

Figure 1. ORTEP structure of 7-X.

Irradiation at 313 nm of a solution of 1 g of 3 and 0.5 g of 4-X in 50 mL of spectrograde acetonitrile for 48 h leads¹³ to the formation of trans- and cis-oxetanes and to the cis-trans isomerization of 3. At low conversions only trans-oxetanes were formed (eq 2). After workup the solution gave residues that could be



separated by column chromatography to give 7-X and 8-X (≥80% chemical yield by means of either VPC or NMR integration). In all instances examined (X = F, Cl, Br, OH), the major isomer $(\sim 60:40)$ was 7-X (see Table I).

The structural assignments were determined by means of ¹³C NMR; the chemical shifts of both isomers could be calculated on the basis of those of 7-H and those of adamantane itself in the manner described above. The question of cis- or trans-nitrile group configuration was determined from the magnitudes of the coupling constants for the oxetane ring protons: they fall within the range 5.5-5.8 Hz, consistent with trans configurations.¹⁴ Finally, the configuration of 7-F was established independently by means of an X-ray diffraction study (see Figure 1).15

In the Diels-Alder reaction, the diene functions as the donor; in the photocycloadditions, the carbonyl π^* state is the nucleophile. Although the mechanisms of the two cycloadditions are different, one being a concerted thermal process and the other involving an exciplex, we believe that bond formation in both cases is assisted by σ delocalization of the electron richer bonds anti to the 5substituent into the incipient σ^* orbital and that these reactions constitute further evidence for the generality of the rule stated above. We note that several other cycloadditions already in the literature exhibit stereoselectivities explicable on the same basis: these include the Diels-Alder reactions of 9,16 the contra-steric



axial [2 + 2] cycloaddition of dichloroketene to methylenecyclohexane to give 10 and 11 in 4:1 ratio,^{17,18} and the contrasting stereochemistry of [1,3]-dipolar cycloaddition of diazomethane to 12 (100% syn) and 13 (100% anti).¹⁹ The explanations offered or discussed were in all instances different from our own.

While we do not wish to assert the hyperconjugation has no rivals as the basis of these effects, it is noteworthy that the rule serves as a simple heuristic device that correctly anticipates the stereochemistry in both thermal and photochemical reactions: bond formation occurs at the face anti to the most electron rich σ bond. This rule can be readily employed to make predictions for the whole, rich variety of pericyclic reactions, and we shall report our results of studies aimed at determining their stereoselectivities in due time.

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Supplementary Material Available: Tables of ¹³C and ¹H NMR data of all compounds mentioned in this paper and X-ray data for compound 7-X (21 pages). Ordering information is given on any current masthead page.

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Specific Deuterium Isotope Effects on the Rates of **Electron Transfer within Geminate Radical-Ion Pairs**

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Recent theories of electron-transfer reactions treat the rearranged high-frequency ($h\omega > kT$) internal vibrational modes quantum mechanically, whereas the low-frequency solvent modes are treated classically.¹ The role of quantum effects in the internal reorganization can, in principle, be investigated by the study of isotope effects. The Franck-Condon factors for electron transfer depend upon vibrational overlap and are proportional to the frequencies of the vibrational modes involved in the transition. Thus, isotopic substitution, which modifies these frequencies, should affect the reaction rate. Several examples of isotope effects

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Table I. Rate Constants for Return Electron Transfer from Cyanoanthracene Radical Anions to Deuteriated and Nondeuteriated Methyl-Substituted Benzene Radical Cations in Acetonitrile at 25 °C

radical cation	radical anion ^a	$-\Delta G_{-et}^{b}$	$k_{\rm d} \ (\times \ 10^{-9} \ {\rm s}^{-1})$	$k_{\rm h} \ (\times \ 10^{-9} \ {\rm s}^{-1})$	$k_{\rm h}/k_{\rm d}$	$(k_{\rm h}/k_{\rm d})_{\rm perMe}^{c}$
toluene	TCA	d	1.88	1.50	1.253	1.253
1,2,3,5-tetramethyl benzene	DCA	2.77	0.80	1.32	1.659	1.135
durene	DCA	2.72	0.98	1.59	1.627	1.129
<i>m</i> -xylene	TCA	2.58	2.97	3.66	1.237	1.112
o-xylene	TCA	2.57	2.96	3.63	1.227	1.108
mesitylene	TCA	2.55	3.77	4.93	1.312	1.095
hexamethylbenzene	DCA	2.53	3.12	5.60	1.796	1.103
<i>p</i> -xylene	TCA	2.50	4.60	6.00	1.299	1.140
1,2,3,5-tetramethylbenzene	TCA	2.27	9.75	11.69	1.20	1.047
durene	TCA	2.22	10.18	12.33	1.21	1.049
hexamethylbenzene	TCA	2.03	14.42	15.89	1.10	1.017

^a DCA = 9,10-dicyanoanthracene, TCA = 2,6,9,10-tetracyanoanthracene. ^bCalculated from $E_{red}(A) - E_{ox}(D)$ in which A = cyanoanthracene and D = methyl-substituted benzenes (ref 8). ^cCalculated according to eq 2. ^d The electrochemical oxidation of toluene is not reversible (ref 10), and so the value of ΔG_{-et} for this reaction cannot be accurately obtained.

