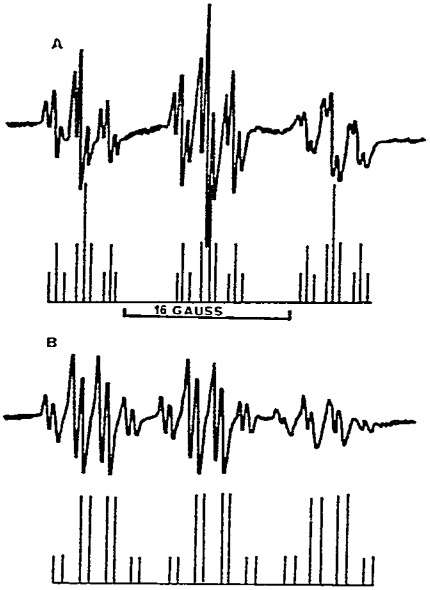


Fig. 3. E.s.r. spectra of nitro-anion radicals photolytically generated from nitrophenyl β-D-glycosides in alkaline isopropyl alcohol solution. A, *p*-nitrophenyl β-D-gluco- and -galactosides; B, *m*-nitrophenyl β-D-gluco- and -galactosides.

constants is included in Fig. 1B. Because of equivalent *ortho*(2) and *para*(1) couplings for the nitroxide from nitrobenzene, the smaller *m*-proton couplings are obscured. However, instead of the quartet (1:3:3:1) of hyperfine lines for these equivalent *ortho*- and *para*-protons, we observe for the nitroxide radical derived from *p*-nitrophenyl β-D-glucopyranoside only a triplet splitting from equivalent *o*-(2) proton couplings. This is due to the replacement of the *p*-proton by the glucopyranoside group. Under these conditions, the *m*-proton couplings can be more easily resolved, and the observations demonstrate that the glycosidic bond is fully preserved in the nitroxide radicals from *p*-nitrophenyl β-D-glucopyranoside. No nitroxide radical can be generated from *p*-nitrophenol in methanol, which is added evidence that no hydrolysis of the glycosidic bond has occurred. Ill-defined spectra were observed in ethanol and isopropyl alcohol, and it was not possible to resolve these sufficiently to obtain coupling constants.

m-*Nitrophenyl β-D-glucopyranoside*. — The spectrum of the nitroxide radical, prepared in an identical manner to that used for *p*-nitrophenyl β-D-glucopyranoside, was more complex for the *m*-nitrophenyl isomer, probably because of overlapping lines. The best fit with the observed spectrum (Fig. 2A) was obtained by using coupling constants $a_{\mathrm{N}} = 11.1$; a_{H}*ortho,para*(3) $= 3.0$, a_{H}*meta*(1) $= 1.0$, and $a_{\mathrm{H}}\beta(2) = 8.0$ gauss, which similarly indicate that the radical has structure **2**. It is possible that the *o*(2) and *p*(1) protons are here not quite equivalent. Slightly differing couplings could

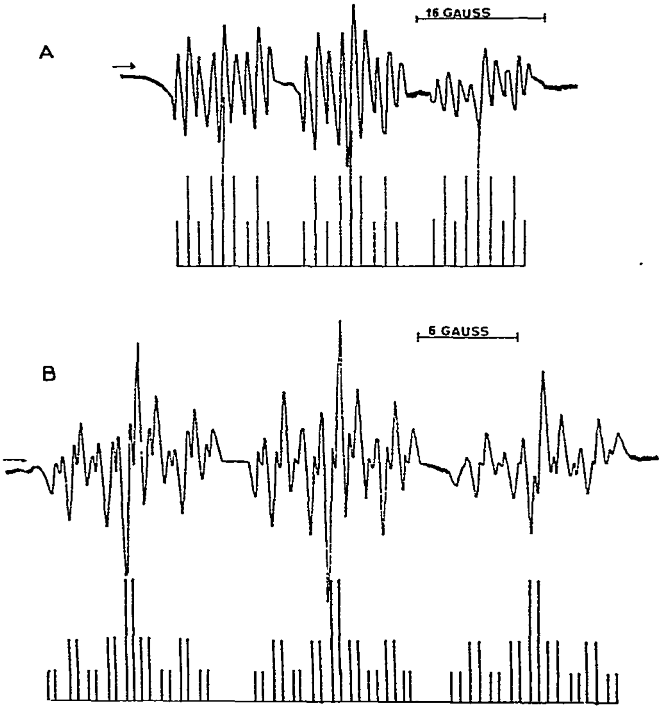
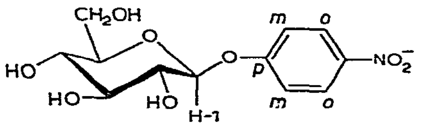


Fig. 4. E.s.r. spectra of nitro-anion radicals electrochemically generated from nitrophenyl β-D-glycosides in acetonitrile. A, *o*-nitrophenyl β-D-glucopyranoside; B, *p*-nitrophenyl β-D-galactopyranoside.

produce some overlapping and, therefore, obscure some of the lines. An exact fit is not possible without the aid of a computer programme.

