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PHOTOINDUCED ELECTRON-TRANSFER REACTIONS OF ARYL GLYCOSIDES*

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ABSTRACT

The photolytic effects of ultraviolet, as well as other electromagnetic, radiation on carbohydrates are of interest in connection with photodegradation of cellulose and potential application in the photolytic cleavage of lignocellulosic bonds. Aryl glycosides, model compounds for lignocellulosic systems, were irradiated under conditions selected to achieve photoinduced electron-transfer. Various anomeric phenyl D-gluco- and D-galacto-pyranoside solutions in acetonitrile saturated with oxygen, air, or nitrogen and containing 1,4-dicyanonaphthalene (DCN) were irradiated at 350 nm for extended periods, and cleavage of the radical cation formed upon electron transfer to give the simple monosaccharide and phenol was observed. In the presence of methanol, it is possible to intercept the cationic intermediate, with formation of the corresponding methyl glycosides. Control experiments conducted in the presence of oxygen, air, or nitrogen in the absence of DCN showed little or no conversion. Comparison of the modes of fragmentation in solution with those observed in the gas phase upon electron impact in the mass spectrometer was made, and mechanisms for the reactions induced by electron transfer under these conditions are proposed.

INTRODUCTION

Considerable attention has been focused on the photolytic effects of ultraviolet, as well as other electromagnetic, radiation on carbohydrates[1,2]. Studies in this area have, no doubt, been stimulated by a desire to understand the photodegradation of cellulose, a process of potential, commercial importance. Cleavage

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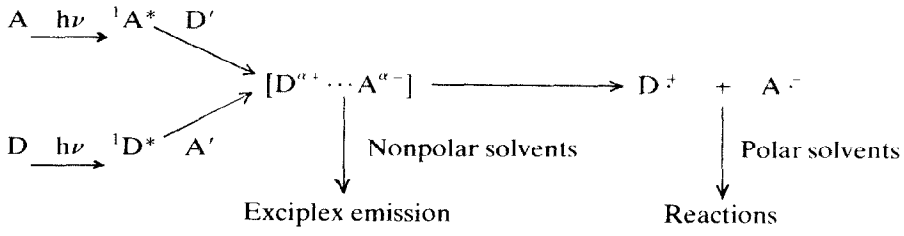
of lignocellulosic bonds by using solar irradiation has potential significance in biomass conversion within our area of interest. Aromatic glycosides constitute reasonable model compounds for lignocellulosics, although the precise linkages between lignins and polysaccharides have not yet been definitively established. Radiation-induced transformations of such compounds incorporating chemically dissimilar groups in the same molecule, namely, carbohydrate and aromatic moieties, are also important for applications to other, naturally occurring biopolymers.

Photoinduced electron-transfer reactions have received widespread attention by photochemists and photophysicists as a result of the pioneering, research results published by Weller[3] and S. G. Cohen[4] and their respective co-workers. In classical, sensitized, photochemical reactions, energy is transferred from a sensitizer to a substrate, resulting in production of a reactive, excited state (usually triplet) of the substrate acceptor. On the other hand, electron-transfer sensitization differs from energy transfer, in that the excited state of the so-called sensitizer has enhanced electron affinity and is capable of accepting an electron from a donor substrate to give a ground-state radical-cation.

More specifically, in a photoinduced, electron-transfer reaction, an acceptor molecule (A) is promoted to its singlet, excited state by absorption of a photon of light. An electron is then transferred from a donor molecule (D) to A *via* an encounter complex, or an exciplex, or both, which, in nonpolar solvents, may undergo exciplex emission. In polar solvents, however, the encounter complex dissociates into radical-cations and -anions, and the former member of this odd-electron pair undergoes reaction. However, the roles may be reversed, and the excited-singlet donor may contribute an electron to the antibonding orbital of the acceptor, to give an unstable radical-anion that undergoes reaction as shown in Scheme 1. It should be noted that dissociation of the encounter complex or exciplex gives rise to ground-state radical-ions that recombine, or otherwise react, in the ground state. In any event, ultimate product neutralityof the conversion is restored by back-donation of an electron from the chemically stable, radical-anion species[5,6]



Scheme 1 Electron-transfer sensitization

The high proportion of aromatic nuclei present in lignin structures offers a vast source of potential, electron-donor sites capable of participating in photo-

induced electron-transfer-sensitized fragmentations of lignocellulosic bonds. Our interest in these areas led to investigation of the utility of these reactions with model systems.

