Mechanistic Aspects of 1,4-Dicyanonaphthalene-Sensitized Phototransformation of Aryl Glycopyranosides[1a]

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Received June 28, 1983

Steady-state irradiation of phenyl glycopyranosides under conditions of photosensitization (electron transfer) by 1,4-dicyanonaphthalene (DCN) leads to the formation of the corresponding monosaccharides (or their methyl derivatives, if methanol is present in the solvent). Mechanistic aspects of this photoreaction have been examined by steady-state fluorescence quenching measurements and 337.1-nm laser flash photolysis. Formation of the DCN radical anion (with yields of 0.18–0.35 δ_{ion}) as well as the DCN triplet (with yields of 0.14–0.27 δ_T) is observed as a result of the electron-transfer quenching of the DCN singlet by phenyl glycopyranosides in acetonitrile and a methanol–acetonitrile (1:10) mixture. Phenoxy radical is also shown to be a transient photoproduct in the latter solvent. Various features of the reaction scheme involving the fragmentation of electron-transfer-derived radical cations of phenyl glycopyranosides into the phenoxy radical and carbonium ions and possible roles of oxygen and methanol in enhancing or inhibiting the yields are discussed.

Under suitable conditions, excited-state-mediated charge-transfer interactions[2-4] of a donor or an acceptor with a substrate lead to the formation of radicals and radical ions that are labile enough to undergo chemical transformations before back electron transfer or charge neutralization may occur. In many cases, the donor or the acceptor, known as the sensitizer, is regenerated in its ground state and acts as the light-absorbing species that initiates photoreactions in a substrate while the substrate itself does not absorb the light. Cyanoaromatics have been popular as electron-transfer sensitizers (acceptors) for use in a variety of light-induced organic reactions such as photooxygenation,[5] photorearrangement/fragmentation,[6] and photoisomerization.[7]

In an earlier paper[8] we have reported on the results of a study concerning the irradiation of several aryl glycopyranosides in solutions in the presence of 1,4-dicyanonaphthalene (DCN) under conditions of photoinduced electron transfer. HPLC analyses of the products obtained under various conditions, namely, in acetonitrile and in acetonitrile/methanol (10:1) saturated with oxygen, air, or nitrogen show the formation of simple monosaccharides, their methyl derivatives, and phenol. A reaction scheme in terms of the fragmentation of electron-transfer-derived radical cations of phenyl glycopyranosides into phenoxy radical and carbonium ions (composed of carbohydrate rings) has been proposed. In this paper we are presenting the mechanistic details, namely, rate constants for DCN singlet quenching and efficiency of electron transfer, as revealed by steady-state fluorescence measurements and time-resolved laser flash photolysis. Interestingly, in addition to DCN radical anion generation, we also observe enhanced formation of the DCN triplet via the charge transfer interaction of the DCN singlet with phenyl glycopyranosides. We point out that the aryl glycopyranosides serve as reasonable models for lignocellulosic materials, and the present work is of potential significance in the field of solar energy and biomass conversion.

Experimental Section

The aryl glycopyranosides, purchased from Sigma, were used as received. The preparation of 1,4-dicyanonaphthalene (DCN) is described elsewhere.[6a,8] Phenol (Baker) was sublimed under

(1) (a) The work described here was supported by the Office of Basic Energy Sciences, U.S. Department of Energy. This is Document No. NDRL-2488 from the Notre Dame Radiation Laboratory. (b) Undergraduate Research Student, Summer 1983.

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Table I. Data Concerning Kinetics of DCN Fluorescence Quenching by Aryl Glycosides and Phenol and Fractions of DCN Singlet Quenching That Result in Ion and Triplet Formation

quencher	solvent	K_{SV}^{F},[a] M^{-1}	$10^{9}k_{q}^{F}$,[b] $M^{-1} s^{-1}$	δ_{ion}[c]	δ_{T}[c]
phenyl α-D-glucopyranoside	MeCN	107	11.2	0.20	0.18
	MeCN/MeOH[d]	94	10.9	0.18	0.14
phenyl β-D-glucopyranoside	MeCN	99	10.4	0.29	0.24
	MeCN/MeOH[d]	84	9.8	0.26	0.20
phenyl β-D-galactopyranoside	MeCN	100	10.5	0.35	0.27
	MeCN/MeOH[d]	85	9.9	0.27	0.20
phenylethyl β-D-galactopyranoside	MeCN	23	2.4		
phenol	MeCN	149	15.7	0.09	0.05

