Mobilities of Radical Cations and Anions, Dimer Radical Anions, and Relative Electron Affinities by Times of Flight in *n*-Hexane

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The mobilities of several radical cations and anions are measured in *n*-hexane using a thin-sheet time-offlight (TOF) technique. We observe the radical cations of N,N,N',N'-tetramethyl-*p*-phenylenediamine, zinc tetraphenylporphine, and pyrene and the radical anions of perfluorobenzene, *p*-benzoquinone, anthraquinone, chloranil, buckminsterfullerene (C₆₀), and octafluoronaphthalene. For all electron acceptors but C₆₀, the dependence of the anionic TOF on acceptor concentration reveals the appearance of the homodimer radical anion at sufficiently high concentrations. The equilibrium constant for the monomer anion/monomer acceptor association reaction is obtained from the concentration studies. A Born-Haber cycle is then applied to estimate the difference between the electron affinities of the monomer and dimer molecules in the gas phase.

1. Introduction

or

Numerous studies on the ionic transport properties of dielectrics such as liquid hydrocarbons have been conducted because of their importance in understanding the process of dielectric breakdown. Many involve the measurement of the mobilities of "intrinsic" cations and anions, those ions that appear when irradiating neat liquid hydrocarbons.¹⁻⁴ In contrast, there is less work concerning the mobilities of "extrinsic" cations and anions in nonpolar media in which donors (D) and/ or acceptors (A) are deliberately introduced. Hummel et al.³ have reported measurements of anionic mobilities of dilute solutions of SF₆, CH₃I, CH₃Br, CH₃Cl, and O₂ in cyclohexane and in 2,2,4-trimethylpentane. Houser and Jarnagin⁵ measured the mobility of the cation of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in hexane and in tridecane. Albrecht and coworkers,^{6,7} in developing a thin-sheet time-of-flight (TOF) technique, reported mobilities for the cations of TMPD⁷ and zinc tetraphenylporphine (ZnTPP)^{6,7} and for the anion of *p*-benzoquinone $(PBQ)^6$ in *n*-hexane.

The thin-sheet TOF technique measures the mobility of photoproduced ions with good precision. (Under favorable circumstances the precision is $\pm 5\%$.) It is also a method in which the ions studied move in the complete absence of counterions. This points to new applications of the method that are obliquely explored for the first time in the present work. For example, it is possible to study the competition between two electron scavengers (A₁, A₂) or between two hole scavengers (D₁, D₂) and by concentration studies ("titration") determine the equilibrium constants, K's, for the charge exchange reactions

$$D_1 + D_2^+ \rightleftharpoons D_1^+ + D_2$$
 (1a)

$$A_1 + A_2^- \rightleftharpoons A_1^- + A_2 \tag{1b}$$

It is only necessary that the mobilities of D_1^+ and D_2^+ and/or A_1^- and A_2^- be detectable and resolvable by the TOF technique and that the time scale of equilibration be a small fraction of

the TOF. As will be described, under favorable conditions one can establish the relative ionization potentials (IPs) and electron affinities (EAs) of chosen species in nonpolar media and in the absence of counterions. In principle, hierarchical pairwise studies could then establish a table of relative IPs and EAs, and application of a Born-Haber cycle could convert this to the corresponding gas-phase table.

The equilibria, eqs 1a and 1b, also point to a principal weakness of the TOF method and others like it. While one can usually prevent primary interference from intrinsic electron photodonors, $\{D_i\}$, of the solvent by eliminating all neat solvent photoelectron generation through appropriate choices of intensity and wavelength of the ionizing radiation, one cannot always eliminate their possible secondary role as unwanted hole acceptors, nor can one confidently neglect possible interference from intrinsic electron acceptors, $\{A_i\}$, of the solvent. One must, therefore, always be alert to the possibility that some unknown D_i and/or A_i may dominate the ionic currents. In this work secondary interference from $\{D_i\}$ of the solvent is eliminated by using a sufficiently high concentration of the extrinsic donor, D, and ensuring that the IP of D in n-hexane is at least ~ 2 eV below that of the solvent, thereby minimizing charge carrier exchange with $\{D_i\}$ during the TOF. Similarly, interference from $\{A_i\}$ is eliminated through the use of a strong extrinsic acceptor, A, at an appropriately high concentration.