The photoinduced cleavage of naturally occurring aryl glycosides upon ultraviolet irradiation (254 nm) was first observed by Tanret[7]. In a subsequent investigation, Heidt[8] studied the photocleavage (254 nm) of a series of glycosides bearing aromatic chromophores. The photoreducing powers of the photolysis mixtures resulting were then used as indices for the relative extent of cleavage to monosaccharides, and the sole evidence that these are produced. It is doubtful whether or not reducing power is, in fact, a reliable criterion by which to judge the extent of liberation of saccharides by photofragmentation in these systems. Reducing power does not provide complete evidence for, or quantitation of, the amount of saccharide produced.

Phillips and colleagues[9] reported physical and analytical data for the ultraviolet photolysis (254 nm) of phenyl β-D-glucopyranoside in aqueous solution. They attributed the difficulties inherent in proposing a valid mechanism for D-glucosidic-bond scission under these conditions to (*a*) a lack of knowledge of the true identity of the products, and (*b*) their invariant quantum-yields under different reaction-conditions. A singlet-state reactive-species was advanced on the basis of the experimental data, and the low quantum-yields were ascribed to solvent caging of radical intermediates.

Yamada and co-workers[10] conducted a more extensive study, in aqueous media, of anomeric aryl glycosides bearing methyl and nitro substituents at various positions on the aglycon. These investigators used paper and gas–liquid chromatography (g.l.c.) to detect the saccharide liberated, but it is unclear from their data whether the reactions observed constituted excited-state photolysis-reactions as defined in the usual sense, or merely ground-state, photoinduced, ionic, hydrolytic reactions.

As a consequence of the reported photolability of aryl glycosides toward direct ultraviolet radiation, we were encouraged in our plan to evaluate electron-transfer sensitization with phenyl α- and β-D-gluco- and -galacto-pyranosides. Additionally, study of the radiation transformations by direct investigation of the compositions of the irradiated solutions has been facilitated by the advent of so-called "high-pressure" liquid chromatography (l.c.), which has several distinct advantages over other methods in this application for routine, quantitative, carbohydrate analysis, including increased speed, higher sensitivity, and excellent reproducibility. For example, aqueous solutions of saccharides can be quantitized without derivatization, or potential loss of sample, and with a minimum of preparation of the sample. Furthermore, it can be used to analyze mixtures containing a much wider range of carbohydrates, including those that are thermally labile, as well as oligo- and poly-saccharides that are insufficiently volatile to be analyzable by g.l.c. Incorporation of multiple detectors for l.c. separations provides information concerning the chemical characteristics of functional groups of the components present in the

sample. With the technologically advanced, commercial analytical-equipment available, it was possible to monitor, simultaneously, the carbohydrate moieties with a differential, refractive-index detector (moderate sensitivity and linear response for quantitation) and the aromatic groups with a variable-wavelength, ultraviolet (u.v.) detector.

We now report the results of ultraviolet irradiation under conditions selected to achieve photoinduced, electron transfer of aryl glycosides, using l.c. to monitor the progress of the reaction. As supporting evidence for the mechanism proposed, laser flash-photolysis experiments are presented, in contrast to the fragmentations observed in electron-impact, mass spectrometry.

EXPERIMENTAL

Materials. — The D-gluco- and D-galacto-pyranosides were obtained commercially (Sigma*), and used without purification. The acetonitrile and methanol were of HPLC grade (Burdick and Jackson). The 1,4-dicyanonaphthalene was prepared according to a procedure described[11] for the conversion of 1-bromonaphthalene into 1-cyanonaphthalene, modified to convert 1,4-dibromonaphthalene[5] into DCN.

Methods. — The technique for irradiating solutions of the glycosides was as follows. A solution (mM–10mM) of the glycoside in acetonitrile containing 0.1mM DCN, in a test tube capped with a serum cap, was saturated with oxygen, nitrogen, or compressed air. Irradiations were conducted by employing a Rayonet RPR-100 chamber-reactor equipped with sixteen 8-W, 254- or 350-nm lamps, and a "merry-go-round" rotating apparatus. Samples irradiated at 254 nm were placed in quartz test-tubes; those treated at 350 nm were contained in Pyrex tubes. The samples were irradiated for various periods of time.

