# Steric Effects in Photoinduced Electron-Transfer Reactions

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Quantum yields for formation of separated radical ions are determined for the electron-transfer reactions of singlet excited cyanoanthracene acceptors with sterically hindered alkylbenzene donors, in acetonitrile. These yields are up to 4 times larger than those for unhindered alkylbenzene donors. The yields are controlled by the competition between separation and return electron transfer in the initially formed radical-ion pairs. From studies of the dependence of the steric effect on the driving force for return electron transfer, it is concluded that the main effect of the steric hindrance is to decrease the magnitude of the electronic coupling matrix element for electron transfer, thus decreasing the return electron transfer rate and increasing the separation yield. The sterically hindered donors can be divided into two groups depending upon whether the substituents on the benzene ring have hydrogens that are capable of hyperconjugative stabilization of the positive charge in the radical cation. The electron transfer reorganization parameters are measurably different for the donors that have these substituents compared to those that lack such hydrogen atoms.

## I. Introduction

Photoinduced electron transfer reactions are often performed in polar solvents such as acetonitrile so that separation of the initially formed geminate radical-ion pairs can occur.<sup>1</sup> The radical-ion pairs are short-lived, and if separation did not occur, chemical reactions would have to be very rapid in order to compete with recombination and other rapid first-order deactivation processes within the radical-ion pairs. Once separated radical ions are formed, however, a wide range of chemical reactions may occur efficiently, because recombination is second order and therefore relatively slow. Therefore, although some chemical reactions have been identified that are fast enough to occur within the geminate radical-ion pairs,<sup>2</sup> the quantum yields for product formation in many photoinduced electron transfer reactions are equivalent to the efficiencies with which separated radical ions are formed.<sup>1b,3</sup> For singlet-sensitized electron transfer between neutral acceptors and donors in acetonitrile, the quantum yields for formation of separated ("free") radical ions,  $\Phi_{sep}$ , are determined by the competition between return electron transfer,  $k_{-et}$ , and separation of the radical-ion pairs (A<sup>--</sup>(S)D<sup>++</sup>),  $k_{sep}$ (Scheme I, eq 1).<sup>1,4a</sup>

$$\Phi_{\rm sep} = \frac{k_{\rm sep}}{k_{\rm -et} + k_{\rm sep}} \tag{1a}$$

$$\frac{k_{-\rm et}}{k_{\rm sep}} = \frac{1}{\Phi_{\rm sep}} - 1 \tag{1b}$$

For efficient formation of separated radical ions, the rate ratio  $k_{-et}/k_{sep}$  should be as small as possible. For typical organic acceptor/donor systems, however, the quantum yields for formation of separated radical ions in acetonitrile are often quite low.<sup>4,5</sup> For example, although quantum yields as high as ca. 0.7 are known,<sup>4e</sup> many acceptor/donor systems form separated radical ions with quantum yields which are less than 0.1, i.e.,  $k_{-et} \gg k_{sep}$ .<sup>4,5</sup> For these radical-ion pairs, reformation of the neutral acceptor and donor in the radical-ion pairs is more efficient than formation of separated radical ions, and the majority of the photon energy is wasted.

In order to understand how to minimize the energy-wasting return electron transfer processes in geminate radical-ion pairs, the factors that control the rates of these reactions have been the subject of many investigations.<sup>4-8</sup> In a series of papers, we have SCHEME I

$$A^{\bullet-}(S)D^{\bullet+} \xrightarrow{k_{tep}} A^{\bullet-} + D^{\bullet+}$$

$$\downarrow^{k_{-e1}}$$

$$A + D$$

been defining the factors that control  $k_{-et}$  in detail, and therefore  $\Phi_{sep}$ .<sup>4</sup> The effects of driving force,<sup>4a</sup> molecular dimension,<sup>4a</sup> molecular charge,4b isotopic substitution,4c separation distance,4d stoichiometry,<sup>4c</sup> solvent polarity,<sup>4f</sup> and external pressure<sup>4g</sup> have been studied. The general conclusions are that the return electron transfer reactions can be satisfactorily accounted for by current conventional nonadiabatic theories of electron transfer. Almost all of the reactions that have been studied are in the Marcus inverted region, i.e., the reaction rate decreases with increasing exothermicity  $(-\Delta G_{-et})$ . In fact, the exothermicity of the return electron transfer reaction is one of the properties of an acceptor/ donor system which can be most usefully varied to optimize  $\Phi_{sep}$ , and the largest values of  $\Phi_{sep}$  are generally associated with the largest  $-\Delta G_{-et}$ .<sup>4,5</sup> Variation of the reaction exothermicity may not always be possible, however, and it is clearly of interest to fully understand how other molecular properties may be manipulated to maximize  $\Phi_{sep}$ .

