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Concentration-Dependent Isotope Effects. The Photocyanation of Naphthalene[†]

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Concentration-dependent isotope effects (IEs) were measured in the competitive photocyanation of naphthalene and perdeuterionaphthalene in acetonitrile in the presence of electron acceptors. The concentration of the reagents naphthalene, cyanide, and oxygen influences the magnitude of the IE. Experiments in which the photocyanation is brought about via selective excitation of an electron acceptor show that the naphthalene-concentration dependence of the IEs is not caused by the naphthalene radical cations, which are intermediates in the photoreaction. This is corroborated by an electrochemical study of (the reactivity of) these radical cations. From these observations and complementary semiempirical PM3 calculations it is concluded that the variation of the IE with naphthalene concentration is due to an excited-state equilibration. A detailed reaction mechanism is proposed to account for the observed IEs.

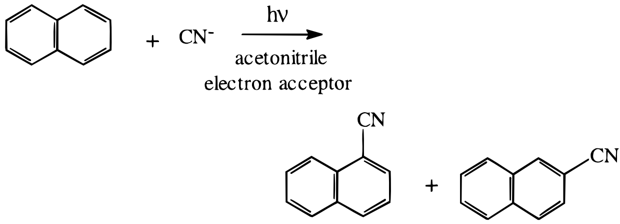
Introduction

The mechanistic implications of isotope effects (IEs) in ground-state reactions are often well understood, and interpretation of these effects is nearly always consistent with the outcome of other mechanistic probes. Therefore, in many mechanistic studies use has been made of these effects.[1] Much less use of IEs is made in the study of photochemical reactions,[2] mainly because of interpretative problems with the magnitude and direction of the effects, which hamper their application in the elucidation of photochemical reaction mechanisms.

The cause of the interpretative problems lies in the multitude of decay paths of the electronically excited states of organic molecules, which all can be affected by isotopic substitution. Deuterium IEs have been reported in detail for photophysical decay processes of relatively few compounds, mainly aromatic hydrocarbons.[3] For a rather small number of photochemical reactions, conclusively interpretable IEs have been reported as well. Clearest is the interpretation of photochemical primary IEs, in which the same concepts can be used as in ground-state primary IEs.[4,5] With secondary IEs the situation is less straightforward. The first observation of a (normal) secondary deuterium IE that could be explained in a way similar to IEs observed in ground-state reactions was reported for the γ-hydrogen abstraction of specifically deuterated bicycloalkyl phenyl ketones.[5] An inverse secondary deuterium IE was observed for the photorearrangement of 2-deuterio-1-iminopyridinium ylide and interpreted cautiously within the framework of ground-state secondary deuterium IE concepts.[6] This proved to be impossible for the photochemical isomerization of dibenzohomobarrelene.[7] This reaction shows an extremely large secondary deuterium IE ($k_H/k_D = 4.8$), which was proposed to originate in different Franck−Condon factors for different reaction paths. Another example of a secondary IE ($k_H/k_D = 1.11-1.16$), which cannot be accounted for within the framework of ground-state concepts, was observed for the intramolecular triplet-sensitized [2+2] cyclization of sesquinorbornatrienes.[8] On the basis of these data, which form a limited selection from the literature, it appears to be difficult to interpret the direction and magnitude of measured secondary IEs in general in mechanistic terms.

A way to overcome this problem is to study IEs in photochemical reactions of which the mechanisms have already been (partially) clarified by other methods. In this way, new explanations for the IEs can be given a firm basis, as in the case of the recently discovered concentration-dependent IE.[9] This phenomenon was reported from our laboratories for the meta photocycloaddition of cyclopentene to *p*-xylene and its perdeuterated isotopologue.[9] The observed IE on the quantum yield of formation of products varied from 1.01 at low concentrations of xylene (0.002 M) to 1.52 at high concentrations (1.333 M), which was attributed to energy transfer via the intermediate formation of xylene excimers. These intermediates allow equilibration between excited xylene-h_{10} and xylene-d_{10} to give excited xylene-d_{10} and xylene-h_{10}, and vice versa. This type of IE can occur in any reaction in which intermediates can exchange excitation energy or charge before reacting to product(s), and it is not a priori limited to photochemical reactions. In this paper we report such phenomena for the photocyanation of naphthalene.

UV irradiation of naphthalene in dry acetonitrile in the presence of cyanide ion and an electron acceptor such as *p*-dicyanobenzene (DCB) results in the clean formation of 1- and 2-cyanonaphthalene (eq 1). The mechanism of this reaction has been studied extensively[10,11] and is postulated to be as depicted in eqs 2−5.[11]



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[†] This paper is dedicated to Prof. Nicholas J. Turro on the occasion of his 60th birthday.

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$$C_{10}H_8 \xrightarrow{h\nu} (C_{10}H_8)^{*S_1} \quad (2)$$

$$(C_{10}H_8)^{*S_1} + DCB \xrightarrow{ET} (C_{10}H_8)^{+\bullet} + DCB^{-\bullet} \quad (3)$$

$$(C_{10}H_8)^{+\bullet} + CN^- \rightarrow 1\text{-}CN{-}C_{10}H_8^{\bullet} + 2\text{-}CN{-}C_{10}H_8^{\bullet} \quad (4)$$

$$1\text{-}CN{-} \text{ or } 2\text{-}CN{-}C_{10}H_8^{\bullet} + \text{oxidant} \xrightarrow{-H\bullet} 1\text{-}CN{-} \text{ or } 2\text{-}CN{-}C_{10}H_7 \quad (5)$$

The singlet excited state of naphthalene is quenched by DCB via electron transfer (ET), leading to the radical cation of naphthalene and the radical anion of DCB (eq 3). The radical cation reacts with cyanide at position 1 or 2 (eq 4), followed by loss of hydrogen from the resulting radicals to yield the products (eq 5). Which reagent functions as the oxidant has thus far not been clarified.