Nevertheless, when deliberately adding an extrinsic D (or A) for a mobility study, some impurity D or A might accompany the solutes and possess an IP or EA such that it becomes the dominant cation or anion in the TOF signal. Purification of D (or A) is helpful but, of course, does not guarantee against such interferences, especially were the impurity to be a particularly powerful hole acceptor or electron acceptor. Invariably one takes pains to purify both the solvent and the extrinsic solutes (D, A) and then assumes that the expected ions (D^+, A^-) are indeed those seen. This is an important assumption that underlies applications of the TOF method and is supported by reasonable behavior of the TOF signals, particularly with regard to their dependence on the concentration of extrinsic D/A.

We have recently improved the thin-sheet TOF technique both in regard to cell design and purification methods. The mobilities of TMPD⁺, ZnTPP⁺, and PBQ⁻ in *n*-hexane are here remeasured. The mobilities of the cation of pyrene and the anions of perfluorobenzene, anthraquinone, chloranil, buckminsterfullerene

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 (C_{60}) ,⁸ and octafluoronaphthalene in *n*-hexane are newly reported. In addition, the concentration of extrinsic acceptors, A, has been varied to the point where dimer anions appear to be formed, as revealed by a reduction in the anionic mobility at high concentrations of added A. Regarding the monomer anion, A_M^- , as the A_1^- and the dimer anion, A_D^- , as the A_2^- of eq 1b, we are able to "titrate" and obtain K for the electron exchange reaction between the monomer anion (A_M^-) and the dimer anion (A_D^-) : $A_M^- + A_M - A_D^-$. Using a Born-Haber cycle, the equilibrium constant, K, is translated into an estimate of the electron affinity difference between the gas-phase monomer (A_M) and homodimer (A_D) .

2. Experimental Section

The thin-sheet TOF technique for mobility measurements in the condensed phase has been described in detail.^{6,7} Its basis is the cylindrical focusing of the excitation light to produce an ~ 0.1 mm thick excitation plane that lies between parallel electrodes and is parallel to them. Multiphoton ionization produces positive and negative ions at an extremely low concentration ($\sim 10^{-11}$ M) in the excitation plane, which, under the influence of the applied electric field, separates into two distinct oppositely charged sheets that travel toward opposite electrodes. The excitation plane is usually placed closer to one electrode, and its position is kept fixed in both a "forwardbiased" configuration and a "reverse-biased" configuration. In the forward-biased configuration the electrode nearer to the excitation plane is the anode (positive electrode) so the anionic sheet travels the shorter distance and the cationic sheet travels the longer distance. In the reverse-biased configuration the cell bias is reversed, and the motions of the sheets are interchanged. If the motions of the charges in these two configurations are considered together, each ionic sheet traverses the full interelectrode distance.

The arrival of a sheet of ions at an electrode is detected by a drop in the photocurrent level, i.e., a "break" in the photocurrent trace. The times at which the breaks occur in the photocurrent trace mark the transit times of the ions. We have consistently chosen the transit time (TOF) to be the midpoint of the break. If τ_{\pm} (+, cation; -, anion) and τ_{\pm}' are the transit times of the ions in the forward-biased and reverse-biased configurations, respectively, then $\tau_{\pm} + \tau_{\pm}'$ is the time taken by the ionic sheet to travel the interelectrode distance, D. The ionic mobilities, μ_{\pm} , are, thus, given by $\mu_{\pm} = (D/E)(\tau_{\pm} + \tau_{\pm}')^{-1}$, where E is the applied electric field. With the present apparatus the precision of μ_+ measured in this way is about 5%. This simple expression for μ_{\pm} is valid only in the absence of space charge effects, which distort the photocurrent trace.⁷ It is also assumed that each ion retains its chemical integrity over the TOF. An "area analysis"⁶ of the photocurrent trace can show whether the first arriver travels the shorter or longer distance. The bias of the applied field then gives the actual sign of the first (and the last) arriving sheet of ions.