A Beckman Instruments HPLC System (Model 322) was used. The components consisted of a dual-piston pump (Model 100A), 20-μL loop-injector (Model 210), LED refractive-index detector (Model 156), and variable wavelength-scanning (Model 165) with a microprocessor-based, programmable, system-controller with CRTL (Model 421). The mobile phase was 7mM sulfuric acid (pH 2.1), prepared with water that had been de-ionized through the Millipore Q system. The acid was filtered twice through a 0.45-μm filter (Millipore, Type HA), and degassed by sonicating *in vacuo*. The purchased column, Aminex HPX-87, Bio-Rad (H^+), was packed with a cross-linked, polystyrene ion-exchange resin, optimized for organic acid or carbohydrate separations, or both, with a guard column of similar material (microguard column, Bio-Rad) preceding the column in the system. The column was operated at ambient temperature and a pressure of ~7 MPa. Prior

*Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U. S. Department of Agriculture over others not mentioned.

to injection, the sample was filtered through a 0.5-μm filter (Millipore FH Type) by using a syringe fitted with a Swinney adapter. The amount of sample injected for each experiment was the same, the sample loop (20 μL) being filled to capacity for each, and the flow rate for elution of the samples was 0.6 mL/min for all. An elution time of ~45 min was sufficient for all separations. Detection with the u.v.-vis 165 detector was conducted in the following way. (*a*) Channel 1 was set at a wavelength of 210 nm, with runs made at a sensitivity of 0.1 aufs; (*b*) rapid scans of peaks detected on channel 1 were made on channel 3, with the peak actuate set to trigger, automatically, the scanning to begin at a peak threshold of 30%. (The scan range was from 190 to 700 nm, with the sensitivity set at 0.1 aufs. The scan rate was 20 $nm.s^{-1}$.); (*c*) channel 2 was set for detection at the wavelength of 254 nm, with the sensitivity set at 0.1 aufs. The rapid scan on channel 3 overrides this channel, but only for the duration of the scan.

Data acquisition from the chromatographic separations was by analog–digital conversation with a Hewlett–Packard Laboratory Automatic System 3354 for data file-handling and post-processing. Retention times were measured from the time of injection of the sample loop into the solvent stream.

The laser flash-photolysis configuration for monitoring transients through absorbance changes in the spectral region of 250–750 nm was used as previously reported[12].

A Finnigan instrument was employed in mass spectrometry by electron impact (70 eV). For analysis a sample was dissolved in the minimal volume of acetonitrile, and deposited within a capillary tube. The solvent was then evaporated, leaving a residue of the sample on the inside of the capillary tube. After insertion into the probe and into the ion source, the samples were heated to 300° in a ballistic fashion. Scanning from mass 33 to 450 was accomplished every 2 s, for a total of 500 scans.

RESULTS AND DISCUSSION

When a solution of phenyl α-D-glucopyranoside in acetonitrile saturated with oxygen and containing 1,4-dicyanonaphthalene (DCN) was irradiated at 350 nm for 72 h, D-glucose was produced (10% of the theoretical yield for total cleavage of the D-glucoside), and residual, starting D-glucoside (20%) was identified; in addition, there were several components as yet unidentified. When compressed air (20% oxygen, 78% nitrogen) was used as the source of oxygen, the yield of D-glucose remained essentially constant (4–5%) throughout the irradiation period for samples taken at 24-h, timed intervals during 72 h. Similar results were obtained with nitrogenated deoxygenated solutions, although a spuriously high value of 12% was measured after 72 h of irradiation. In experiments conducted in the absence of DCN under otherwise identical conditions, in acetonitrile solutions respectively saturated with oxygen, air, and nitrogen, no evidence for saccharide formation was discernible by l.c., and the starting material was completely recovered, as shown in Table I.

TABLE I

EFFECTS OF ELECTRON-TRANSFER SENSITIZATION WITH UV IRRADIATION (350 nm) ON ARYL GLYCOSIDES

Pyranoside	*Solvent*	*Sparging Gas*	*Time of irradiation (h)*	*Product yield (%)*	*Product*			*Starting material recovered (%)*	*Color of reaction mixture*
Phenyl α-D-gluco-	MeCN	oxygen	72	10	D-glucose			20	yellow
		air	24	4					yellow
			48	5					yellow
			72	4					lt. yellow
		nitrogen	24	5					yellow
			48	6					yellow
			72	12					lt. yellow
	(no DCN)	oxygen	72	0	0			100	colorless
	(no DCN)	air	72	0	0			100	colorless
	(no DCN)	nitrogen	72	0	0			100	colorless
Phenyl β-D-gluco-		oxygen	72	40	D-glucose			20	yellow
		air	24	17				9	yellow
			48	17				trace	yellow
			72	17				sl. trace	yellow
		nitrogen	24	22				25	yellow
			48	21				14	yellow
			72	19				3	lt. yellow
	(no DCN)	air	72	3				83	colorless
	(no DCN)	nitrogen	72	3				88	colorless
	MeCN–MeOH (10:1)	air	24	33	Me β-D-glucoside	33	Me α-D-glucoside	17	yellow
			48	39		39		10	yellow
			72	36		49		4	yellow