[a] ±10%. [b] Calculated from the relationship $K_{SV}^{F} = k_{q}^{F}\tau_{F}$, where τ_{F} is DCN fluorescence lifetime (9.5 ns in MeCN and 8.6 ns in 10:1 MeCN/MeOH, v/v). [c] Obtained from eq 10 and 11 (see text) at [Q] = 8-10 mM for glycopyranosides and 30 mM for phenol, ±10%. [d] 10:1 v/v.

vacuum. Acetonitrile (Aldrich, gold label) was fractionally distilled under an atmosphere of nitrogen, and methanol (Aldrich, gold label) was used without further purification.

The fluorescence measurements were carried out in an SLM photon-counting spectrofluorimeter with right-angle geometry between the directions of excitation and observation of emission. The essential features of the apparatus are presented elsewhere.[9] All absorption spectra were recorded in a Cary 218 spectrophotometer with 1-nm band-pass. The laser flash photolysis experments were performed by using nitrogen laser pulses (337.1 nm, 2-3 mJ, ~8 ns) from a Molectron UV-400 laser system. Details of the kinetic spectrophotometer and signal/data processing system are available in previous papers.[9,10]

Results

(a) Fluorescence Quenching. The steady-state fluorescence of DCN (emission maximum, λ_{max} = 380 nm and lifetime, τ_{F} = 9.5 ns in MeCN) is efficiently quenched in the presence of millimolar concentrations of phenyl-substituted glycopyranosides. The Stern–Volmer quenching constants (K_{SV}^{F}) were obtained from linear plots based on the equation $I_{0}/I = 1 + K_{SV}^{F}[Q]$, where I and I_{0} are the fluorescence intensities (monitored at λ_{max}) in the presence of the quencher at concentration [Q] and in its absence, respectively. Table I contains the data concerning K_{SV}^{F} and the biomolecular rate constants (k_{q}^{F}) for fluorescence quenching calculated from the relation $K_{SV}^{F} = k_{q}^{F}\tau_{F}$ by using τ_{F} = 9.5 ns in MeCN and 8.6 ns in 1:10 MeOH/MeCN (v/v).

(b) Laser Flash Photolysis. Upon laser flash photolysis of DCN in the presence of phenyl glycopyranosides (8-10 mM) in deaerated MeCN or 1:10 MeOH/MeCN (v/v), transient absorptions at 350-650 nm assignable to the DCN radical anion (DCN⁻·) and the DCN triplet (³DCN*) are observed on a microsecond time scale. The former is characterized by a sharp and intense peak at 390 nm, and the latter displays a broad absorption maximum at 455 nm. In addition, relatively strong spectral absorptions due to both species are noticed at 280-300 nm. Figure 1 shows the transient absorption spectra obtained with phenyl β-D-glucopyranoside in MeCN and phenyl α-D-glucopyranoside in 1:10 MeOH/MeCN (v/v) under deoxygenated conditions. The assignments of the transient species as DCN⁻· and ³DCN* are based on spectral comparisons and sensitivity toward oxygen; details regarding the kinetic and spectral behaviors of DCN⁻· and ³DCN* generated under well-defined conditions are available elsewhere.[6a,7c]

The oxygen quenching rate constant (k_{q,O_2}) for DCN⁻· is much higher[7c] than that for ³DCN*; in air-saturated
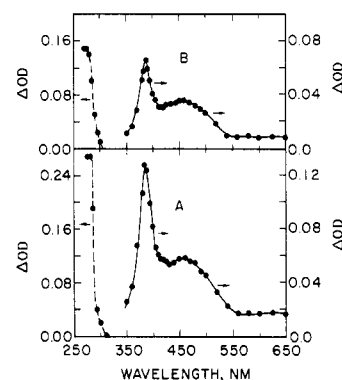