The photoconductivity cell has been modified to allow the use of Macor (machinable glass-ceramic, Corning) spacers which accurately fix the interelectrode distance, D. In the present work, D = 0.503 cm and the applied voltage is 2.99 kV. We have also introduced more extensive purification procedures than previously employed.^{6,7}

N,N,N',N'-Tetramethyl-*p*-phenylenediamine (TMPD, 98%), pyrene (99%), *p*-benzoquinone (PBQ, 98%), perfluorobenzene (PFB, 99%), chloranil (CA, 99%), C₆₀, and octafluoronaphthalene (OFN, 96%) were purchased from Aldrich Chemical. Anthraquinone (ATQ, 99%) was purchased from Fluka Chemika-Biochemika, and zinc tetraphenylporphine (ZnTPP) was pur-

chased from Porphyrin Products. TMPD, pyrene, PBQ, ATQ, and CA were purified by vacuum sublimation. PFB was stored over a mixture of silica gel and molecular sieves to remove any water present. The n-hexane (95%, HPLC grade) was purchased from J. T. Baker and fractionally distilled on a 4 ft column. The middle third of the distillate was refluxed with sodium under argon for about 12 h and then distilled under argon. C₆₀, OFN, and ZnTPP were used without further purification. The sample solutions were prepared in air because the presence of dissolved oxygen does not appear to affect the identities of the observed charge carriers or their mobilities. In fact, many attempts by this laboratory to demonstrate a change in the TOFs of charge carriers as oxygen is deliberately added to "freeze-pump-thaw" degassed samples have failed. Presumably oxygen does not successfully compete for photoelectrons with the intrinsic and extrinsic electron acceptors in our samples. The concentrations of electron donors and acceptors in the samples were [TMPD] = 2×10^{-6} M, [ZnTPP] = $[pyrene] = 10^{-6} \text{ M}, [perfluorobenzene] \equiv [PFB] = 10^{-9} \text{ to } 0.05$ M, [p-benzoquinone] \equiv [PBQ] = 10⁻⁹ to 10⁻³ M, [anthraquinone] = $[ATQ] = 10^{-9}$ to 2×10^{-4} M, [chloranil] = $[CA] = 10^{-9}$ to 10^{-4} M, [octafluoronaphthalene] = [OFN] = 10^{-9} to 0.08 M, and $[C_{60}] = 10^{-9}$ to 10^{-5} M.

Between experiments involving different acceptors and/or donors, the photoconductivity cell is disassembled and cleaned as follows: (1) precleaning all parts in detergent (PEX from Peck's Products Co.), (2) soaking the metallic parts in a saturated solution of KOH in ethanol, the Teflon parts and quartz windows in chromic acid, and the Macor spacers in methanol and hexane, and (3) rinsing all parts with deionized water. While usually this procedure appears to be satisfactory, it seems to be inadequate in removing C_{60} . In this case, soaking the cell parts in benzene removes all traces of C_{60} . This additional cleaning step is included in all but the earliest C_{60} experiments.

Laser excitation was provided by a Continuum Nd:YAG laser at either the second harmonic (532 nm) or the third harmonic (355 nm).

All mobility measurements were made at room temperature (24 $^{\circ}$ C).

3. Results and Discussion

3.1. Cations. Figures 1, 2, and 3 show the photocurrent traces seen from solutions of 2×10^{-6} M TMPD in *n*-hexane (with 532 nm excitation), 10^{-6} M ZnTPP in *n*-hexane (with 532 nm excitation), and 10^{-6} M pyrene in *n*-hexane (with 355 nm excitation), respectively. In most experiments in which an explicit photoelectron donor is present, the intensity of excitation was adjusted to eliminate any significant photocurrent from *n*-hexane alone. Ionization was triphotonic at 532 nm and biphotonic at 355 nm. Thus, at the chosen intensities and wavelengths, the total energy of excitation effectively never exceeded 7 eV. The IPs of TMPD, ZnTPP, and pyrene in *n*-hexane are 5.0, ~5.1, and ~6.6 eV, respectively (see Appendix A). Since they are at least 2 eV below that of the solvent (~8.6 eV⁹), we can neglect any secondary interference from the intrinsic donors, {D_i}, of the solvent.