In continuation of this theme, therefore, we have investigated the effect of steric interactions on  $\Phi_{sep}$ , and on the rates of return electron transfer in the geminate radical-ion pairs. In several previous investigations, steric effects have been observed on the rates of second-order, intermolecular electron transfer reactions,<sup>9</sup> although in other studies, the lack of observed steric effects has been taken as evidence against rate-determining electron transfer in bimolecular reactions.<sup>10,11</sup> Furthermore, it is not necessarily easy to predict the effects of steric crowding on the rates of electron transfer in radical-ion pairs from results on second-order reactions. Although the return electron transfer reactions in radical-ion pairs are bimolecular, they are first-order and not diffusionlimited. As a result, they exhibit many of the properties of the rigidly linked acceptor/donor systems that have proven to be particularly useful in recent years as test cases for electron-transfer theories.<sup>12</sup> Steric effects have, however, been observed on the photophysical properties of exciplexes,13 which are closely related to the radical-ion pairs studied here, and there have also been many observations of steric effects on energy-transfer processes,14 which are also closely related to electron-transfer reactions. Of

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particular relevance to the present work are the results of Jones and Chatterjee<sup>15</sup> and Gassman and De Silva,<sup>16</sup> who observed that increasing steric bulk in the radical-ion pairs can in fact lead to increases in  $\Phi_{sep}$ . In the former study, the steric effects were attributed mainly to an increase in the separation distance between the acceptor and donor in the radical-ion pair as a result of steric crowding.

In the present work we have also clearly demonstrated that  $\Phi_{sep}$  can be increased upon the addition of steric bulk to the reactants. In addition, we have studied the steric effect in a homologous series of reactions so that the driving force dependence can be determined. In this way, the influence of steric interactions on the various factors that control  $\Phi_{sep}$  could be evaluated.

## **II.** Results and Discussion

**Experimental Strategy.** Most current theories of electron transfer cast the rate in the form of a golden rule expression<sup>17</sup> (eq 2a),

$$k_{-\rm et} = \frac{4\pi^2}{h} V^2 \,\rm FCWD \tag{2a}$$

$$FCWD = \sum_{j=0}^{\infty} F_j (4\pi\lambda_s k_B T)^{-1/2} \exp\left[-\frac{(\Delta G_{-et} + jh\nu_v + \lambda_s)^2}{4\lambda_s k_B T}\right]$$
(2b)

$$F_j = \exp(-S)\frac{S^j}{j!}$$
  $S = \frac{\Lambda_v}{h\nu_v}$ 

i.e., as the product of an electronic coupling matrix element (V)and a Franck-Condon weighted density of states (FCWD). In a commonly used description, the FCWD depends upon the reaction free energy ( $\Delta G_{-et}$ ), a reorganization energy associated with rearranged low-frequency modes ( $\lambda_s$ ), and a reorganization energy,  $\lambda_v$ , associated with a representative averaged high frequency mode  $(v_v)$  (eq 2b).<sup>17</sup> The dependence of  $k_{-et}$  on the FCWD results in the familiar Marcus "normal" region  $(k_{-et})$ increases with increasing exothermicity when  $-\Delta G_{-et} \lesssim \lambda_v + \lambda_s$ and Marcus "inverted" region  $(k_{-et}$  decreases with increasing exothermicity when  $-\Delta G_{-et} \gtrsim \lambda_v + \lambda_s$ ). As discussed above, most of the return electron transfer reactions in radical-ion pairs that have been studied are in the inverted region. In this case, for a constant value of  $-\Delta G_{-et}$ ,  $k_{-et}$  should decrease with decreasing  $\lambda_s$ ,  $\lambda_{v}$ , or  $\nu_{v}$ . Because V is a scaling factor, k<sub>-et</sub> also decreases with decreasing V.

For return electron transfer in the inverted region in a polar solvent, increasing the steric bulk of one of the reactants in a radical-ion pair is expected to decrease  $k_{-et}$  (and thus increase  $\Phi_{sen}$ ) compared to a less sterically crowded but otherwise similar radical-ion pair, on the basis of the following considerations. Electronic coupling between the radical anion and radical cation may decrease with increased steric crowding because of a larger average separation of the ions in the pair, thus decreasing V and therefore  $k_{-et}$ .<sup>17,18</sup> The steric effect might also decrease the solvation of the radical ion in the pair because of shielding of the polar solvent molecules, thus lowering  $\lambda_s$  and decreasing  $k_{-et}$ .<sup>19</sup> Increasing steric bulk by altering molecular structure might also change the reorganization parameters associated with the rearranged high frequency modes,  $\lambda_v$  and  $v_v$ . If these are decreased, then  $k_{-et}$  would again be expected to decrease. Finally, increased steric bulk in one of the partners in a radical-ion pair might also result in a change in  $k_{sep}$ , which also has to be taken into account.