Figure 1. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of DCN (0.5 mM) under deaerated conditions in the presence of (A) phenyl β-D-glucopyranoside (13 mM, MeCN) and (B) phenyl α-D-glucopyranoside (9 mM, 1:10 MeOH/MeCN, v/v). The spectra correspond to 300 ns following the laser flash.
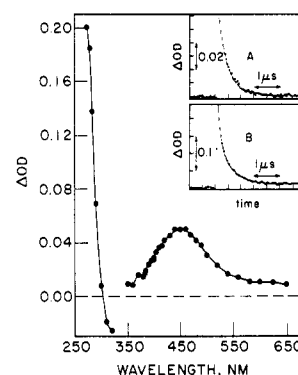

Figure 2. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of DCN (0.5 mM) in air-saturated MeCN in the presence of 13 mM phenyl β-D-glucopyranoside. The spectrum corresponds to 200 ns following the laser flash. The inserts A and B show experimental traces for decay of transient absorption at 455 and 280 nm, respectively.

MeCN the lifetimes (τ) of the two species are 50 and 400 ns, respectively. Thus, it was possible to monitor the triplet in aerated solutions at a time (~200 ns) following the laser flash when the decay of the radical anion was practically complete. Figure 2 shows the transient spectrum observed with phenyl β-D-glycopyranoside in air-satured MeCN and two kinetic traces at 280 and 455 nm, respectively, corresponding primarily to the decay of the triplet.

After the completion of the decay of DCN⁻· and ³DCN* in air-saturated solutions, we expected to observe transient absorptions due to the radical cations derived from electron transfer from the aryl glycopyranosides and/or the phenoxy radical formed via decomposition of the radical cations. Phenoxy radical is known[11] to have absorption maxima at

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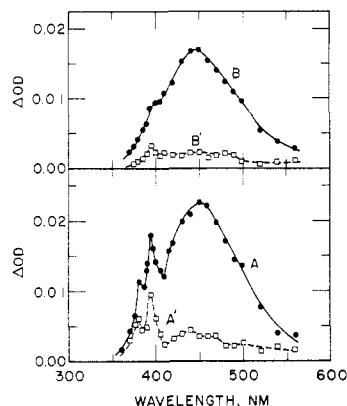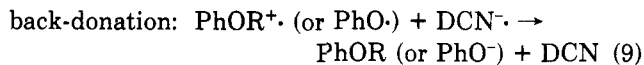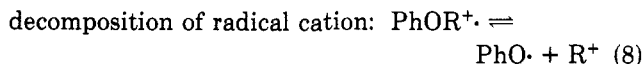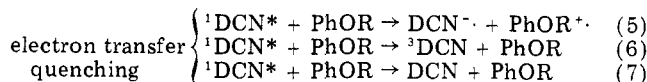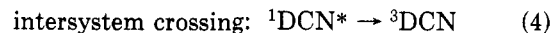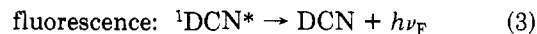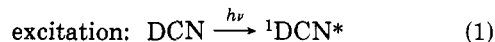
Figure 3. Transient absorption spectra observed at 200 (A) and 900 ns (A') following the laser flash in an air-saturated MeCN solution containing 0.5 mM DCN and 15 mM phenol and at 500 ns (B) and 1.4 μs (B') following the laser flash in air-saturated 1:10 MeOH/MeCN (v/v) containing 0.5 mM DCN and 0.3 mM phenyl β-D-glucopyranoside.