This mechanism is analogous to that of the anodic cyanation of naphthalene, which starts with the oxidation of naphthalene to its radical cation, followed by the reaction of this intermediate with cyanide. In a solution open to air the resulting arenyl radicals lose hydrogen to yield the products.[12] These, 1- and 2-cyanonaphthalene, are formed in the same ratio as observed in the photochemical cyanation, demonstrating the analogy between the photochemical and electrochemical reactions.[13]

We report here the IEs observed in the abovementioned photocyanation of naphthalene and perdeuterionaphthalene at systematically varied concentrations of *all* reagents. To understand more about the causes of the measured IEs the photocyanation was also performed by selective excitation of the electron acceptor 9,10-dicyanoanthracene. Furthermore, the reactivity of the radical cation of naphthalene was studied via electrochemical means. The study was completed with semiempirical PM3 calculations of the IEs on energy exchange equilibrations of the lowest singlet and triplet excited states of naphthalene with the ground state and on the analogous charge-transfer equilibration of its radical cation.

Experimental and Computational Details

Experiments. The photochemical reactions were performed at 20 °C under stirring in a 100 mL cylindrical Pyrex reaction vessel open to the air, in which a tube was immersed, that contained the lamp (Hanau TNN-15/32 low-pressure mercury arc (254 nm) or Hanau TQ81 high-pressure mercury arc) and a cooling liquid. Irradiations were performed at 254 nm (low-pressure lamp, quartz tube, water as cooling liquid), at >300 nm (high-pressure lamp, Pyrex tube, water) or at >330 nm (high-pressure lamp, Pyrex tube, acetone). For actinometry ($\lambda_{exc} = 254$ nm; 20 °C) the photohydrolysis of 3-nitroanisole (3.5×10^{-3} M) in a 0.1 M NaOH water/methanol (9:1) solution (quantum yield = 0.22)[14] was used. The disappearance of starting materials and appearance of products was studied as a function of time, using an internal standard (1-pentadecanol) and the kinetics described earlier.[15] This was done by removing aliquots (1.00 mL) of the reaction mixture at appropriate times, injecting them in a water/ether mixture (to remove the salts), and analyzing the ether layer by means of gas chromatography (GC). An analogous method without internal standard was used for the determination of the IEs. All irradiations were performed in triplicate, except those at the two highest naphthalene concentrations which were performed in duplicate. All electrochemical experiments were performed in duplicate. The GC analysis of every sample was performed at least five times. In the competition experiments the ratio of naphthalene to perdeuterionaphthalene was 1:1. Measured IEs on reactions refer to the ratio of cyano-derivatives arising from naphthalene and those from perdeuterionaphthalene. The experimental errors are given as σ_{n-1} standard deviations.

Equipment. GC analyses were carried out with a Packard model 433 gas chromatograph (50 m CP SIL5-CB, ∅ = 0.25 mm) and a flame ionization detector. Hydrogen was used as the carrier gas at an inlet-pressure of 72 kPa. GC analysis was performed at 90 and 117 °C for analysis of isotopologues of naphthalene and cyanonaphthalenes respectively, followed by a rise to 250 °C to clean the column from high boiling trace products for the next run. Injection and detection temperature were 250 and 275 °C, respectively.

Low-resolution mass spectra were obtained with a GC-MS setup consisting of a Packard model 438A gas chromatograph (25m CP−SIL 19 CB, ∅ = 0.32 mm) using helium as carrier gas, coupled with a Finnigan Mat ITD 700 mass spectrometer using electron impact and chemical ionization. UV spectroscopy was performed using a Varian DMS 200 spectrophotometer. Fluorescence emission spectra were recorded on a Spex Industries, Inc. Fluorolog II spectrofluorimeter.

Semipreparative electrochemistry was carried out in a two-compartment electrochemical cell open to the air with platinum working and counter electrodes and a saturated calomel reference electrode (SCE). The potential source used was a PAR Model 174 Polarographic Analyzer. All reported potentials from the literature or from our own experiments are with respect to the SCE.

Reagents and Solvents. Naphthalene (Aldrich) and perdeuterionaphthalene (Aldrich) were sublimed twice before use; DCB, 1-cyanonaphthalene, and 9,10-dicyanoanthracene (all Aldrich) were sublimed once. 9,9′-bis(*N*-methylacridinium nitrate) (BMA), 1,3,5-tri-*tert*-butylbenzene and 2,4,6-triphenylpyrylium tetrafluoroborate (TPP) (all Aldrich), and 1-pentadecanol (Janssen Chimica) were used as received. 1-Cyanoperdeuterionaphthalene was synthesized from perdeuterionaphthalene by bromination[16] followed by cyanation with cuprous cyanide in DMF.[17] 2-Cyanonaphthalene was prepared analogously from 2-bromonaphthalene.[17] *N*-methylacridinium iodide (MA) was synthesized according to the literature procedure.[18] Acetonitrile (Janssen, Spectrophotometric grade or A. C. S. reagent) was dried on activated molecular sieves (Janssen, 4 Å) and used without further purification.

Calculations. All calculations were performed using the programs VAMP (based on AMPAC 1.0 and MOPAC 4.0) and MOPAC 6.01, using the PM3 parameters.[19] Properties of radicals and radical cations were evaluated using the ROHF formalism.[20] Equilibrium IEs were calculated on the basis of calculated zero-point energy differences.[21]

Results

Absorption and Emission. The absorption coefficients of naphthalene and perdeuterionaphthalene were determined in acetonitrile at 254 nm, the wavelength of irradiation used in most of the photochemical experiments. Multiple measurements of freshly prepared solutions yielded values of $\epsilon_H = 2632 \pm 21$ and $\epsilon_D = 2709 \pm 32$ (M^{-1} cm^{-1}). This implies an IE of 0.97 ± 0.01 on the absorbance.