Two radical-ion pairs are usually considered in photoinduced electron-transfer reactions in polar solvents, i.e., the contact (CRIP) and solvent-separated (SSRIP) radical-ion pairs.<sup>1a,4d</sup> In general it is not known whether a CRIP is always formed in bimolecular electron transfer reactions in polar solvents, or





SCHEME III

Ered V (vs SCE)

 $E_{0,0}(^{1}A^{*}) = eV$ 



whether the CRIP is bypassed with direct formation of the SSRIP.<sup>20</sup> For the cyanoanthracene acceptor/alkylbenzene donor systems, however, this issue has been addressed by studying CRIP emission efficiencies as a function of solvent polarity,<sup>20a</sup> and by comparing the emission efficiencies and radical-ion yields for the bimolecular reaction with those obtained by excitation of ground-state CT complexes.<sup>20a,4d</sup> It was found that when the driving force for formation of the radical-ion pairs is high, the SSRIP are formed directly, without the intermediacy of the CRIP. Formation of the CRIP only occurs when the driving force is small. Under these conditions, however, the driving force for the corresponding return electron transfer reaction is large, and as a result of the Marcus inverted region effect, return electron transfer in the CRIP is slow compared to solvation to form a SSRIP. For the cyanoanthracene/alkylbenzene systems in acetonitrile, therefore, CRIP formation either does not occur, or when it does, return electron transfer in the CRIP is unimportant. For these reasons the return electron transfer reactions are assumed to occur only in the SSRIP for the present systems, and the dynamics of the CRIP are ignored.<sup>21</sup>

Measurements of Separation Yields. The excited state electron acceptors are 9,10-dicyanoanthracene (DCA) and 2,6,9,10tetracyanoanthracene (TCA) (Scheme II).<sup>4a</sup> The donors are the sterically hindered benzene derivatives shown in Scheme III. The reactions of the radical-ion pairs of these donors can be compared to those of the noncrowded, simple alkyl-substituted benzene donors we have studied previously.<sup>4</sup>

The sterically hindered donors can be divided into two groups. The first consists of those in which hydrogens  $\alpha$  to the benzene ring can contribute to hyperconjugative stabilization of the positive charge, i.e., the substituted dimethylindan compounds 1-4. The second group consists of donors in which hyperconjugative stabilization by  $\alpha$  hydrogens is not possible, i.e., the donors 5-9. Although tetraisopropylbenzene and hexaethylbenzene both have  $\alpha$  hydrogens, the steric crowding that occurs in the  $\alpha$ -isopropyl and  $\alpha$ -ethyl substituents forces the methyl groups above and below the plane of the benzene ring. As a consequence, the  $\alpha$  hydrogens are in the plane of the ring, which minimizes their hyperconjugative interactions.

Diffusive quenching of the excited singlet states of the cyanoanthracenes by the electron donors in acetonitrile results

TABLE I: Quantum Yields for Separated Ion Formation,  $\Phi_{sep}$ , for Sterically Hindered Substituted Benzene Donors with Cyanoanthracene Acceptors

acceptor	donor <sup>b</sup>	$-\Delta G_{-\mathrm{et}}^c$	Φsep	$(\Phi_{sep})_{nc}{}^d$	$k_{\rm et}/k_{\rm sep}^e$	$(k_{\rm et}/k_{\rm sep})_{\rm nc}^{d}$
DCA	1	2.81	0.582	0.344	0.719	1.91
DCA	2	2.73	0.403	0.245	1.48	3.08
DCA	3	2.59	0.307	0.135	2.26	6.38
DCA	4	2.54	0.208	0.111	3.80	7.98
DCA	8	2.68	0.549	0.205	0.820	3.87
DCA	9	2.55	0.397	0.112	1.52	7.94
TCA	1	2.34	0.113	0.0517	7.83	18.32
TCA	2	2.26	0.0861	0.0408	10.62	23.50
TCA	3	2.12	0.0665	0.0302	14.03	32.06
TCA	4	2.07	0.0625	0.0282	15.00	34.52
TCA	5	2.57	0.364	0.125	1.75	7.02
TCA	6	2.47	0.266	0.0830	2.76	11.04
TCA	7	2.45	0.325	0.0769	2.08	12.00
TCA	8	2.21	0.109	0.0369	8.15	26.12
TCA	9	2.08	0.0736	0.0283	12.59	34.36

<sup>a</sup> DCA = 9,10-dicyanoanthracene, TCA = 2,6,9,10-tetracyanoanthracene. <sup>b</sup> See Scheme III for structures of donors. <sup>c</sup> Determined with eq 3, using values for the redox potentials given in Schemes II and III. <sup>d</sup> Predicted value for a noncrowded radical-ion pair with a  $-\Delta G_{-et}$  equal to that for the sterically hindered system.<sup>23</sup> <sup>c</sup> Calculated using eq 1b.