We assume that no unknown strong hole acceptor accompanies the extrinsic donor, D, and, therefore, assign the cationic TOFs in Figures 1, 2, and 3 to TMPD⁺, ZnTPP⁺, and pyrene⁺, respectively. The corresponding mobilities are 10 × 10^{-4} (TMPD⁺), 3.8×10^{-4} (ZnTPP⁺), and 7.0×10^{-4} cm² V⁻¹ s⁻¹ (pyrene⁺). With the viscosity of *n*-hexane at 24 °C given by $\eta = 0.304$ cP,¹⁰ the "Stokes' law¹¹" radii ($r_{\pm} = e/6\pi\eta\mu_{\pm}$) are 2.8, 7.3, and 4.0 Å, respectively. The mobilities and Stokes radii of these extrinsic cations are listed in Table 1.



Figure 1. Photocurrent traces for 2×10^{-6} M TMPD in *n*-hexane with 532 nm excitation. The position of the excitation plane is kept fixed in both of the traces. Each trace shows two breaks. The field in trace A is forward-biased; the second break corresponds to the arrival of the cation at the negative electrode after traveling the longer distance. The field in trace B is reverse-biased; the first break corresponds to the arrival of the cation after traveling the shorter distance. The mobilities of the cation and anion are 10×10^{-4} and 7.5×10^{-4} cm² V⁻¹ s⁻¹, respectively.



Figure 2. Photocurrent traces for 10^{-6} M ZnTPP in *n*-hexane with 532 nm excitation. The position of the excitation plane is kept fixed in both of the traces. Trace A is forward-biased; the second break corresponds to the arrival of the cation after traveling the longer distance. Trace B is reverse-biased; the first break corresponds to the arrival of the cation after traveling the shorter distance. The mobilities of the cation and anion are 3.8×10^{-4} and 5.1×10^{-4} cm² V⁻¹ s⁻¹, respectively.

The new mobility, 10×10^{-4} cm² V⁻¹ s⁻¹, for TMPD⁺ significantly departs from those previously reported: 7.6×10^{-4} cm² V⁻¹ s⁻¹ in a TOF experiment by Houser and Jarnagin⁵ and 6.4×10^{-4} cm² V⁻¹ s⁻¹ from this laboratory⁷ by the thin-sheet TOF method. The TOF method of Houser and Jarnagin is based on the same concept as our thin-sheet TOF technique, i.e., the creation of a sheet of charge between and parallel to coplanar electrodes. Houser and Jarnagin do this by masking the



Figure 3. Photocurrent traces for 10^{-6} M pyrene in *n*-hexane with 355 nm excitation. The position of the excitation plane is kept fixed in both of the traces. Trace A is forward-biased; the second break corresponds to the arrival of the cation after traveling the longer distance. Trace B is reverse-biased; the first break corresponds to the arrival of the cation after traveling the shorter distance. The mobility of the cation is 7.0×10^{-4} cm² V⁻¹ s⁻¹. The anionic part of trace B shows two breaks, indicating the presence of two different anions. The transit times of these anions cannot be resolved in the anionic part of trace A, the mobilities of the anions corresponding to the first and second breaks in the anionic part of trace B are 7.4×10^{-4} cm² V⁻¹ s⁻¹, respectively.