Naphthalene and strong electron acceptors form charge-transfer complexes with two charge-transfer bands.[22] In aceto-

TABLE 1: Quantum Yields of Formation of 1- and 2-Cyanonaphthalene from Naphthalene at $\lambda_{exc} = 254$ nm with 18-Crown-6 KCN and Various Electron Acceptors (with Their Reduction Potential) in Acetonitrile[a]

electron acceptor (concentration; reduction potential)	$[C_{10}H_8]$	quantum yield of 1-cyano-naphthalene	quantum yield of 2-cyano-naphthalene
TPP[b] (0.8;−0.29)	8.8	$<10^{-5}$	$<10^{-5}$
BMA[c] (0.8;na.)	2.4	$<10^{-5}$	$<10^{-5}$
MA[d] (0.9;−0.46)	2.4	$<10^{-5}$	$<10^{-5}$
DCA[e] (0.8;−0.89)	8.2	3.3×10^{-3}	4.6×10^{-4}
9-CA[f] (0.8;−1.56)	8.0	5.2×10^{-3}	7.1×10^{-4}
DCB (0.8;−1.64)	7.5	1.5×10^{-2}	2.0×10^{-3}
DCB (0.8) + 1,3,5-tri-*tert*-butylbenzene (28.2)	1.33	2.4×10^{-2}	3.9×10^{-3}
DCB (0.8) + argon[g]	7.5	8.1×10^{-3}	1.2×10^{-3}

[a] All concentrations in mM; reduction potentials in *V* versus SCE; [18-crown-6 KCN] = 18.0 mM. [b] TPP = 2,4,6-Tetraphenylpyrylium tetrafluoroborate. [c] BMA = 9,9′-bis(*N*-methylacridinium nitrate); na = not available. [d] MA = *N*-methylacridinium iodide. [e] DCA = 9,10-dicyanoanthracene. [f] 9-CA = 9-cyanoanthracene. [g] The reaction was performed under an argon atmosphere.

nitrile with DCB no such bands are observed, which is due to the relatively high reduction potential of this acceptor (−1.6V[23]).[24] Therefore the charge-transfer behavior of naphthalene and perdeuterionaphthalene was studied using tetracyanoethene (reduction potential: 0.24 V[23]).[25] Maximum charge-transfer absorptions were found for naphthalene at 558.4 and 427.1 nm and for perdeuterionaphthalene at 559.0 and 428.1 nm. This implies isotopic differences of 55 and 156 cal/mol, respectively (corresponding to IEs of 1.10 and 1.31, respectively, at 20 °C).[26]

The energy of a charge-transfer transition is proportional to the ionization potential of the donor molecule.[22] The two charge-transfer transitions observed have energies of 51.2 and 67.0 kcal/mol, respectively, and are ascribed to electron transfer from the HOMO and HOMO-1 of naphthalene to tetracyanoethene. This difference of 15.8 kcal/mol is close to a reported value in CCl_4 of 14.9 kcal/mol[22] and to the calculated difference between HOMO and HOMO-1 energies using the PM3 parametrization: 13.8 kcal/mol.

The fluorescence of naphthalene is quenched by DCB. Kinetics with this quencher, however, could not be accurately determined because of the efficient fluorescence of DCB itself in the spectral region of interest. Stern−Volmer constants were therefore determined for both isotopologues using 9-cyanoanthracene as quencher, and found to be identical within experimental error ($k_q\tau = 1200 \pm 150$ M^{-1}). The quenching process presumably follows the Rehm−Weller kinetics, and its rate equals the rate of diffusion in acetonitrile.[27] On the basis of these data the fluorescence lifetimes[28] of both isotopologues in acetonitrile solutions open to air were 63 ± 8 ns, in agreement with the general notion that the effect of perdeuteration on the fluorescence lifetimes of polycyclic aromatic hydrocarbons is (almost) nonexistent.[3,29] The radiative lifetimes of both naphthalene and perdeuterionaphthalene are reported to be 96 ns in deoxygenated cyclohexane.[30] At the naphthalene concentrations used, no excimer fluorescence was observed.

Photochemistry. When naphthalene is irradiated in a non-degassed acetonitrile solution, containing cyanide and a suitable electron acceptor, two products result: 1- and 2-cyanonaphthalene, in a ratio of about 7:1. To minimize effects due to ion pairing of cyanide to its counterion, the complex of potassium cyanide with 18-crown-6 ether (18C6 KCN) was used as the source of cyanide.[31] The quantum yields of product formation depend on the electron acceptor (Table 1), but the ratio of product−isomers does not. The data show DCB to be the preferred electron acceptor of the ones under study, and DCB was therefore used in most of the other experiments. It is noteworthy that even if DCB is only present in catalytic quantities with respect to naphthalene it is not consumed during the reaction.

TABLE 2: Isotope Effects on the Formation of 1-Cyanonaphthalene and Product Ratios at Varying Total Naphthalene Concentrations (in mM) in Acetonitrile ($\lambda_{exc} = 254$ nm) with DCB as Electron Acceptor[a]

entry	$[C_{10}L_8]$	isotope effect	ratio 1-CN/2-CNC$_{10}$L$_7$
1	0.63	0.96 ± 0.02	*d*
2	1.01	0.98 ± 0.02	7.27 ± 0.55
3	1.33	1.04 ± 0.02	8.00 ± 0.68
4	3.62	1.10 ± 0.02	7.27 ± 0.45
5	7.50	1.16 ± 0.02	7.29 ± 0.40
6	16.00	1.20 ± 0.01	7.04 ± 0.59
7	32.50	1.31 ± 0.01	8.10 ± 0.70
8	64.50	1.35 ± 0.02	8.05 ± 1.35
9	1.33[b]	1.07 ± 0.02	6.31 ± 0.43
10	7.50[c]	0.98 ± 0.02	7.35 ± 0.39

[a] [DCB] = 0.8 mM; [18-crown-6-KCN] = 18 mM. [b] 28.2 mM 1,3,5-tri-*tert*-butylbenzene was added. [c] IE determined in separate experiments for naphthalene and perdeuterionaphthalene. [d] Due to the small amount of photoproducts formed, no consistent ratio could be obtained.

IEs on the product formation were studied in two ways: (a) "intraexperimentally", in which naphthalene and perdeuterionaphthalene in a 1:1 ratio were irradiated in one reaction vessel, and (b) "interexperimentally", where two experiments were performed independently in separate reaction vessels, one with the hydrogen and one with the deuterium compound.

IEs on the formation of both 1- and 2-cyanonaphthalene were measured by GC analysis.[32] The deuterated compounds have shorter retention times than their hydrogen isotopologues on all GC columns which were tested for this purpose (OV 101, Carbowax, CP SIL5, CP SIL19). Base line separation was achieved between the starting materials naphthalene and perdeuterionaphthalene. For 1-cyanonaphthalene and 1-cyanoperdeuterionaphthalene peak-valley ratios > 10 were obtained; for 2-cyanonaphthalene and 2-cyanoperdeuterionaphthalene peak-valley ratios fell from about 8 at high product concentrations to about 3 at the lowest product concentrations.