in radical-ion pair formation.<sup>4</sup> The quantum yields for formation of separated radical ions were determined using the transient absorption technique described previously, and the data are summarized in Table I.4a Efficient, i.e., nearly diffusioncontrolled, electron-transfer quenching of the 'TCA\* occurred with all of the donors of Scheme III. Not all of the donors quenched the <sup>1</sup>DCA<sup>\*</sup> efficiently, however, and the acceptor/ donor combinations studied (Table I) were limited to those in which the bimolecular quenching rate constant was  $\geq 5 \times 10^9 \text{ s}^{-1}$ . The  $\Phi_{sep}$  are related to  $k_{-et}$  and  $k_{sep}$  as indicated in eq 1. From the  $\Phi_{sep}$  data, values can only be obtained for the ratio  $k_{-et}/k_{sep}$ , rather than the individual rate constants. The rate constant ratio  $k_{-\rm et}/k_{\rm sep}$  decreases with increasing  $\Phi_{\rm sep}$ . The rate constant ratios are also given in Table I together with the free energies for the return electron transfer reaction for each pair  $(-\Delta G_{-et})$  determined using eq 3.4a

$$-\Delta G_{-\rm et} = E_{\rm D}^{\rm ox} - E_{\rm A}^{\rm red} \tag{3}$$

As discussed above, in previous studies we determined the  $\Phi_{sep}$ , and therefore  $k_{-et}/k_{sep}$ , for the reactions of DCA and TCA with simple alkyl-substituted benzene derivatives.4ª In that work a clear relationship was found between  $\log(k_{-et}/k_{sep})$  and  $-\Delta G_{-et}$ , as shown in Figure 1. The  $\log(k_{-et}/k_{sep})$  values for the simple alkyl-substituted donors decrease with increasing exothermicity (increasing  $-\Delta G_{-et}$ ) due to a decrease in  $k_{-et}$  as a consequence of the Marcus inverted region effect. It is assumed that  $k_{sep}$  is constant for the simple alkyl-substituted benzenes, which represent a set of donors with closely related structures.<sup>22</sup> The curve drawn through the data points corresponds to a theoretical dependence of  $k_{-\rm et}/k_{\rm sep}$  on  $-\Delta G_{-\rm et}$ . The rate constant  $k_{-\rm et}$  is calculated as a function of  $-\Delta G_{-et}$  using eq 2, with 1.72 eV for  $\lambda_s$ , 0.2 eV for  $\lambda_v$ , and 1400 cm<sup>-1</sup> for  $v_v$ .<sup>4d</sup> A value for the electronic coupling matrix element V of 10.8 cm<sup>-1</sup> then gives the best fit to the data, if  $k_{sep}$ is assumed to be  $5 \times 10^8 \text{ s}^{-1.4d}$  If  $k_{\text{sep}}$  is  $8 \times 10^8 \text{ s}^{-1}$ , then V would be 13.7 cm<sup>-1</sup>.4h

Also included in Figure 1 are the  $\log(k_{-et}/k_{sep})$  data for the sterically hindered donors studied here. It is clear that the  $k_{-et}/k_{sep}$  are smaller for the sterically hindered donors, because these data points are all lower than the theoretical curve for the nonsterically hindered donors. An interesting comparison is provided by the reactions of <sup>1</sup>TCA<sup>+</sup> with mesitylene ( $\Phi_{sep} = 0.093$ ),<sup>4a</sup> 1,3,5-triisopropylbenzene ( $\Phi_{sep} = 0.18$ ),<sup>24</sup> and 1,3,5-tri*-tert*-butylbenzene ( $\Phi_{sep} = 0.33$ , Table I). The steric crowding increases as the substituent is changed from methyl to isopropyl to *tert*-butyl, and the separation yield increases correspondingly. However, direct comparison is not valid because the oxidation potential of