395–405 nm (λ_{max} = 3 × 10^3 M^{-1} cm^{-1} at 402 nm in water).[11a] Laser flash photolysis of DCN in the presence of phenol (15–30 mM) under conditions of nearly complete quenching of DCN fluorescence shows the formation of both DCN⁻· and ³DCN*, but in smaller yields than under comparable quenching by phenyl glycopyranosides (see later). When the solution is air-saturated, sharp transient absorption due to phenoxy radical becomes discernible with λ_{max} at 395 nm following the decay of DCN⁻· and ³DCN*. This is illustrated in Figure 3A,A'. Similar experiments with the phenyl glycopyranosides as quenchers of ¹DCN* in air-saturated 10:1 MeCN/MeOH show a small but distinct absorption at 395 nm, suggesting that the phenoxy radical is formed in these cases also. The transient spectra at 370–560 nm obtained with phenyl β-D-glucopyranoside and air-saturated 1:10 MeOH/MeCN are presented in Figure 3B,B'. The reasons why the transient absorption due to phenoxy radical is found to be weak in the experiments with phenyl glycopyranosides as quenchers are as follows: (i) at the highest concentrations attainable for the phenyl glycopyranosides (near saturation), ¹DCN* is quenched by the sugars only to the extent of ~50%, (ii) oxygen (K_{SV}^F = 127 M^{-1} in MeCN)[7c] in air-saturated solutions quenches ¹DCN* competitively, lowering the yields of electron-transfer-derived radical ions, and (iii) the decomposition of the phenyl glycopyranoside radical cations into phenoxy radicals and carbonium ions of the sugars is probably less than quantitative (see later). Because of the weak character of the absorption and its overlap with that of DCN⁻· and ³DCN* we could not ascertain the exact time scale in which the breakdown of the radical cations of phenyl glycopyranosides occurs, although the observation of the phenoxyl radical at ~250 ns following the laser flash sets an upper limit on the lifetimes of the radical cations.

On the basis of the observations concerning DCN fluorescence quenching and formation of ³DCN*, DCN⁻·, and phenoxy radical as a result of the quenching, the overall interaction of the DCN singlet with phenyl glycopyranosides and phenol may be described by the following discrete steps (eq 1–9; PhOR ≡ phenyl glycopyranoside or phenol).

excitation: $DCN \xrightarrow{h\nu} {}^1DCN^*$ (1)

internal conversion: ${}^1DCN^* \rightarrow DCN$ (2)

fluorescence: ${}^1DCN^* \rightarrow DCN + h\nu_F$ (3)

intersystem crossing: ${}^1DCN^* \rightarrow {}^3DCN$ (4)

electron transfer quenching
$$\begin{cases} {}^1DCN^* + PhOR \rightarrow DCN^{-\cdot} + PhOR^{+\cdot} & (5) \\ {}^1DCN^* + PhOR \rightarrow {}^3DCN + PhOR & (6) \\ {}^1DCN^* + PhOR \rightarrow DCN + PhOR & (7) \end{cases}$$

decomposition of radical cation: $PhOR^{+\cdot} \rightleftharpoons$
$$PhO\cdot + R^+ \quad (8)$$

back-donation: $PhOR^{+\cdot}$ (or $PhO\cdot$) + $DCN^{-\cdot} \rightarrow$
$$PhOR \text{ (or } PhO^-) + DCN \quad (9)$$

In polar solvents, the processes 5 and 7 probably occur[2,12] through a common singlet ion pair, ${}^1(DCN^{-\cdot}\cdots PhOR^{+\cdot})$, formed via electron transfer in the initially formed encounter complex, and may be considered to be the outcome of the dissociation of the caged ion pair into separated radical ions and back-donation of electron within the ion pair, respectively. On the other hand, the formation of ³DCN* (process 6) through electron-transfer quenching presumably involves transition of the singlet ion pair to a triple configuration.[12] For practical purposes, it is worthwhile to determine the fractions of the quenching events that account for the formation of triplet and radical ions (denoted by δ_T and δ_{ion}, respectively), that is, the relative importance of the processes 5–7. A comparison of end-of-pulse absorbance due to ³DCN* (ΔOD_0^T) at 455 nm in the absence of a quencher with those due to DCN⁻· (ΔOD^{ion}) at 390 nm and ³DCN* (ΔOD^T) at 455 nm observed in the presence of a quencher at concentration [Q] enabled us to estimate δ_{ion} and δ_T on the basis of eq 10 and 11. We used values[7c] of 2.2 × 10^4 and 7 × 10^3 M^{-1} cm^{-1}

$$\delta_{ion} = \phi_T^0 \left(\frac{\Delta OD^{ion}}{\Delta OD_0^T} \right) \left(\frac{\epsilon_T}{\epsilon_{ion}} \right) \left(\frac{1 + K_{SV}^F[Q]}{K_{SV}^F[Q]} \right) \quad (10)$$