The interpretation of GC peak integrations in terms of IEs hinges on known response factors of the flame ionization detector for the different isotopologues. Therefore, 1-cyanonaphthalene-d_7 was synthesized independently, and response factors were measured for this compound and its h$_7$-isotopologue, and for naphthalene and perdeuterionaphthalene. The IEs on the response factors were 1.013 ± 0.010 and 1.017 ± 0.007, respectively, at the detection temperature of 275 °C, and independent of the amount of aromatic compound injected. These values are equal within experimental error, and IEs are not corrected for possible differences between them.

The IEs measured at various total naphthalene concentrations ($[C_{10}L_8]$; L = H, D) are given in Table 2, together with the 1-CN−C$_{10}$L$_7$/2-CN−C$_{10}$L$_7$ ratios. For entries 2−8 these ratios average out to 7.57 ± 0.45. Entry 9 presents an IE and product ratio of a reaction in which part of the naphthalene radical cations are created as free ions by using 1,3,5-tri-*tert*-butylbenzene as cosensitizer.[33] All entries refer to intraexperimental IEs, except entry 10, which presents an interexperimental IE. The IE results of entries 1−8 are graphically represented in Figure 1.

The IEs on the formation of product were also measured by using 9,10-dicyanoanthracene (DCA) as electron acceptor and

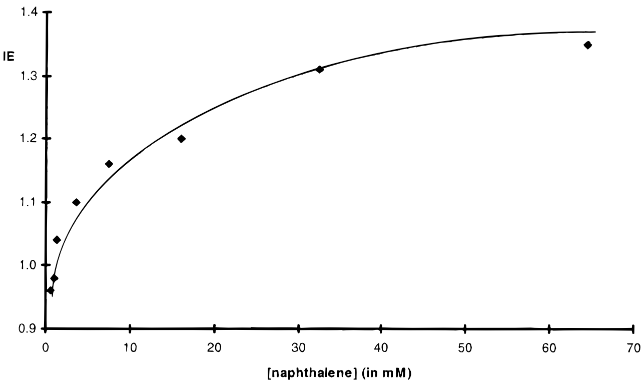


Figure 1. Isotope effects on the formation of 1-cyanonaphthalene in the photocyanation of naphthalene in acetonitrile ($\lambda_{exc} = 254$ nm), with DCB as electron acceptor, with varying naphthalene concentration.

TABLE 3: Isotope Effects on the Formation of 1-Cyanonaphthalene in Acetonitrile, with DCA as Electron Acceptor at Various Wavelengths of Excitation

λ_{exc} (nm)	$[C_{10}L_8]$[a]	isotope effect
254	4.7	1.07 ± 0.02
254	16.0	1.16 ± 0.02
254	29.0	1.30 ± 0.01
>300	5.0	1.06 ± 0.03
>300	16.0	1.15 ± 0.02
>330	12.0	1.00 ± 0.02
>330	16.0	1.00 ± 0.02

[a] All concentrations in mM; [9,10-dicyanoanthracene] = 0.8 mM; [18-crown-6 KCN] = 18.0 mM.

irradiating the solution at $\lambda_{exc} = 254$ nm, > 300 nm, and > 330 nm, respectively (Table 3). At the first two wavelengths of excitation, the same variation in the magnitude of the IEs with varying naphthalene concentration is observed as with DCB as electron acceptor. At $\lambda_{exc} > 330$ nm, there is no IE. In this case, the acceptor is excited exclusively (eq 6) and the radical cation of naphthalene is formed via electron transfer to the excited acceptor (eq 7). Energy transfer from the excited acceptor to ground-state naphthalene (eq 7a) is energetically not possible. Thus, under these reaction conditions the singlet excited state of naphthalene is not involved in the photocyanation.

$$\mathrm{DCA} \xrightarrow{h\nu} (\mathrm{DCA})^{*S_1} \tag{6}$$

$$(\mathrm{DCA})^{*S_1} + C_{10}H_8 \xrightarrow{\mathrm{ET}} \mathrm{DCA}^{-\bullet} + (C_{10}H_8)^{+\bullet} \tag{7}$$

$$(\mathrm{DCA})^{*S_1} + C_{10}H_8 \nrightarrow \mathrm{DCA} + (C_{10}H_8)^{*S_1} \tag{7a}$$

The IEs on the formation of product with DCB as ET sensitizer were also measured at various concentrations of *all* reagents other than naphthalene (Table 4). Using constant $C_{10}L_8$ concentrations, the concentration of cyanide was systematically varied. Furthermore, the effect of the total salt concentration was tested by combining a low cyanide concentration with a high total salt concentration (0.52 mM KCN, 17.48 mM $KClO_4$, entry 2). Variation of the DCB concentration from 0.8 to 8.0 mM, using 3.6 mM as the total naphthalene concentration and 18 mM cyanide, yielded no significant variation of the observed IE and product ratios (data not in table). In the absence of oxygen (entry 6), 1- and 2-cyanonaphthalene are still the dominant products, but dihydrocyanonaphthalenes and small amounts of several trace products are also formed. It is likely that, in solutions open to air, oxygen functions as the final oxidant. This is based on the fact that the photocyanation does not proceed in the absence of a catalytic amount of DCB, but that no DCB is consumed. This suggests that DCB is the initial electron acceptor, and that oxygen picks up the electron from DCB radical anion, yielding oxygen radical anion.

TABLE 4: Intraexperimental IEs on the Formation of 1-Cyanonaphthalene (in Acetonitrile, $\lambda_{exc} = 254$ nm, DCB as Electron Acceptor) with Varying Cyanide and Oxidant Concentrations (All Concentrations in mM)[a]

entry	$[C_{10}L_8]$	[cyanide]	atmosphere	isotope effect	ratio 1-CN/2-CNC$_{10}$L$_7$
1	16.0	0.52	air	1.04 ± 0.03	6.02 ± 0.23
2	16.0	0.52[b]	air	0.99 ± 0.02	6.50 ± 0.51
3	16.0	2.7	air	1.14 ± 0.01	6.16 ± 1.06
4	16.0	18.0	air	1.20 ± 0.01	7.04 ± 0.59
5	7.5	18.0	air	1.16 ± 0.02	7.29 ± 0.40
6[c]	7.5	18.0	argon	2.5 ± 0.4	6.73 ± 0.39

[a] [DCB] = 0.8 mM. [b] 17.48 mM 18-crown-6 $KClO_4$ was added. [c] Experiment performed in duplicate.