Figure 1. Plots of the logarithm of the ratio of the rates of return electron transfer,  $k_{\text{et}}$ , to separation,  $k_{\text{sep}}$ , vs exothermicity,  $-\Delta G_{\text{et}}$ , for radicalion pairs with 9,10-dicyanoanthracene and 2,6,9,10-tetracyanoanthracene as acceptors. The corresponding quantum yields for formation of separated radical ions,  $\Phi_{\text{sep}}$ , are shown on the right-hand axis. The small squares are for nonsterically hindered alkyl-substituted benzene donors (data from ref 4a). The thin curve represents a theoretical dependence for these data on  $-\Delta G_{\text{-et}}$ .<sup>23</sup> The filled circles are for the dimethylindan donors 1–4. The heavy curve for these data is the same as that for the vertical scale.<sup>23</sup> The open circles are for the sterically hindered donors 5–9. The dashed curve for these data is the same as that for the donors 1–4, with  $\lambda_s$  decreased by 0.1 eV (see text).<sup>23</sup>

the donor also decreases slightly in the same order, from 2.11 V vs SCE for mesitylene<sup>4a</sup> to 2.01 V for 1,3,5-tri-*tert*-butylbenzene. Thus, the exothermicity of the tri-*tert*-butylbenzene reaction is actually smaller than that for the mesitylene reaction, which, all other factors being equal, would normally lead to a larger  $k_{-et}$  and thus smaller  $\Phi_{sep}$ . A predicted separation yield for a noncrowded radical-ion pair with a value of  $-\Delta G_{-et}$  equal to that of the TCA/1,3,5-tri-*tert*-butylbenzene radical-ion pair (2.45 eV), ( $\Phi_{sep}$ )<sub>nc</sub>, can be obtained from the theoretical  $k_{-et}/k_{sep}$  curve for the simple alkyl-substituted donors (Figure 1). This value is in fact 0.077 (Table I), which is 4.3 times smaller than the measured yield for the TCA/1,3,5-tri-*tert*-butylbenzene system.

Predicted radical-ion separation yields for noncrowded radicalion pairs with values of  $-\Delta G_{\text{-et}}$  appropriate for all of the sterically hindered systems ( $(\Phi_{\text{sep}})_{nc}$ ) are included in Table I. From these data it is clear that the measured separation yields are significantly increased by steric crowding of the donor molecules, by factors of ca. 1.6-4.3. A more informative measure of the steric effect is provided by the comparison between the measured  $k_{-et}/k_{sep}$  for the sterically hindered donors and predicted values for noncrowded radical-ion pairs,  $(k_{-et}/k_{sep})_{nc}$ . The rate ratios for the sterically hindered systems are between ca. 2 and 6 times smaller than those for equivalent noncrowded cases. It is clearly of interest to determine which of the molecular properties discussed above is responsible for these effects.

Analysis of Yield Data in Terms of Nonadiabatic Electron Transfer Theories. Obviously the changes in the rate constant ratios may be a consequence of changes in  $k_{sep}$ ,  $k_{-et}$ , or both. The purpose of studying the steric effect as a function of the driving force for electron transfer is to isolate the effects on  $k_{-et}$ . The first part of this discussion, therefore, focuses on the steric effects on the return electron transfer processes. The influence of steric bulk on the electron transfer matrix element, V, is estimated by assuming the  $k_{sep}$  is the same for both crowded and noncrowded pairs. The possible steric effects on  $k_{sep}$  and the consequences for the determination of the steric effect on V are discussed later.

As noted above, the effect of the steric interactions may be to influence  $k_{-et}$  by changes in the reorganization parameters, and/ or by changes in the electronic coupling matrix element, V. Since V is simply a scaling factor for  $k_{-et}$  (eq 2), changes in this parameter



Figure 2. Plots of the logarithm of the ratio of the rates of return electron transfer to separation,  $(k_{-et}/k_{sep})$ , for radical-ion pairs with the sterically hindered dimethylindan donors 1-4 (filled circles), and the sterically hindered donors 5-9 (open circles), versus the corresponding predicted values for noncrowded donors of the same electron transfer driving force,  $(k_{-et}/k_{sep})_{nc}$ . The slopes given in the figure are those for the approximately linear plots of both sets of data. The thin line has a slope of unity and an intercept of zero (the identity line).

will not change the driving-force dependence for  $k_{-et}$  or for the rate ratio  $k_{-et}/k_{sep}$ . If, however, the reorganization parameters are different, then the driving force dependence for the rate ratio  $k_{-et}/k_{sep}$  will be changed. Because the sterically hindered benzenes give radical-ion pairs with varying exothermicities for return electron transfer (Table I), the driving-force dependence of the steric effect can be evaluated.

A fairly sensitive way to detect differences in the reorganization parameters ( $\lambda_s$ ,  $\lambda_y$ , and  $\nu_y$ ) for two sets of electron transfer reactions is to plot the electron transfer rate data for one set of reactions versus that for the other set at the same  $\Delta G_{-et}$ . For data that occurs only in either the normal or inverted regions, and over a limited range of  $-\Delta G_{-et}$ , such a plot will be approximately linear. If the two sets of data have the same reorganization parameters, the plot will have a slope of unity. A plot with a slope deviating from unity would indicate that one or more of the reorganization parameters is different. A plot of the current data in this form is shown in Figure 2. For each of the sterically hindered donors, the  $\log(k_{-et}/k_{sep})$  values are plotted against the corresponding (i.e., same  $-\Delta G_{-et}$ ) ratio predicted for noncrowded cases, log- $(k_{-et}/k_{sep})_{nc}$ . Also included in Figure 2 is a line of unit slope and zero intercept. Data points will fall on this line, the identity line, if the rate ratio values  $k_{-et}/k_{sep}$  are identical to  $(k_{-et}/k_{sep})_{nc}$ . Points deviating from this line indicate a difference in the electron transfer parameters for the two sets of data.