$$\delta_T = \left(\frac{\phi_T^0}{K_{SV}^F[Q]} \right) \left[(1 + K_{SV}^F[Q]) \left(\frac{\Delta OD_T}{\Delta OD_T^0} \right) - 1 \right] \quad (11)$$

for the extinction coefficients (ϵ_{ion} and ϵ_T) of DCN⁻· and ³DCN* at 390 and 455 nm, respectively, in both MeCN and 1:10 MeOH/MeCN (v/v). The intrinsic triplet yields (ϕ_T^0)[13] of DCN in deaerated MeCN and 1:10 MeOH/MeCN were 0.19 and 0.15, respectively. The data concerning δ_{ion} and δ_T are presented in Table I.

We found that the DCN triplet is not quenched to any significant extent by any of the aryl glycopyranosides (k_q < 2 × 10^7 M^{-1} s^{-1}). Although the triple is produced under singlet quenching conditions with yields (δ_T) comparable to those of intrinsic intersystem crossing (ϕ_T^0), no tangible amount of radical ions, DCN⁻· and PhOR⁺·, is formed by way of triplet quenching.

We have indicated reversibility in the dissociation of the radical cation in eq 8. While for phenol (R = H) the dissociation[14] is entirely in favor of the phenoxyl radical,

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(12) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster R., Ed.; Academic Press: New York, 1979, pp 1–78.

(13) ϕ_T^0's were measured by comparing end-of-pulse absorbance changes (ΔOD's) due to DCN and benzophenone triplets observed by laser flash photolysis of solutions optically matched at the laser wavelength (337.1 nm).

(14) The pK_a of the radical cation from phenol is -2.0. See: Dixon, W. T.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1221–1230; **1978**, *74*, 432–439.

there is a possibility that in an aprotic solvent (acetonitrile), the fragmentation of the cations of phenyl glycopyranosides is incomplete. When methanol is present in the solvent, this "scavanges" the glycopyranoside-related carbonium ion (R^+), forming anomeric mixtures of methyl glycosides (eq 12). This can explain why phenoxy radical

$$R^+ + CH_3OH \rightarrow \overset{+}{\underset{H}{R}OCH_3} \rightleftharpoons ROCH_3 + H^+ \quad (12)$$
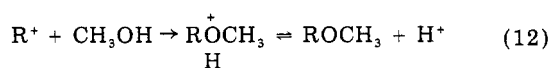
is observed in reasonable yields in the course of laser flash photolysis in 1:10 MeOH/MeCN while practically none is observed in neat MeCN. That the trapping by methanol can be important is also suggested by the fact that the yields of products (glucose, galactose, or their methyl derivatives) in steady-state irradiation under electron-transfer-sensitized conditions are[8] significantly enhanced when methanol is present.

Discussion

The quenching of DCN fluorescence by phenyl glycopyranosides occurs with rate constants below but close to the limit of diffusion control. Comparatively, phenylethyl β-D-galactopyranoside is ineffective as a quencher. This is not surprising because, assuming that the oxidation potentials of a phenylethyl glycopyranoside and a phenyl glycopyranoside are not much different from those of toluene ($E_{1/2}^{ox} = 1.98$ V in MeCN vs. Ag/0.1 M Ag$^+$)[13] and anisole ($E_{1/2}^{ox} = 1.76$ V in MeCN vs. SCE),[13] respectively, the free energy change of electron transfer from the former would be less negative by $\sim$13 kcal/mol than that from the latter. The free energy of electron transfer from a ground-state donor to an excited-state acceptor is given[2b,d] by eq 13, where $\Delta E_{0,0}$ is the excitation energy of DCN and

$$\Delta G_{et} = -\Delta E_{0,0} + E_{1/2}^{ox} - E_{1/2}^{red} + W_p - W_r \quad (13)$$

the W's represent the coulombic work in bringing together the product radical ions to form an ion pair or the reactant partners to form an association complex. Using the reduction potential of DCN ($E_{1/2}^{red} = -1.67$ V in MeCN, vs. Ag/0.1 M AgNO$_3$)[6c] and assuming that $\Delta E_{0,0}$ corresponds to the fluorescence maximum (380 nm) observed in MeCN, we estimate[1] a value of -5.5 kcal/mol for ΔG_{et} of electron transfer between the DCN singlet and a phenyl glycopyranoside. This value, though negative, is higher than the -10 kcal/mol estimated[2] as the threshold ΔG_{et} for diffusion-controlled rate constants for electron-transfer quenching of singlets.