TABLE 5: Intraexperimental IEs on the Formation of 1-Cyanonaphthalene in the Anodic Cyanation of Naphthalene at Two Naphthalene Concentrations (in mM) and Three Oxidation Potentials (in *V* versus SCE)[a]

$[C_{10}L_8]$	*V*	isotope effect	1-CN/2-CNC$_{10}$L$_7$
3.6	1.40	1.04 ± 0.02	5.91 ± 0.29
15	1.175	1.02 ± 0.01	5.17 ± 0.10
15	1.25	1.01 ± 0.01	5.70 ± 0.13
15	1.40	1.01 ± 0.01	5.42 ± 0.20

[a] [KCN] = 2.5 mM.

Electrochemistry. Semipreparative electrochemistry was carried out to investigate the role of naphthalene radical cations in the determination of the IEs observed in the photochemical reactions. IEs in the anodic cyanation were measured at concentrations of naphthalene and perdeuterionaphthalene of 7.5 mM each and 1.8 mM each, and at a cyanide concentration of 2.5 mM, using three different oxidation potentials (1.175−1.40 V versus SCE) (Table 5). The ratio 1-CN−$C_{10}L_7$/2-CN−$C_{10}L_7$ was determined to be 5.55 ± 0.38 (averaged over all averaged values for each experiment). No systematic variation of this ratio was observed with varying naphthalene concentrations and oxidation potential. The ratio is significantly different from that obtained in the photochemical experiments.

Calculations. PM3 calculations were performed to calculate the equilibrium IEs which could be expected if the reactions depicted in eqs 8−10 would occur. The method used has been discussed in detail before.[21] These reactions involve equilibration of the first singlet and triplet excited states of naphthalene isotopologues via energy transfer, and the analogous equilibration between isotopologous naphthalene radical cations via electron transfer. The first equilibrium may occur at high concentrations of naphthalene, at which singlet excited naphthalene can transfer its energy to another naphthalene molecule before decaying via bimolecular electron transfer to DCB or unimolecular decay to the ground state. The second equilibrium is calculated to show that such an IE is not restricted to singlet states, although under the reaction conditions used the singlet state is the reactive one.[10] Equation 10 represents the equilibration that can take place both in the electro- and photochemical experiments. If a radical cation lives long enough (due to low cyanide concentration), it can transfer its charge to its isotopologue. This would lead to IEs that depend on the cyanide concentrations used.

$$C_{10}H_8 + (C_{10}D_8)^{*S_1} \overset{K}{\rightleftarrows} (C_{10}H_8)^{*S_1} + C_{10}D_8 \qquad (8)$$

HOMO−LUMO excitation:

$$\Delta H = -165 \text{ cal/mol}; \quad K = 1.33$$

CISD-calculation: $\Delta H = -$ (calculation not successful)[34]

$$C_{10}H_8 + (C_{10}D_8)^{*T_1} \overset{K}{\rightleftarrows} (C_{10}H_8)^{*T_1} + C_{10}D_8 \qquad (9)$$

HOMO−LUMO excitation:

$$\Delta H = -157 \text{ cal/mol}; \quad K = 1.31$$

CISD-calculation: $\Delta H = -56$ cal/mol; K = 1.10

$$C_{10}H_8 + (C_{10}D_8)^{+\bullet} \overset{K}{\rightleftarrows} C_{10}D_8 + (C_{10}H_8)^{+\bullet} \qquad (10)$$

$$\Delta H = -141 \text{ cal/mol}; K = 1.27$$

For the calculation of excited-state properties two methods were tested: representation of the lowest singlet state by HOMO−LUMO excitation, or as calculated by the use of configuration interaction using singly and doubly excited configurations (=CISD). CISD-calculations were performed with 10 orbitals: the HOMO-4 up to the LUMO+4, yielding 978 configurations. The 100 configurations with the lowest energy were then used in the configuration interaction to describe the molecular state.

As far as reproduction of experimental energies is concerned, the HOMO−LUMO excitation representation of the lowest singlet is better than the CISD-calculation: $E_{S1} = 97$ and 76 kcal/mol, respectively, with experimental values of 90−95 kcal/mol.[23,35] Calculated values for E_{T1} of 51 and 40 kcal/mol respectively were obtained, where 61 kcal/mol is the experimental value.[23] These results compare favorably with ab initio calculations with large and flexible ANO-type basis sets which calculated the S_1 and T_1 energies of naphthalene to be 104 and 78 kcal/mol, respectively (CASSCF),[36a] or 82 and 69 kcal/mol, respectively (CASPT2).[36b] Our results also show that, in the reproduction of experimental excited-state data, PM3 is no significant improvement over MNDO, which calculates the S_1 and T_1 states to have energies of 98 and 57 kcal/mol, respectively.[37]

Inclusion of explicit configuration interaction using the PM3 parametrization does not lead to a better but, in contrast, to a worse fit of the calculated energies with the experimental excited-state energies. It is therefore not to be expected that the second derivatives of the energy with respect to the nuclear coordinates, which are calculated to obtain the zero-point energies, are predicted better by the data obtained via CISD calculations than by data calculated without inclusion of any extra electron correlation correction. Therefore, the HOMO−LUMO excitation data are supposedly more reliable for the calculation of the equilibrium IEs (eqs 8 and 9). IEs are given in reaction enthalpies (in cal/mol) and, assuming $\Delta S = 0$, in the corresponding equilibrium constant at 293 K, the temperature at which all experiments were performed.