Table II. Deuterium Isotope Effect, k_h/k_d , on the Rates of Return Electron Transfer within Geminate Pairs of TCA Radical Anions and Perdeuteriated or Selectively Deuteriated Alkylbenzene Radical Cations

radical cation	perdeuteriated	methyl deuteriated	ring deuteriated
toluene	1.25 ± 0.04	1.22 ± 0.04	1.00 ± 0.03
p-xylene	1.30 ± 0.03	1.28 ± 0.03	1.01 ± 0.03

on electron-transfer reactions have been reported;² however, in several of these cases the origin of the effect is questionable,³ and no systematic studies for a series of related compounds have been reported yet. Theoretical studies suggest that k_h/k_d should depend upon the electron-transfer reaction free energy (ΔG_{et}) .⁴ Specifically, for pure quantum effects, it is predicted that only normal isotope effects should be observed $(k_h/k_d > 1)$, that k_h/k_d should be approximately unity when the reaction exothermicity is equal to the total reorganization energy (i.e., the sum of the solvent and vibrational reorganization energies, $\lambda_s + \lambda_v$), and that k_h/k_d should increase as ΔG_{et} increases above $\lambda_s + \lambda_v$, i.e., in the Marcus "inverted region".⁵ Previous studies, however, have not fully tested these predictions, and, indeed, the inverted region has only recently been observed experimentally.⁶ We have reported that return electron transfer within geminate radical ion pairs, eq 1, provides

$$A^{\bullet-}/D^{\bullet+} \to A + D \tag{1}$$

an excellent example of the inverted region and also that this system is sensitive to small changes in the molecular structure of the ion pairs.⁷ We now report the results of the first systematic study of the effect of isotopic substitution on the rates of electron transfer for reactions in the inverted region.



Figure 1. Ratios of rate constants for return electron transfer within geminate radical ion pairs of cyanoanthracene radical anions with undeuteriated and perdeuteriated alkyl benzene radical cations in acetonitrile at 25 °C, as a function of the reaction free energy (ΔG_{-et}). In the top half of the figure are plotted the rate ratios (k_h/k_d) obtained directly from the experimental data; in the bottom half of the figure the rate ratios are corrected for the number of methyl groups on the benzene donor $((k_{\rm h}/k_{\rm d})_{\rm perMe})$.

Rates of return electron transfer within geminate radical ion pairs of 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) radical anions and the radical cations of perdeuteriated methyl-substituted benzene derivatives, k_{d} , were determined by using the method previously described.⁷ The rates are summarized in Table I together with the corresponding rates for radical ion pairs of the undeuteriated parent donors, $k_{\rm h}$, which were reported previously.7b The free energies of the electrontransfer reactions for both sets of ion pairs were calculated by using the relation $\Delta G_{-\text{et}} = E_{\text{red}}(A) - E_{\text{ox}}(D)$.⁸ For both sets of radical-ion pairs, the rates of the electron-transfer reactions decrease with increasing reaction exothermicity, as expected for reactions in the inverted region.^{5,7} In each case, however, the reactions with deuteriated radical cations are slower than the

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corresponding reactions of the undeuteriated radical cations, $k_{\rm h}$ $> k_{d}$

Of particular interest is the effect of selective isotopic substitution. As shown in Table II, for toluene and p-xylene, ring deuteriation leads to no or insignificant isotope effect, whereas methyl deuteriation results in almost the same isotope effect as perdeuteriation. These remarkable specific isotope effects are similar to others observed previously in charge-transfer complex absorption spectra^{9a} and in the nonradiative decay of exciplexes in the gas phase.9b-g The methyl-specific isotope effect is consistent with significant changes in the methyl carbon-hydrogen and ring carbon-methyl carbon bond lengths upon ionization of the substituted benzene.9 These specific bond length changes are consistent with significant hyperconjugative stabilization of the substituted Lenzene radical cations by the ring methyl groups.^{9a,d-g}