The slope of the plot for the dimethylindan donors 1-4 is in fact quite close to unity, 1.03, but is displaced below the identity line. This means that the driving-force dependence for these donors is very much the same as that for the simple alkylsubstituted donors (implying similar reorganization parameters for both sets of compounds), but that the  $k_{-et}/k_{sep}$  values are uniformly smaller. The fact that the reorganization parameters for compounds 1-4 and the nonsterically hindered donors are similar is further illustrated by the theoretical curve that can be drawn through the data for the dimethylindan donors shown in Figure 1. This curve is identical to that for the simple alkylsubstituted donors (the same  $\lambda_s$ ,  $\lambda_v$ , and  $\nu_v$  were used), except that it is displaced vertically downward. The displacement corresponds to a decrease in the ratio  $k_{-et}/k_{sep}$  for the sterically hindered donors by a factor of 2.3, which is the average of the ratio of the  $(k_{-\rm et}/k_{\rm sep})_{\rm nc}$  and the  $k_{-\rm et}/k_{\rm sep}$  values of Table I.

In contrast to the dimethylindan donors, the slope of the plot shown in Figure 2 for the donors 5-9, 1.25, is distinctly greater

than unity. The data points are also displaced below the identity line. For electron-transfer reactions in the inverted region, this indicates that one or more of the reorganization parameters  $\lambda_a$ ,  $\lambda_{v_1}$  and  $\nu_v$  is measurably *smaller* for these donors compared to those for the noncrowded series.

The fact that the reorganization parameters for the dimethylindan-type donors, 1-4, are essentially unchanged compared to the methyl-substituted donors indicates that the increased  $\Phi_{sep}$ for these donors is caused either by a decrease in  $k_{-et}$  as a result of a corresponding decrease in the electronic coupling matrix element V, or by an increase in  $k_{sep}$ . As discussed in more detail below, however, an increase in  $k_{sep}$  is unlikely for the present systems, whereas a decrease in V is entirely reasonable. In the simplest interpretation, the effect of steric crowding in the SSRIP can be considered to increase the average separation distance between the radical anion and the radical cation  $\pi$  systems. It is well-known that V depends upon the distance between the acceptor and the donor and in fact an exponential dependence is usually assumed.<sup>17,18</sup> The separation of the  $\pi$  systems in the SSRIP is not well-defined, however, because the SSRIP is a dynamic species and the separation distance fluctuates. An averaged distance is usually assumed, therefore, and this distance for a radical-anion/ radical-cation pair in acetonitrile is often taken to be ca. 7 Å.<sup>1a</sup> A simple estimate of the effect of steric crowding on the distance between the two  $\pi$  systems can be obtained from consideration of the difference in the van der Waals size of the sterically hindered radical cations compared to the noncrowded radical cations. From simple molecular models, the bulky substituents on the donors 1-4 extend the van der Waals surfaces by ca. 1.3 Å compared to the simple alkyl-substituted donors. Thus, a simple interpretation is that, in the sterically hindered SSRIP, the average separation of the  $\pi$  systems is increased by ca. 1.3 Å. The ratio of two matrix elements,  $V_1/V_2$ , for the same donor/acceptor reacting at two at distances  $r_1$  and  $r_2$ , is shown in eq 4.

$$V_1/V_2 = \exp[\beta(r_2 - r_1)/2]$$
 (4)

In eq 4,  $\beta$  determines the distance dependence of V. Values for  $\beta$  of ca. 1.1 Å<sup>-1</sup> have been estimated previously for noncovalently linked systems in homogeneous media.25 Therefore, for an increase in separation distance of 1.3 Å, V would be expected to decrease by a factor of ca. 2. Because the reorganization parameters for the uncrowded and the dimethylindan donors appear to be essentially the same, the FCWD of eq 2 are the same and therefore  $k_{-et}$  would be expected to change simply by the square of the change in V, i.e., the  $k_{-et}$  for the sterically hindered radical-ion pair should be smaller than that for a nonhindered pair by a factor of ca. 4. Instead, the  $k_{-et}/k_{sep}$ for the dimethylindan donors are on average smaller than the  $(k_{-\rm et}/k_{\rm sep})_{\rm nc}$  by only a factor of 2.3. Assuming that the  $k_{\rm sep}$  are the same for both sets of donors, the factor of 2.3 corresponds to the change in  $k_{-et}$ , which in turn corresponds to a decrease in V by a factor of ca. 1.5.