Furthermore, calculations were performed to investigate the potential energy surface for hydrogen atom abstraction from 1-cyano-1-*H*-naphthyl radical (the intermediate formed after attack by CN^- at position 1 of naphthalene radical cation) by oxygen radical anion and by oxygen. For the reaction with oxygen radical anion, the saddle point on this surface was found at a geometry with the C−H bond to be broken at 1.352 Å and the H−O bond length equal to 1.486 Å (Figure 2a). The activation enthalpy was calculated to be <2 kcal/mol. For the reaction with oxygen, the activation barrier was calculated to be 28 kcal/mol, and the transition state was calculated with the C−H bond to be broken equal to 1.444 Å, as well as the H−O bond equal to 1.413 Å (Figure 2b). Grid calculations with systematic variation of both the C−H and O−H distances to simulate the potential energy surface of the hydrogen abstraction by the radical anion of oxygen show a slight minimum in the potential energy surface around r(C−H) = 1.3 Å and r(O−H) = 1.7 Å. This suggests that oxygen radical anion possibly forms a weak hydrogen-bonded complex with 1-cyano-1-*H*-naphthyl radical before abstracting the hydrogen atom.

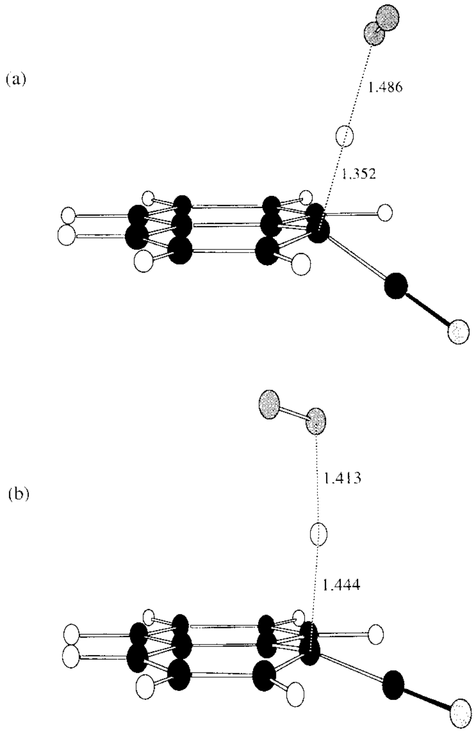
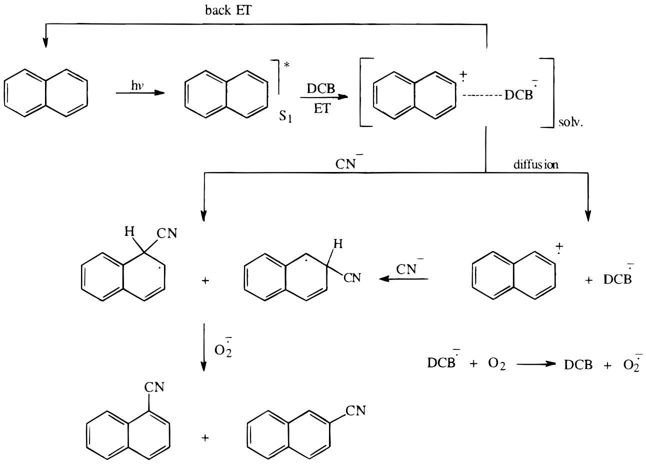


Figure 2. Transition states for hydrogen abstraction from 1-cyano-1-*H*-naphthyl radical by (a) the radical anion of oxygen and (b) by oxygen.

Discussion

Photochemical Cyanation. The photocyanation of naphthalene in acetonitrile in the presence of electron-accepting sensitizers smoothly yields two products: 1- and 2-cyanonaphthalene, in a ratio of about 7:1. This ratio is in line with the calculated charge distribution in the naphthalene radical cation. The calculated charge at position 1 is +0.09, while at position 2 it is −0.05; when the charge of the bound hydrogen atoms is added to that of the carbon atoms this yields values of +0.25 and +0.09. Both methods for the determination of the electrostatic attraction of the nucleophile therefore show a preference for position 1. Attack at this position is also favored because the resulting radical has a lower energy than the 2-cyano-2-*H*-naphthyl radical ($\Delta H_f = 93.8$ versus 97.5 kcal/mol), due to more extensive resonance. The attack must be relatively fast under the reaction conditions used, since inverse IEs would have resulted on the product formation if the combination reaction would have been rate limiting.[38] The *n*-cyano-*n*-*H*-naphthyl radicals lose hydrogen easily to oxygen

SCHEME 1: Postulated Mechanism for the Photocyanation of Naphthalene



radical anion. The calculated barrier for hydrogen atom transfer from 1-cyano-1-*H*-naphthyl radical to oxygen radical anion is <2 kcal/mol, while that to oxygen is 28 kcal/mol. This is tantamount to a relative rate of 10^{17} at equal concentrations of oxygen and oxygen radical anion at room temperature. Therefore, transfer of the hydrogen atom from the radical will almost exclusively occur to oxygen radical anion, despite the fact that this is present in much lower concentrations than oxygen. The reason that oxygen and oxygen radical anion were calculated as hydrogen atom abstractors and not DCB radical anion is the large rise in observed IE (from 1.16 to 2.5) under low $[O_2]$ conditions. This primary IE points to a change in the rate-limiting step, making the hydrogen abstraction step limiting due to the low $[O_2^{-\bullet}]$. The measured IE is in line with the structure calculated for the transition state for formation of 1-cyanonaphthalene, which shows significant C−H bond lengthening (r(C−H) = 1.352 Å). Experimental evidence for the hypothesis that DCB picks up the electron from naphthalene, as well as that its radical anion transfers this extra electron to oxygen, comes from the observation that DCB is only needed in catalytic amounts and that it is not consumed in the reaction. The control experiment without DCB showed hardly any product formation on the time-scale studied, while in the experiments with reduced oxygen concentration DCB (present in 0.7% of the amount of $C_{10}L_8$) is also not consumed. Under those conditions dihydrocyanonaphthalenes, resulting from disproportionation of *n*-H-*n*-CN-naphthyl radicals, are formed besides cyanonaphthalenes, in quantities slightly less than the cyanonaphthalenes (8.0 and 7.1% respectively, after 16% conversion). The fact that the amount of cyanonaphthalenes is consistently slightly larger than the amount of dihydrocyanonaphthalenes shows that some oxygen is still present, which can reoxidize the small amount of DCB radical anion formed. The whole reaction scheme is summarized in Scheme 1.