TABLE 1: Mobilities, μ_{\pm} , and Stokes Radii,^{*a*} r_{\pm} , of Ions in *n*-Hexane at 24 °C

ion	$(\times 10^{-4} cm^2 V^{-1} s^{-1})$	r_{\pm} (Å)
TMPD ⁺	10 (7.6 ⁵)	2.8
ZnTPP ⁺	3.8	7.3
pyrene ⁺	7.0	4.0
C ₆₀ -	5.6	5.0
p-benzoquinone ⁻	8.0	3.5
(p-benzoquinone) ₂	5.4	5.2
anthraquinone ⁻	8.7	3.2
(anthraquinone)2 ⁻	5.7	4.9
chloranil ⁻	9.3	3.0
(chloranil)2 ⁻	7.6	3.7
perfluorobenzene ⁻	8.9	3.1
(perfluorobenzene)2 ⁻	7.4	3.8
octafluoronaphthalene ⁻	9.4	3.0
(octafluoronaphthalene)2 ⁻	6.0	4.7

^{*a*} $r_{\pm} = e/(6\pi\eta\mu_{\pm})$ where $\eta = 0.304$ cP¹⁰ for *n*-hexane at 24 °C.

photoconductivity cell so that the light from a xenon lamp enters the cell through a slit that confines the excitation to a 0.1-0.2 cm region close to one electrode. We obtain much better spatial resolution from our laser-based thin-sheet TOF technique: cylindrical focusing creates a charge layer with a width of the order of 10^{-2} cm, and the interelectrode distance is spacer defined. On the other hand, we suspect that the much lower mobility of 6.4×10^{-4} cm² V⁻¹ s⁻¹ seen in the second work is possibly due to the intrusion of an unknown cationic interference, since purification there was not as painstaking as in the current study. (An example of the intrusion of an impurity acceptor is given below.) Thus, the improved purification procedures and increased precision of the present experiments lead us to suggest that the correct mobility of TMPD⁺ in *n*-hexane at 24 °C is 10×10^{-4} cm² V⁻¹ s⁻¹. Intrinsic Anions. In these cationic TOF studies no extrinsic electron acceptors have been intentionally added. In the absence of an extrinsic acceptor, the solvent itself invariably provides unknown electron acceptors, $\{A_i\}$, producing anions with TOF signals that characteristically have breaks that are much more gradual than those of extrinsic cations. In addition, their TOFs vary considerably from solvent batch to solvent batch. Finally, we have mentioned the possibility that the extrinsic material brings with it some unknown, dilute, but favorable acceptor.

The anionic TOF in these extrinsic cation systems are fairly representative of the intrinsic behavior of different solvent batches. In Figure 1 (TMPD), the anionic mobility is $\sim 7.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; in Figure 2 (ZnTPP), it is $\sim 5.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The pyrene experiment (Figure 3) is exceptional in this regard: there are two anionic breaks corresponding to two separate sheets of anions in the reverse-biased TOF trace (Figure 3B). The second anionic break is quite sharp and indicates a mobility of $\sim 5.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The first break is much less resolved and corresponds to a mobility of $\sim 7.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The presence of two anionic breaks in Figure 3B indicates that two types of acceptors capture photoelectrons and that charge exchange equilibration (eq 1b) has not been achieved on the time scale of the TOF time resolution (~0.015 s) and probably not during the TOF (~0.15 s) as well. The kinetics of charge carrier competition (eqs 1a and 1b) and the corresponding TOF waveforms will be discussed in a separate publication.¹³ Interestingly, the mobility of the faster anion (~7.4 × 10⁻⁴ cm² V⁻¹ s⁻¹), while not atypical for that of an intrinsic anion, is also close to that of the pyrene cation (7.0 × 10⁻⁴ cm² V⁻¹ s⁻¹), and one might speculate that it is the pyrene anion. Pyrene can act as an electron acceptor: its electron affinity is 0.58 eV.^{14,15} The pyrene anion has been observed in the gas phase following low-energy (0–15 eV) electron impact¹⁶ and in the condensed phase where the photodetachment spectra of the pyrene anion in nonpolar solvents¹⁷ have been obtained.