		nitrogen	24	27	37	13	yellow
			48	29	38	6	yellow
			72	30	41	4	yellow
	(no DCN)	air	72	0	0	64	colorless
	(no DCN)	nitrogen	72	0	0	68	colorless
Phenyl β-D-galacto-	MeCN	air	24	44	D-galactose	1	yellow
			48	20		0	colorless
			72	6		0	colorless
		nitrogen	24	60		6	yellow
			48	48		0	colorless
			72	25		0	colorless
	(no CDN)	air	72	0		98	colorless
	(no DCN)	nitrogen	72	0		94	colorless
	MeCN–MeOH (10:1)	air	23	92	Me D-galactoside (α + β)	8	yellow
			48	95		1	yellow
			72	100		0	yellow
		nitrogen	24	91		8	yellow
			48	85		0	colorless
			72	87		0	colorless
	(no DCN)	air	72	0		100	colorless
	(no DCN)	nitrogen	72	0		100	colorless
Phenethyl β-D-galacto-	MeCN–MeOH (10:1)	air	24			57	colorless
			48			56	colorless
			72			50	colorless
		nitrogen	24			86	colorless
			48			68	colorless
			72			64	colorless
	(no DCN)	air	72			100	colorless
	(no DCN)	nitrogen	72			67	colorless

No photolability was observed under any of the conditions outlined when methyl α-D-glucopyranoside was irradiated, even in the presence of DCN. Presumably, in the absence of an aryl substituent, radical-ion formation by electron transfer is disfavored because the oxidation potential of the substrate is inordinately high.

The anomeric phenyl β-D-glucopyranoside was studied under the irradiation conditions (350 nm) described for phenyl α-D-glucoside (with and without DCN, and under oxygen, air, or nitrogen). The extent of consumption of the β anomer under conditions equivalent to those employed with the α anomer was enhanced, and the amount of D-glucose produced and unidentified products formed were increased substantially (see Table I). The highest yield of cleavage products is obtained when oxygen, instead of air, is present as the saturating atmosphere. As in the case of phenyl α-D-glucopyranoside, the yield of D-glucose from phenyl β-D-glucopyranoside remains fairly constant over the duration of irradiation, and likewise varies with the atmosphere present. We attribute the marked difference in reactivity observed between the α and β anomer, *i.e.*, four times as much D-glucose is liberated from the β as from the α anomer under identical conditions, to more-favorable interaction between the encounter complex, leading to electron transfer from the β anomer to DCN. Control reactions in the absence of DCN (under otherwise identical conditions) were conducted, and the proportion of D-glucose liberated was found to be 6% under oxygen, 3% under air, and 3% under nitrogen after irradiation for 72 h; however, the overall conversion levels are only 18, 17, and 12%, respectively (*cf.*, values in Table I).

It is interesting to compare the results of direct irradiation (254 nm) of phenyl β-D-glucopyranoside at higher energies in acetonitrile solution with those obtained under electron-transfer conditions. Whereas 85% of the phenyl β-D-glucoside is consumed upon irradiation during 24 h, only 17% of the D-glucose is recovered from the product mixture. Similar results are obtained after deoxygenating the system, although less D-glucoside (76%) was consumed. When aqueous solutions of phenyl β-D-glucoside are irradiated (254 nm) under similar conditions, 50% of the aryl D-glucoside is consumed in the oxygenated systems, and 27% of the D-glucose is liberated. The proportion of D-glucose produced rises to 34% and the conversion level to 67%, when the aqueous solution is de-aerated with nitrogen prior to illumination. It is significant that there is a marked difference in energy of ~125 kJ/mol (~30 kcal/mol) between radiation at 254 nm and 350 nm, which is relevant for potential, commercial applications.

Acetonitrile solutions of an epimer, phenyl β-D-galactopyranoside, were irradiated under photoinduced electron-transfer, sensitization conditions (350 nm, DCN). From the results shown in Table I, it may be seen that the highest conversion into D-galactose occurred at 24 h, with the yield decreasing markedly after 72 h of irradiation under conditions of sparging with air and nitrogen. The conversion of the starting material is, however, complete after 48 h of irradiation. Measurable conversion (2–6%) in the control experiment was detected, despite the absence of DCN.