Naphthalene Concentration-Dependent Isotope Effects in the Photocyanation of $C_{10}L_8$. The photocyanation of naphthalene unambiguously shows an IE that is dependent on the $C_{10}L_8$ concentration, when hydrogen and deuterium isotopologues are competing for photons and material reagents (Table 2, Figure 1). When the $C_{10}L_8$ concentration is low, 0.63 mM, the IE equals the IE measured interexperimentally, as well as the difference in absorbance at 254 nm (0.96, 0.98, and 0.97, respectively). Therefore it seems plausible that the IE at low total naphthalene concentrations is caused by differences in absorbance between naphthalene and perdeuterionaphthalene: the relative concentration of excited $C_{10}H_8$ and excited $C_{10}D_8$ determines the magnitude of the IE.

At higher $C_{10}L_8$ concentrations the IE increases substantially, approaching a plateau value around 1.35 at 64 mM. This concentration dependence can be caused by any of the steps in which naphthalene and perdeuterionaphthalene are competing to acquire the ability to yield product. Since the reaction is known to proceed via the lowest excited singlet state of naphthalene under the reaction conditions used,[10] a concentration dependence involves this state or some intermediate directly following or preceding this. Three steps are clearly imaginable. First, excited naphthalene can transfer its excitation energy to ground-state perdeuterionaphthalene and vice versa (eq 8). At higher $C_{10}L_8$ concentrations more energy exchange can take place. Therefore, kinetic IEs will approach the equilibrium IE for energy exchange. Second, it is well-known that radical cations of aromatic compounds form dimers with neutral aromatics.[39] For naphthalene the association constant in benzonitrile has been reported to be 520 M^{-1}.[40] Via this reversible dimer formation exchange of charge might occur between isotopologous radical cations (eq 10). On the basis of the absence of binaphthyl formation in the photochemical cyanation, as well as on the basics of the IEs observed in the electrochemical and photochemical experiments (vide infra), this is unlikely. Third, it has recently been proposed that concentration-dependent photoinduced electron transfer does occur between cyanoanthracenes and naphthalene in acetonitrile.[41] With increasing naphthalene concentration, electron transfer results not only in a 1:1 radical ion complex, but increasingly and more also in the formation of a 1:2 complex,[41,42] in which the positive charge is distributed over two naphthalene molecules. It is unlikely that 1:2 complexes are involved in the concentration-dependent IEs since they display an increased rate of back electron transfer with respect to analogous 1:1 complexes.[41] This would result in a smaller amount of product after a fixed time of irradiation, which is incompatible with our experimental results.

We therefore propose the concentration dependence of the IE on product formation to be caused by the reversible energy exchange between excited naphthalene and ground-state perdeuterionaphthalene (eq 8). This is in line with the observation that the IE = 1.00 if photocyanation takes place without excitation of naphthalene (λ_{exc} > 330 nm, DCA as sensitizer), at a concentration of $C_{10}L_8$ at which IE = 1.15 (λ_{exc} > 300 nm; DCA), 1.16 (λ_{exc} = 254 nm; DCA), or 1.20 (λ_{exc} = 254 nm; DCB) if naphthalene can be photoexcited (Table 3).

The energy exchange might occur (a) at contact distance (via excimer formation)[9] or (b) via singlet−singlet energy transfer via either a long-range (Förster) or a short-range mechanism.[43] (a) Two arguments suggest that excimers are not involved in this process. First, excimer fluorescence could only be observed at naphthalene concentrations much larger (>0.5 M)[44] than those used in the reaction under study (<0.065 M). Second, the formation of naphthalene excimers is less likely than that of naphthalene radical cation dimers: the association constant of naphthalene excimer (0.72 M^{-1})[45] is much lower than that of naphthalene radical cation dimer (520 M^{-1}),[40] while the rates of the quenching reaction of excited naphthalene by DCB and naphthalene radical cation by cyanide are very similar.[46] Binaphthyl products are expected if radical cation dimers are intermediates, but since those products are not observed, the intermediacy of excimers is even less likely. (b) On the other hand, singlet−singlet energy transfer via the Förster mechanism is also unlikely. The calculated concentrations at which energy transfer via this mechanism becomes important for naphthalene and perdeuterionaphthalene are 1.1 and 0.5 M,[47] substantially higher than the concentrations used in this study. This leaves as a last possibility that energy transfer between $C_{10}H_8$ and $C_{10}D_8$ occurs via a short-range mechanism.

With regard to the calculations of the equilibrium IEs, it should be noted that they point to the right direction and magnitude of the observed IE, but are not useful to discriminate between different IE-effecting steps (eqs 8−10), since the calculated IEs vary only over a small range (1.27−1.33) for very different processes.

Isotope Effects in the Anodic Cyanation of Naphthalene. The above conclusion that, under the reaction conditions chosen, the equilibration of eq 10 is not important is confirmed by the IEs obtained in the electrochemical study. The anodic cyanation of naphthalene shows an IE close to one (1.01−1.04), practically independent of the total naphthalene concentration used. This means that the radical cation−nucleophile combination must be faster than the equilibration of eq 10. If this equilibration would have been completed before further reaction would take place, an IE > 1.10 would be expected (on the basis of the charge-transfer spectra), and the computations suggest this to be 1.27.[48] By performing the electrochemical experiments at varying potentials around the half-wave potential of naphthalene (1.26 V versus SCE),[49] the concentration of radical cations produced was varied substantially. As can be seen from the data in Table 5, electrolyses performed at 1.25 or 1.17 V give identical results as those performed at 1.40 V. Therefore it can be concluded that, as long as enough cyanide is available, the equilibration of eq 10 does not take place, not even at high oxidation potentials at which the amount of naphthalene radical cations formed is limited by diffusion of the naphthalene to the electrode, rather than by oxidation rates of naphthalene residing near the electrode.[50]

Cyanide Concentration-Dependent Isotope Effects in the Photocyanation of $C_{10}L_8$. Upon decrease of the cyanide concentration from 18 to 0.52 mM, the IE decreases from 1.20 to 1.04 (Table 4). As added 18-crown-6 $KClO_4$ does not increase the IE (Table 4, entry 2), the change in solvent polarity by decreasing salt concentrations is unimportant. Quenching of excited $C_{10}L_8$ by cyanide is an inefficient process,[51] and therefore will hardly influence the equilibration of eq 8. If any quenching would occur, however, an increase in the cyanide concentration hampering the equilibration would reduce the IE instead of increasing it as is observed. This suggests that the overall observed IE can be influenced by reaction steps occurring after the equilibration of eq 8. The first such step, quenching of singlet excited naphthalene by DCB, occurs with a rate which is diffusion controlled (vide supra) and will not be subject to an IE. To explain the variation of the IE with the concentration of cyanide we postulate that after the quenching a geminate radical ion pair is formed, which can undergo any of the following three processes (Scheme 1): (1) back electron transfer, to give back the reactants naphthalene and DCB; (2) diffusion of the radical ions out of the solvent cage, followed by capture of cyanide by free naphthalene radical cation; (3) reaction of naphthalene radical cation with cyanide in the solvent cage.[52] The relative importance of the three processes depends on the concentration of cyanide and so will the IEs associated with each step.