The observed kinetic isotope effect (Table I) seems to depend on the reaction exothermicity and on the number of methyl groups on the benzene ring. Thus, isotope effects per methyl group, $(k_h/k_d)_{perMe}$, are calculated with eq 2 in which n is the number of methyl groups on the donor.

$$(k_{\rm h}/k_{\rm d})_{\rm perMe} = (k_{\rm h}/k_{\rm d})^{1/n}$$
 (2)

In Figure 1 are plotted (k_h/k_d) and $(k_h/k_d)_{perMe}$ as a function of reaction free energy. The plots clearly show that the magnitude of the isotope effect increases with increasing reaction exothermicity (ΔG_{-et}) . Previously, we have shown that the maximum rate of return electron transfer for the undeuteriated donors, i.e., the rate for which the Franck-Condon factors are maximized and the reaction activation energy is minimized, occurs for a reaction exothermicity of 1.9 eV. According to the figure, at this value of ΔG , the $k_{\rm h}/k_{\rm d}$ ratio approaches a value of unity. This observation is in clear agreement with the theoretical predictions of Jortner et al. for isotopic quantum effects.⁴ The Franck-Condon factors for the electron-transfer process are reduced as a result of changes in the frequencies of the rearranged vibrational modes. In addition to the frequency changes, the extent of hyperconjugation should decrease with deuteriation due to the stronger C-D bond, and thus the internal reorganization could decrease. Thus, the isotope effects observed here could also contain contributions from changes in the internal reorganization energy, λ_{v} .

Many treatments of electron-transfer reactions assume that the rearranged vibrational modes can be approximated by a single average vibrational frequency, often ca. 1500 cm^{-1} which is typical of carbon-carbon skeletal stretching modes.^{6,7} However, the present deuterium isotope effects suggest that higher frequency modes may have to be taken into account. Indeed, in the radiationless transitions of the triplet states of aromatic hydrocarbons in the gas phase, the role of high-frequency (ca. 3000 cm⁻¹) carbon-hydrogen modes is well established, although for these processes, isotope effects are observed upon deuteriation of the ring hydrogens.¹¹ Although the present results do not say anything about lower frequency modes, they suggest that contributions of the high-frequency carbon-hydrogen modes to the single averaged frequency in single mode models should not be underestimated, at least for the reactions of alkyl-substituted aromatic radical cations, in which hyperconjugation can be significant.

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Hydrogen-Deuterium Exchange of Diborane in Superacid Solution through Diboranonium $(B_2H_7^+)$ and Diboranium (B₂H₅⁺) Ions^{1a,b}

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The gaseous positive ion chemistry of diborane 1 was studied by mass spectrometry, including ICR studies.² Aside from the preparation of simple carborane cations,^{3,4} the behavior of diborane 1 in superacidic media has not been previously explored, although the interaction of B_2H_6 with HF(DF) was the subject of theoretical⁵ and spectroscopic studies.⁶ We report herein the slow proton/deuterium exchange of B_2H_6 , 1, in the superacidic FSO3D.SbF5 (deuterio Magic acid)/SO2ClF medium at low temperatures involving the corresponding isotopomeric diboranonium ions (protonated diborane) $B_2H_7^+$ ions. The structure of the $B_2H_7^+$ ion has also been probed by ab initio theoretical calculations.

When triply distilled diborane, (B_2H_6) 1,⁷ was mixed with 1:1 FSO₃D·SbF₅ (deuterio Magic acid)/SO₂ClF at -78 °C, most of the diborane dissolved with no detectible gas evolution, and a colorless solution was obtained. An immediate ¹¹B and ²H NMR⁸ analysis did not reveal any initial proton-deuterium exchange. After 24 h, however, at -78 °C, such analysis showed protondeuterium exchange. Direct NMR study of the superacidic solution of diborane did not reveal the presence of any observable cation and was indicative only of a complex mixture of exchanged boranes. After warming to room temperature analysis of the products also showed the formation of some BF_3 and H_2 as well as SO₂ and SbF₃. By using standard vacuum line techniques, a portion of diborane was removed and condensed onto frozen THF. Upon warming, the thawed THF solution was subjected to ²H NMR spectroscopic analysis. The proton decoupled ²H NMR showed a peak at 2.5 ppm indicating proton-deuterium exchange in B_2H_6 . The peak at 2.5 ppm is identical with that of THF·BD₃ obtained by reacting B_2D_6 with THF. Partially exchanged diboranes (B₂H₅D to B₂HD₅) which form THF-BD₂H and TH-F-BDH₂ adducts also show similar ²H NMR spectra. In a further experiment a gas-phase sample was also subjected to FT-infrared analysis.⁹ The spectrum obtained is complex as would be expected from a B_2H_6 , B_2H_5D , etc. mixture wherein the deuterium is at

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