The smaller than expected changes in  $k_{-et}$ , and hence V, may be partially caused by the fact that the increase in the separation distance in the SSRIP is less than the increase in the van der Waals surface of the alkyl substituents. Configurations of the radical anion/solvent/radical cation are certainly possible in which the increase in the separation distance between the  $\pi$  systems in the sterically hindered radical-ion pairs is less than 1.3 Å. Furthermore, the assumption of an exponential distance dependence may be an oversimplification. The magnitude of the electronic coupling matrix element V is determined by the overlap of the wave functions of the radical anion and the radical cation in the SSRIP. Although the overlap of the parts of the wave functions associated with the  $\pi$  system of the sterically hindered radical cations may well be decreased compared to those of the simple alkyl-substituted radical cations, there is extensive delo-

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calization of charge into the substituents in alkyl-substituted benzene radical cations. The bulky substituents may increase the separation distance between the two  $\pi$  systems; however, the change in the distance between the radical anion and the substituents must be smaller. Thus, an increase in separation distance is difficult to define quantitatively, although an overall decrease in electronic coupling can be reasonably understood.

The results for the dimethylindan donors, 1-4, suggest that changes in the reorganization parameters are minimal. It is somewhat surprising that no change in the solvent-reorganization energy can be detected. A decrease in this parameter might have been expected because the sterically hindered radical cations are presumably somewhat less solvated than the noncrowded radical cations. However, it is possible that the expected decrease in  $\lambda_s$ is balanced by a corresponding increase in another contribution to the total reorganization parameters, so that the overall change is undetectable. Alternatively, the effects of steric crowding on the solvent-reorganization energy might simply be too small to be detected.

The reorganization parameters for the donors 5-9 are measurably smaller than those for both the donors 1-4 and the sterically nonhindered donors. The most obvious difference between the donors 5-9 and 1-4 is that hydrogen hyperconjugation is not possible for the former. Hyperconjugation delocalizes the positive charge into the hydrogen atoms of the alkyl substituent groups. Thus, vibrational modes associated with the substituent groups contribute to  $\lambda_{v}$ , the reorganization energy associated with the reactant localized high-frequency modes. The modes associated with a CR<sub>3</sub> substituent, whether C-R stretching or CR<sub>3</sub> wagging or breathing, must occur with higher frequency when R is hydrogen compared to when R is alkyl. Thus the contributions to  $v_v$  from the substituents should be of lower frequency when hydrogens  $\alpha$  to the benzene ring are replaced by alkyl groups. Qualitatively this conclusion is consistent with observations of deuterium isotope effects. We have previously reported that substitution of the hydrogens on methyl-substituted benzenes by deuteriums causes a reduction in  $k_{-et}$ , in a manner that is qualitatively similar to that observed for the donors 5-9.4c

Simulations of the data shown in Figure 1 for the donors 5-9, using eq 2, indicate, however, that the change in driving-force dependence cannot be accounted for by changes in  $v_v$  alone, i.e., a decrease in  $\lambda_v$  and  $\lambda_s$  is also required. A good fit to the data can be obtained by, for example, using the same parameters used to fit the dimethylindan donors, with the  $\lambda_s$  decreased by 0.1 eV, as indicated by the dashed curve in Figure 1. Other combinations of  $\lambda_{v}$  and  $\lambda_{s}$  also give good fits to the data, however, provided their sum is less than the total reorganization energy for the uncrowded donors. As a result, it is not possible to determine which of the reorganization energies is most changed compared to the simple alkyl-substituted donors. A decrease in  $\lambda_s$  for the donors 5–9 and not for 1-4 might be reasonable, because the absence of hydrogen hyperconjugation in compounds 5-9 should result in a somewhat different charge distribution in the radical cations compared to those of 1-4. In addition, the substituents on the donors 5-9 may be simply more sterically crowded than those on the donors 1-4, resulting in larger changes in the reorganization parameters.<sup>26</sup> Because the changes in the reorganization parameters cannot be determined quantitatively, it is also not possible to determine the change in the electronic coupling matrix element for the donors **5–9.** The most reasonable assumption is that the V is decreased to a similar extent for both sets of donors.