Deuterium kinetic IEs are known to exist on the back electron transfer from aromatic radical cations to the radical anion of cyanoanthracene. Methyl-deuterated methylbenzenes show a decreased rate of back electron transfer compared to their hydrogen isotopologues.[53] On the other hand, the effect of ring deuteration in toluene and *p*-xylene was very close to zero,[53] as was the isotopic shift in charge-transfer spectra of benzene versus perdeuteriobenzene with tetracyanoethene.[26] Charge-transfer spectra of naphthalene and perdeuterionaphthalene, however, do show isotopic shifts (vide supra). The lowest energy charge-transfer bands show shifts of 55 and 156 cal/mol, respectively, comparable to the values for the isotopic shift observed for toluene-h_8 and -d_8 and hexamethylbenzene-h_{18} and -d_{18} with tetracyanoethene (117 and 206 cal/mol, respectively).[26] The radical cations of these alkylbenzenes show kinetic IEs for back electron transfer to cyanoanthracene radical anions up to 1.8![53] The kinetic IE has been demonstrated to increase with the driving force for back electron transfer,[53] in line with theoretical predictions.[54] The radical ion pair under study has a driving force of 3.2 eV (E_{ox}(naphthalene) = 1.60 V, E_{red}(DCB) = −1.60 V), at least 0.4 eV more exergonic than the examples given in ref 53. It seems therefore reasonable to suppose there will be a normal kinetic IE of substantial magnitude on the back electron transfer within the geminate radical ion pair of naphthalene and DCB (eq 11).

$$[C_{10}L_8^{+\bullet} \cdots DCB^{-\bullet}] \rightarrow C_{10}L_8 + DCB \qquad (11)$$

How does this influence the observed IEs on product formation with varying cyanide concentration? With decreasing cyanide concentration the IE decreases. To explain the reduction in the impact of the singlet energy exchange of eq 8 which causes the IE, one has to assume that either cyanide acts as an agent promoting the diffusion of naphthalene radical cation from the solvent cage which it shares with DCB radical anion or that cyanide reacts *within* the solvent cage with the radical cation. The latter process is more plausible. At lower cyanide concentrations more back electron transfer will occur, thereby decreasing the ratio $C_{10}H_8^{+\bullet}/C_{10}D_8^{+\bullet}$. This will lead to a reduction of the IE, as observed. Chemical evidence for the (partial) reaction of cyanide and naphthalene radical cation *within* the solvent cage can be found in the fact that the photochemical reaction of naphthalene with cyanide results in a different 1- to 2-cyanonaphthalene ratio (7.6:1) than the electrochemical experiments (5.6:1). The radical cations in the latter reaction are formed close to a positively charged electrode from which they diffuse away quickly. Since the reaction with cyanide is slower than diffusion controlled,[11] cyanide can react with the more or less free ions in that case. The geminate radical ion pair being somewhat more selective for reaction with cyanide ion than the free radical ion is consistent with the observation that the ratio of 1-cyanonaphthalene/2-cyanonaphthalene seems to increase slightly with increasing cyanide concentration (Table 4, entries 1, 3, and 4).

Attempts were made to create free naphthalene radical cations by photochemical means. Experiments using a positively charged electron acceptor (TPP or MA) or a doubly charged one (BMA), to obtain geminate ion pairs with a very short lifetime due to the lack of Coulombic attraction or the creation of Coulombic repulsion after electron transfer,[55] failed to yield significant amounts of cyanation product (Table 1). In view of the high reduction potentials of these three cationic sensitizers, this is presumably caused by a very efficient energy-wasting back electron transfer.[56] Biphenyl (oxidation potential: 1.96 V),[56] which is used in numerous cases to create aromatic radical cations outside the initial solvent cage,[57] has a radical cation which is a strong enough electron acceptor to oxidize naphthalene. It was, however, cyanated very effectively itself, thereby hampering the analysis. The use of 1,3,5-tri-*tert*-butylbenzene (oxidation potential: 2.01 V[33]) was more successful (see Table

1). The quantum yield increased by a factor of 1.6, and the ratio of 1-cyano- to 2-cyano-derivative dropped well below the average value in the absence of 1,3,5-tri-*tert*-butylbenzene (6.31 versus 7.57) and approached the value obtained in the electrochemical experiments (5.55). These data support the hypothesis that part of the naphthalene radical cations are created via oxidation by 1,3,5-tri-*tert*-butylbenzene radical cation, and therefore as free ions. For reaction with free ions the 1-CN− to 2-CN−$C_{10}L_7$ ratio is lower. The higher quantum yield (Table 1, entry 7) is due to the reduced importance of energy-wasting back electron transfer.[58]

Concluding Remarks

The present study shows: (1) the usefulness of the concept of concentration-dependent IEs in the study of reaction mechanisms, (2) the necessity for adaptation of the proposed mechanism for the photocyanation of naphthalene on the basis of the observed concentration-dependent IE with variation of the cyanide concentration, and (3) the (to the best of our knowledge) first two examples of concentration-dependent IEs in a photochemical reaction proceeding via electron transfer: one involving energy exchange between an electronically excited molecule and its ground-state isotopologue (eq 8) and the other involving electron transfer within a ground-state ion pair (eq 11). Concentration-dependent IEs are therefore not limited to photochemical reactions, but can be found in *any* reaction in which intermediates have the possibility to transfer reactivity to an isotopologue, before leading to product(s).

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(32) This method of measuring IEs is both quantitatively superior to and significantly faster and cheaper than analysis by GC/MS.

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