Thus, we observed steady-state production of D-glucose by electron-transfer photosensitization of phenyl α- and β-D-glucopyranoside; in contrast, with phenyl β-D-galactopyranoside, the proportion of D-galactose produced decreases with increase in irradiation time. It appears that the free sugars are subject to secondary reactions.

In order to intercept the presumed, cationic intermediate as a photostable product, 10% of methanol was incorporated into the acetonitrile solvent, and the reactions were conducted under reaction conditions similar to those already outlined. The production of the anomeric methyl α- and β-D-glucopyranoside by cleavage of phenyl β-D-glucopyranoside is indicated in Table I. After saturation with air, the total proportion of methyl D-glucosides produced by irradiation for 24 h is 66%; after 48 h, 78%; and after 72 h, 85%. The corresponding yields under a nitrogen atmosphere were 64% (24 h), 67% (48 h), and 71% (72 h). The conversion levels of the initial glycoside are comparable to those observed without the methanol, but it is apparent that the methyl D-glucosides are photostable products, the yields of which reflect the actual cleavage of the aryl glucoside without the complications of secondary reactions inherent when the free sugar is produced. It is interesting that, in these trapping experiments, the yield of the α is slightly higher than that of the β anomer, as is listed in Table I. The control reactions performed in the absence of DCN confirmed that electron transfer is necessary in order that cleavage of the aryl glycoside may proceed upon photolysis. The identification of the anomers and products was achieved by chromatography, utilizing authentic standards, or by addition of known amounts of standards (from which yields could also be calculated), or both.

Similar results were obtained on irradiation of phenyl β-D-galactopyranoside in acetonitrile containing 10% of methanol. From the data given in Table I, it is apparent that the yields for the production of methyl D-galactoside are 85% or higher. In this case, separation of the anomers was not achieved. The extent of conversion of the starting material is consistent with that observed without added methanol and, again, trapping of the methyl D-galactosides indicated much higher yields of the cleavage product than were obtained under the previous reaction-conditions. With compressed air for aeration, the yields of methyl D-galactosides increased to 100%, indicating total conversion of the starting material; however, with nitrogen sparging, the proportion of methyl D-galactosides decreased slightly with irradiation time.

Much lower levels of conversion were observed on irradiation of phenethyl β-D-galactopyranoside under conditions of electron-transfer sensitization by incorporating methanol in the acetonitrile. None of the products expected (from cleavage of the type observed with the phenyl glycosides) were detected (*e.g.*, D-glucose, methyl D-glucoside, D-galactose, and methyl D-galactoside).

Irradiation of a solution of phenol in acetonitrile containing 10% of methanol, in the presence of DCN, produced marked changes with time in the u.v.-absorbing components as monitored by l.c. These chromatograms, as well as

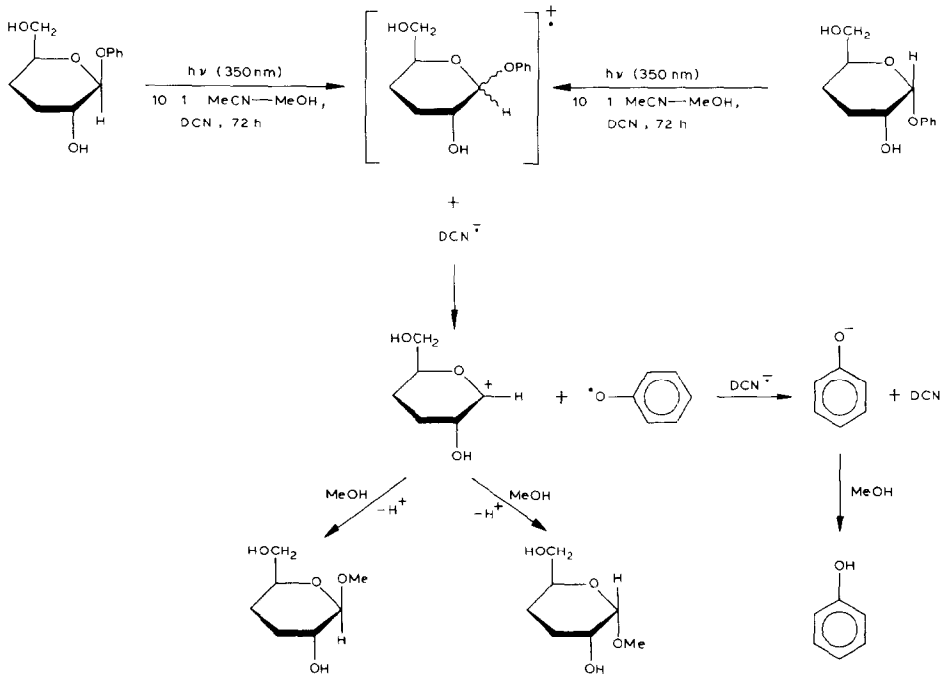
that of the phenol standard, were compared with those obtained from the irradiated samples already discussed. Separation patterns for phenol, or for degradation products from irradiation of phenol, were examined, and correlations were detected in all cases of irradiation of aryl glycosides, except for phenethyl D-galactoside. The complexity of the components, detected by u.v., in the l.c. separations increased with time of irradiation in the presence of DCN, and under the conditions where methanol was not present, as might be expected from the trends observed in monitoring the carbohydrate components. After irradiation, chromatograms of the control samples displayed little or no change from those of the starting materials.