As expected from the fact that the site of electron transfer from the phenyl glycopyranosides is the phenoxy moiety, there are no drastic variations in k_q^F, δ_{ion}, or δ_T with respect to the three glycopyranoside residues. However,

the observed trend in δ_{ion}, that is α-glucopyranoside < β-glucopyranoside < β-galactopyranoside, is significant because the product yield from steady-state irradiation under DCN sensitization also follows[8] this order, in general. Interestingly, phenol is a stronger quencher of DCN fluorescence than any of the phenyl glycopyranosides; in terms of both δ_{ion} and δ_T, however, it is much less effective (Table I). The fact that phenol behaves as a strong, "physical" quencher of DCN fluorescence should be duly recognized because its accumulation in the system in the course of steady-state photolysis prevents the photoreaction from being quantitative (owing to the energy-wasting role of phenol as a competitive quencher when the concentration of the substrate, phenyl glycopyranoside, is decreased).

For all of the three phenyl glycopyranosides, K_{SV}^F values are smaller in 1:10 MeOH/MeCN than in neat MeCN (Table I). This lowering of K_{SV}^F is in part due to the smaller τ_F of DCN in the presence of methanol. From a practical point of view the effect of a smaller K_{SV}^F in a MeOH + MeCN mixture can be compensated for by using higher concentrations of the sugar derivatives, these compounds being more soluble in methanolic mixtures. More importantly, methanol reacts with the carbonium ion, R^+ (eq 12), and thus facilitates the decomposition of phenyl glycopyranoside radical cation, PhOR$^+$· (eq 8), which, otherwise, receives an electron from DCN$^-$· (back-donation, eq 9) to regenerate the substrates in the ground state. Thus, the enhancement[8] of product yields in MeOH/MeCN mixtures relative to neat MeCN becomes explainable.

Although ^{3}DCN* is formed in nonnegligible yields under ^{1}DCN* quenching by phenyl glycopyranosides, it does not seem to have any important role in the overall scheme of the photoreaction under deaerated conditions except that its formation, like process 7, constitutes a channel for energy wastage. In aerated or oxygenated solutions, however, the oxygen quenching of ^{3}DCN* generates singlet oxygen, a potential oxidant[17] for phenols. Also, apart from the fact that oxygen is a competitor in quenching ^{1}DCN* ($K_{SV}^F = 127$ M^{-1} in MeCN), its presence makes important differences in the overall reaction scheme by quenching DCN$^-$· (most probably forming superoxide anion, O$_2^-$·)[18] and the phenoxy radical (probably forming a peroxy radical); the kinetics of the interactions of O$_2^-$· with phenyl glycopyranoside radical cations and phenoxy radical via back-donation of electron or peroxide formation would be substantially different from that of back-donation from DCN$^-$· (eq 9). The experimental observation that the product yields are in general enhanced[8] in the presence of oxygen under steady-state DCN-sensitized irradiation suggests that oxygen plays a beneficial role, possibly by providing scavengers (^{1}O$_2$*, ^{3}O$_2$, and O$_2^-$·) for phenol and phenoxy radical and by inhibiting the regeneration of phenyl glycopyranosides from the radical cations via back-donation of electrons.

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(16) W's in acetonitrile were calculated by using the relationship W(kcal/mol) = 9.10$Z_A Z_B/d$, where Z_A and Z_B are the ion charges (+1 and −1 for product ions and 0's for reactant partners) and d is the internuclear distance in the ion-pair of association complex (taken to be 8 Å). See: Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *Chem. Phys. Lett.* **1979**, *61*, 522–525; *J. Am. Chem. Soc.* **1979**, *101*, 4815–4824.

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(18) On the basis of the reduction potential of −0.57 V of O$_2$ (in water, vs. SCE),[5b] the free energy change of electron transfer from DCN$^-$· to O$_2$ is estimated to be −18 kcal/mol.