Nitro-anion radicals. — The production of the nitro-anion radicals by photolysis of the glycosides in alkaline isopropyl alcohol solution was rapid. No radical anion could be observed for *o*-nitrophenyl β-D-glucopyranoside or galactoside due to their extremely rapid hydrolysis[10].

p-*Nitrophenyl β-D-gluco- and -galactopyranosides.* — The nitro-anion radical from these glycosides exhibited a 27-line spectrum (Fig. 3A). Here again the *p*-proton coupling is absent, indicating that structure **3** is the most likely one for these radical anions. For this *p*-nitro-anion radical of phenyl β-D-gluco- or -galactopyranoside,



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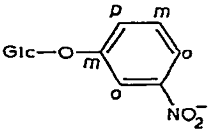

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the coupling constants are $a_N = 15.28$, $a_H ortho(2) = 3.24$, and $a_H meta(2) = 0.84$ gauss. The last two couplings are assigned on the basis that coupling to *o*-protons is larger than to *m*-protons[6,11].

m-*Nitrophenyl β*-D-*gluco- and -galactopyranosides.* — A 24-line spectrum was observed for the nitro-anion radicals from these glycosides (Fig. 3B), and the coupling constants are $a_N = 14.34$, $a_H ortho,para = 3.24$, and $a_H meta(1) = 1.05$ gauss. One *m*-proton coupling is absent and, therefore, **4** is the structure of these radical anions.

No nitro-anion radical was observed for *m*- or *p*-nitrophenol, which is further evidence that the glycosidic bond was intact. The nitrogen coupling is smaller than in the case of the *p*-substituted glycosides and also the *m*-proton coupling is somewhat larger. Previously, it has been shown that nitro-anions with *p*-substituted ether groups exhibit large nitrogen couplings[6,7]. Table I gives a comparison of the values which have been found. Our observed nitrogen coupling, $a_H = 13.0$ gauss, for the parent nitrobenzene anion is lower than those previously reported. This may be due to the use of isopropyl alcohol as a solvent instead of aqueous methanol and ethanol[6] or aqueous acetone[7]. On this basis, both *m*- and *p*-substituted glycoside nitro-anions have higher a_N values than the corresponding *p*-substituted ether derivatives. For the *p*-glycoside, $a_N = 15.28$ gauss, and this can be directly compared with previous data, but no a_N values for *m*-substituted ether nitro-anions have been reported. No coupling to H-1 of the pyranosyl group is observed, whereas the coupling to the methyl or methylene protons of the *p*-substituted ether groups is 0.3–0.4 gauss[6]. This difference may be due to limitation placed on the modulation we are able to use, which is determined by the concentrations of radical anion which can be generated. An excess of decomposition products would probably lead to broadening of hyperfine lines.

A feature of the spectra of the anions we have observed, and of most *p*-substituted nitrobenzene anions, is the broadening and consequent loss in intensity of the high- and low-field components, that is for the M_I (nitrogen) $= \pm 1$ transitions. These features cannot be adequately explained at the present time[6].

Nitro-anions can more readily be generated electrolytically, and by using this method the nitro-anion radical from *o*-nitrophenyl *β*-D-glucopyranoside, not previously prepared, could be observed (Fig. 4A). Also, in the spectra of *p*-nitrophenyl glucoside and galactoside anions, the small coupling (0.3–0.4 gauss) to H-1 of the glycopyranosyl group could be identified. Better resolution was observed in the spectrum of the galactoside anion (see Fig. 4B), but we have no explanation for this. No coupling to this proton could be observed for the *o*- or *m*-nitrophenyl *β*-D-glucopyranoside anions, probably due to inequivalence of the *o*- and *p*-protons having a broadening effect on the hyperfine lines.