Color transformations were detected for most of the reactions, and these constitute another aspect of the changes wrought by irradiation with electron-transfer sensitization by DCN. Generally, the mixtures turned yellow within the first 24 h of irradiation, except for phenethyl β-D-galactoside (see Table I). Irradiation of phenol plus DCN induced the same type of color change. In several systems, the yellow solutions were subsequently bleached either to a lighter shade of yellow or to colorless. The most striking example of this change was observed with phenyl β-D-galactoside. In contrast to the clear starting-solutions, formation of turbidity or cloudiness in some of the solutions after irradiation was another noticeable change.

The 70-eV, electron impact, mass spectra of all of the aryl glycosides studied are characterized by the absence of a peak for the molecular ion, as has previously been reported for phenyl β-D-glucopyranoside[13]. For the phenyl α- and β-D-gluco- and -galacto-pyranosides, the base peak was at *m/z* 94 ($PhOH^{+}$), indicating that the cationic fragment consisted of phenol. The fragmentation patterns in the gas phase thus differ markedly from those in solution, where the solvent plays a role. On the other hand, the spectrum of phenethyl β-D-galactopyranoside exhibits the base peak at *m/z* 105, suggesting that it is caused by $PhCH_2CH_2^{+}$.

Laser flash-photolysis experiments were conducted with aryl glycosides in acetonitrile solution containing DCN, simulating the previous experimental conditions. Characterization of the transient absorption-spectra of the DCN radical-anion confirmed that the aryl glycosides are, indeed, active as donors in the electron-transfer reactions proposed, but the spectrum of the phenoxy radical was obscured by the other components, so that its formation could not be verified.

From the experimental results obtained, the mechanism shown in Scheme 2 is proposed, in order to explain the photoinduced, electron-transfer sensitization of aryl glycosides. The photostability of the methyl D-glucosides indicates that an aryl group is required in order that radical-ion formation *via* electron-transfer sensitization may occur in these systems. Laser flash-photolysis confirmed that the irradiation conditions are favorable for electron transfer from the aryl glycosides, to give the DCN radical-anion. The proposed carbonium ion formed on the carbohydrate ring provides a rationale for detection of the methyl glycoside anomers among the reaction products. Their fairly even distribution in the products indicates a cationic center equally accessible from either side of the plane of the molecule. Phenol, or



Scheme 2. Mechanism for photoinduced, electron-transfer reaction of aryl glycosides, with 1,4-dicyanonaphthalene (DCN) as the sensitizer, in methanol–acetonitrile.

its irradiative degradation-products, or both, were detected in the reaction products after irradiation under these conditions.

CONCLUSIONS

Photoinduced, electron-transfer sensitization, with 1,4-dicyanonaphthalene as the sensitizer, effects cleavage of aryl glycosides at much lower energy-levels (ultraviolet irradiation of 350 nm) than previously reported. The photolability was greatest with the β anomer in the case of phenyl D-glucoside, with fragmentation to D-glucose and phenol. Higher yields of the glycose were obtained from the phenyl D-galactosides than from the phenyl D-glucosides. The results obtained in the presence of methanol, which traps the cationic intermediate as the photostable methyl glycoside, indicated almost quantitative cleavage. The proximity of the aromatic group to the linkage contributes significantly to the effectiveness of the cleavage to the glycoside. A mechanism for the electron-transfer reaction is proposed.

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