In the discussion of the steric effects on V, it was assumed that  $k_{sep}$  for the SSRIP of the sterically hindered and nonhindered donors are the same. In fact, because V and  $k_{sep}$  both merely scale the  $k_{-et}/k_{sep}$  ratio, from the experiments described here it is not strictly possible to determine the relative importance of changes in V and changes in  $k_{sep}$ . The separation process represents diffusion in a coulomb potential. The diffusion

coefficients of the radical-ions depend inversely upon their radii;27 therefore it might be expected that  $k_{sep}$  will be smaller for the sterically hindered radical-ions compared to the noncrowded radical-ions. If  $k_{sep}$  does decrease, then the effect on  $k_{-et}$  is actually larger than that predicted by assuming that  $k_{sep}$  is unchanged. Under these circumstances, the decrease in the electronic coupling matrix element with steric crowding is correspondingly larger. However, any increase in the separation distance in the SSRIP as a result of steric crowding might also decrease the coulombic stabilization of the pair (which also depends inversely upon separation distance<sup>28</sup>), resulting in an increase in  $k_{sep}$ . This effect will probably be small, however, since an increase in the separation distance in the SSRIP from 7 to 8.3 Å (see above) corresponds to a decrease in the coulombic stabilization energy of only ca. 8 meV in acetonitrile.<sup>28</sup> Nevertheless, this effect may counterbalance the effect of the change in diffusion coefficient to some extent, so that the overall change in  $k_{sep}$  may be very small.

In summary, therefore, if  $k_{sep}$  for the storically hindered donors decreases compared that for the simple alkyl-substituted donors, then the actual changes in V and  $k_{-et}$  are larger than discussed above, and if  $k_{sep}$  increases, then the corresponding changes in Vand  $k_{-et}$  are smaller.

## **III.** Conclusions

Substitution of simple alkyl groups by more sterically crowded substituents results in an increase in the quantum yields for formation of separated radical ions in bimolecular photoinduced electron transfer reactions in acetonitrile. The results are most reasonably explained as being mainly as the result of a decrease in the electronic coupling matrix element for return electron, which increases the separation yield. Depending upon the specific nature of the substituent, however, changes in the reorganization parameters can also be detected. The results suggest that useful increases in the formation of separated radical ions can be achieved by using sterically hindered donors such as those described here. For example, when using tetracyanoanthracene as the acceptor, fairly high separation yields are obtained using the tert-butyl substituted benzenes as donors. These donors are thus good cosensitizers for this acceptor,<sup>4a</sup> and their radical cations are sufficiently oxidizing ( $E^{ox}_{D} > 2 \text{ V vs SCE}$ ) to be useful with a wide range of other substrates.

## **Experimental Section**

All experiments were performed in acetonitrile, which was degassed using freeze/pump/thaw cycles (Baker HPLC grade, used as received). The cyanonanthracene acceptors were available from previous work.<sup>4a</sup> All of the donors were available commercially. Donors 1-4 were obtained from American Petroleum Institute Standard Reference Materials (Pittsburgh, PA) and used as received. 1,3-Di-tert-butylbenzene (Wiley), tert-butylbenzene (Kodak), and 1,3,5-tri-isopropylbenzene (Aldrich) were distilled. 1,4-Di-tert-butylbenzene (Aldrich), 1,3,5-tri-tert-butylbenzene (Aldrich), 1,2,4,5-tetraisopropylbenzene (Aldrich), and hexaethylbenzene (Kodak) were recrystallized from ethanol. The oxidation potentials (Scheme III) of the donors 1-4, 8, and 9 were measured as described in ref 4a, using the technique of square-wave voltammetry;<sup>29</sup> those of 5-7 are from ref 30. The reduction potentials and the excitation energies given in Scheme II were taken from ref 4a. The quantum yields of radical-ions,  $\Phi_{sep}$ , given in Table I are averaged values from three to five different samples. The values were found to be reproducible to within ca.  $\pm 5\%$ . The quantum yields were measured using the transient absorption technique that is described in detail in ref 4a. Correction was made for incomplete interception of the excited acceptor. The correction factors were obtained from the efficiency of fluorescence quenching of the excited acceptors. The concentrations of the donors ranged from 0.04 to 0.2 M and the interception efficiencies ranged from ca. 80% to 95%.

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(21) Note that this may not be generally true for all acceptor/donor systems, and in fact it has been shown that for the fumaronitrile/trans-stilbene pair, contact radical-ion pairs are both produced in the bimolecular electron transfer reaction in acetonitrile, and contribute to the return electron transfer processes.20b

(22) There is very little scatter in the data and there is no reason to suspect that  $k_{sep}$  decreases in a regular manner with increasing  $-\Delta G_{-\alpha}$ .

(23) Calculated using 1.72 eV for  $\lambda_{s}$ , 0.2 eV for  $\lambda_{v}$ , 1400 cm<sup>-1</sup> for  $\nu_{v}$ , 10.8 cm<sup>-1</sup> for V, and  $5 \times 10^8$  s<sup>-1</sup> for  $k_{sep}$ . For further details, see the text. (24) This data is not included in Table I and Figure 1.

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