The nitrogen and proton coupling constants obtained are summarised in Table II, together with those for the parent anion. Our observed a_N for the nitrobenzene anion, 11.12, is larger than that previously reported[4]. The only difference in the conditions is our use of tetra-*tert*-butylammonium, instead of tetra-*n*-propylammonium, cations which may be responsible for a higher electron density at the nitrogen atom. The a_N value for the *m*-nitro-anion is the same as the parent anion value in acetonitrile, which makes the a_N value anomalously high for this anion in isopropyl alcohol.

TABLE I

COMPARISON OF COUPLING CONSTANTS FROM *p*-SUBSTITUENT ETHER AND *p*- AND *m*-SUBSTITUENT GLYCOSIDE AROMATIC NITRO-ANION RADICALS

Substituent	a_N		$a_H$ortho(*2*)[f]	$a_H$meta(*2*)	a_{OCH_2}
p-H[a]	13.6		3.3	1.1	
p-H[e]	13.0	(13.3)	3.45	1.15	
p-OBu[a]	14.5		3.4	1.1	0.4
p-OEt[a]	14.4	(14.4)	3.4	1.0	0.4
p-OMe[a]	14.3	(14.25)	3.4	1.1	0.34
p-Glucopyranoside	15.28		3.24	0.84	[d]
p-Galactopyranoside	15.28		3.24	0.84	
m-Glucopyranoside	14.34		3.24[b]	1.05[c]	[d]
m-Galactopyranoside	14.34		3.24[b]	1.05[c]	

[a] Reference 6 (7); [b] a_H*ortho,para* (3); [c] a_H*meta* (1); [d] a_{OCH_2} not observed; [e] this work; [f] number of equivalent protons.

TABLE II

NITROGEN AND PROTON COUPLING CONSTANTS FOR NITRO-ANION RADICALS OF *o*-, *m*-, AND *p*-NITROPHENYL β-D-GLYCOSIDES ELECTROLYTICALLY REDUCED IN ACETONITRILE

Substituent	a_N	$a_H$ortho	$a_H$para	$a_H$meta	a_{OCH}
H	11.12	3.40 (2)[a]	3.79 (1)	1.12 (2)	
p-Glucoside	12.13	3.38 (2)		1.10 (2)	0.4
p-Galactoside	12.31	3.38 (2)		1.10 (2)	0.43
m-Glucoside	11.12	3.75 (2)	3.75 (1)	1.12 (1)	
o-Glucoside	12.43	3.39 (1)	3.39 (1)	1.09 (2)	

[a] Number of equivalent protons given in brackets.

The a_N value for *o*-nitrophenyl β-D-glucopyranoside is higher than for the parent anion. Since hydrogen bonding can occur between the glycoside group, *via* HO-2 and the nitro group, out of plane rotation of the nitro-group could result. Such rotation has previously been invoked to account for high a_N values when bulky groups are present[12].

Calculation of the σ constant for the glycoside groups. — Bowers[13] has applied a modification of the Hammett rate equation to correlate the effects of substituents in e.s.r. studies, namely, $\log_{10}(a_N^X/a_N^H) = \rho\sigma_X$, where a_N^X is the nitrogen coupling constant for a substituent other than hydrogen in the *para* position, and a_N^H is the nitrogen coupling constant for the unsubstituted nitrobenzene, σ_X is dependent on the particular substituent (X) and ρ is dependent on the solvent used rather on the reaction series as in the original equation. Table III summarises the nitrogen coupling constants for p-OH, $-OCH_3$, and $-H$ in a variety of solvents, together with the coupling constant ratios (a_N^X/a_N^H). p-Galactoside (OGal) and -glucoside (OGlc) data are also included in the two solvents, acetonitrile and isopropyl alcohol. It is evident that the coupling constant ratios for p-OGal and -OGlc are very close to that for $-OCH_3$ and, therefore, much lower than for -OH. Using the ρ value -0.295 for acetonitrile[13], the values $\sigma_{OGal} = -0.15$ and $\sigma_{OGlc} = -0.13$ are obtained by the above equation, compared with $\sigma_{OCH_3} = -0.16$ and $\sigma_{OH} = -0.42$.

TABLE III

COMPARISON OF NITROGEN COUPLING CONSTANT DATA FOR p-SUBSTITUTED NITROBENZENE ANIONS IN DIFFERENT SOLVENTS

Solvent	a_N^X					a_N^X/a_N^H			
	OH	*OCH$_3$*	*OGal*	*OGlc*	*H*	a_N^{OH}/a_N^H	$a_N^{OCH_3}/a_N^H$	a_N^{OG}/a_N^H (*OGal*; *OGlc*)	
HCONMe$_2$[a]	13.9	10.6			9.75	1.425	1.087		
Me$_2$SO[a]	13.59	1.93			9.87	1.377	1.107		
MeCN[a,d]	13.88[a]	11.57[a]	12.31[d]	12.13[d]	11.12[d] 10.32[a]	1.345[a]	1.121[a]	1.11[d]	1.09[d]
Aqueous MeOH[b] or EtOH		14.3			13.6		1.051		
Aqueous Me$_2$CO[c]		14.25			13.3		1.071		
i-PrOH[d]			15.28	15.28	13.0				1.175

[a]Refs. 3, 4, and 13; [b]Ref. 6; [c]Ref. 7; [d]This work.

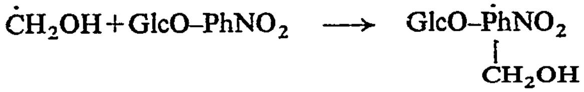
These results indicate that glycosidic groups have a similar electron-donating capacity to OCH_3, and therefore the glycosidic link is an ether type of linkage. The slightly more negative σ constant, indicating a greater electron-donating capacity for the galactoside group, could be significant, but without comparable values for other glycopyranosides this conclusion cannot be fully substantiated. However, as Bowers has shown, the a_N constant is extremely sensitive to the electron-donating or -withdrawing powers of p-substituents. Therefore, it is possible that this method could detect much smaller differences in these properties for very similar groups than has been possible by other techniques. For example, pulse radiolysis studies of aryl glucosides indicate that steric features appear to exert almost as significant an influence on the reactivity towards e_{aq}^- as do polar effects. This method, therefore, cannot be effectively used to quantitatively compare electron-withdrawing or -donating powers of various substituent groups. In this investigation, no such problems arise, and the main argument against the value of the nitrogen coupling constant not being an absolute one for σ constant determinations is that concerning out-of-plane rotation of the nitro group, but this is minimal for p-substituents[12].

Mechanism of radical formation. — The formation of nitrophenyl β-D-glycosidic nitroxide radicals during photolysis of the glycoside in neutral methanol may satisfactorily be accounted for by reactions *1–4* postulated by Chachaty and Forchioni[1]. The quantum yields for glycosidic scission[15], which is the main chemical reaction observed during the photolysis of aryl glycosides, are low (~0.01) and are only marginally influenced by the nature of the aglycone. This observation is consistent with the slow rate of formation of the glycoside nitroxide radicals in neutral, alcoholic solution and by the retention of the glycosidic bond in both nitroxide and nitro-anion radicals. Due to radiative and radiationless transitions[16], deactivation of the excited state may efficiently compete with the abstraction reaction *2* which yields the precursor radical necessary for nitroxide radical formation.

Apart from deactivation of the excited state, competing side reactions would also account for our observation that nitroxide radical production is extremely slow. These can be summarised as follows:

$$2\dot{C}H_2OH \longrightarrow (CH_2OH)_2 \qquad (7)$$

$$2GlcO{-}Ph\dot{N}O_2H \longrightarrow GlcO{-}PhNO_2 + GlcO{-}PhNO + H_2O \qquad (8)$$



$$\dot{C}H_2OH + GlcO{-}PhNO_2 \longrightarrow GlcO{-}\underset{\substack{|\\ CH_2OH}}{\dot{P}h}NO_2 \qquad (9)$$

Dimerisation of the hydroxymethylene radical (reaction *7*) and disproportionation of the hydrogen adduct radical (reaction *8*) will successfully compete with reaction *3*. The latter reaction leads to partial regeneration of the parent molecule and, if of a comparable rate to reaction *3*, would partially account for the slow rate of formation of the nitroxide radical. Scavenging of $\dot{C}H_2OH$ by the substrate could occur *via* reaction *9*, and the most probable fate of the resulting radical is dimerisation.

In alkaline isopropyl alcohol, the production of the nitro-anion radical is extremely rapid due to ionisation of the hydrogen adduct radical (reaction *6*). A steady-state concentration could not, however, be maintained due to alkali-catalysed hydrolysis of the glycosidic bond, thus making the nitro-anion radical unstable. Scission of this bond leads to the production of D-glucose and probably a *p*-nitrophenol radical anion. This anion would not be stable under these conditions, as indicated earlier in this paper and reported elsewhere[6], and would probably dissociate rapidly to give more-stable products.

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