The sharpness of the TOF break corresponding to the slow anion (μ - = 5.7 × 10⁻⁴ cm² V⁻¹ s⁻¹) in Figure 3B is not characteristic of the waveform of intrinsic electron acceptors, which produce anionic breaks that are considerably less defined. We have reason to believe that this particular pyrene sample has been contaminated with C₆₀ (μ - = 5.6 × 10⁻⁴ cm² V⁻¹ s⁻¹), because the prior experiment was our first study of a solution of C₆₀ in *n*-hexane. Only later did we discover that our normal cleaning procedure failed to fully remove traces of C₆₀. Use of benzene succeeded in removing all traces of C₆₀ (see Experimental Section).

3.2. Anions. **3.2.1.** Monomer Anions. The observation of extrinsic anions in TOF experiments is somewhat complicated by the presence of intrinsic electron acceptors, $\{A_i\}$, which have unknown identities and concentrations. Whether the photoproduced electrons are scavenged by the extrinsic or by the intrinsic electron acceptors will depend on the relative electron affinities (EAs) and concentrations of the acceptors. The introduction of extrinsic electron acceptors with sufficiently large electron affinities and at sufficiently high concentration ought to (and does) overcome the electron acceptors used in this work have large electron affinities, ranging from about 0.9 to 2.8 eV.¹⁸⁻²¹

To demonstrate the electron scavenging success of an extrinsic electron acceptor in competition with the intrinsic acceptors, $\{A_i\}$, a study of the anionic mobility as a function of the concentration of the extrinsic electron acceptor is carried out. Figure 4 shows the results of such a study for octafluo-



Figure 4. Photocurrent traces for 2×10^{-6} M TMPD and octafluoronaphthalene in *n*-hexane with 532 nm excitation. The position of the excitation plane is kept fixed in all of the traces. The concentration of octafluoronaphthalene is (A) 0, (B) 10^{-9} , (C) 5×10^{-9} , (D) 10^{-8} , (E) 5×10^{-8} , (F) 5×10^{-7} , and (G) 10^{-5} M. The first break in each trace corresponds to the arrival of TMPD⁺ ($\mu_+ = 10 \times 10^{-4}$ cm² V⁻¹ s⁻¹) after traveling the shorter distance. The second break corresponds to the arrival of the anion after traveling the longer distance. The anionic mobility ($\times 10^{-4}$ cm² V⁻¹ s⁻¹) is (A) 7.5, (B) 8.6, (C) 9.1, (D) 9.2, (E) 9.3, (F) 9.4, and (G) 9.4.

ronaphthalene (OFN) using 532 nm excitation. The position of the excitation plane is kept fixed for all of the photocurrent traces. The concentration of OFN is varied from 0 to 10^{-5} M, while the concentration of the extrinsic photodonor, TMPD, remains constant at 2×10^{-6} M. In this solvent batch the intrinsic electron acceptors, {A_i}, scavenge the photoelectrons produced during the photoionization of TMPD to form anions having a mobility of 7.5×10^{-4} cm² V⁻¹ s⁻¹ (trace A). As the concentration of OFN is increased, the anionic mobility is seen to increase. When $[OFN] = 5 \times 10^{-7} \text{ M}$ (trace F), the anionic mobility has become 9.4×10^{-4} cm² V⁻¹ s⁻¹. This mobility is the same as that found at 10^{-5} M OFN (trace G). We can therefore conclude that when $[OFN] \ge 5 \times 10^{-7}$ M, the intrinsic electron acceptors are no longer competitive, and essentially all of the photoelectrons are scavenged by OFN. The mobility of the OFN radical anion is then taken to be $9.4 \times 10^{-4} \text{ cm}^2$ V^{-1} s⁻¹. The forward-biased and reverse-biased photocurrent traces for 2 \times 10⁻⁶ M TMPD and 10⁻⁵ M OFN in *n*-hexane (532 nm excitation) are shown in Figure 5.

Similar concentration studies have been undertaken for the other extrinsic electron acceptors. Samples containing 10^{-5} M perfluorobenzene in *n*-hexane (355 nm excitation), 10^{-7} M anthraquinone in *n*-hexane (352 nm excitation), 10^{-6} M *p*-benzoquinone in *n*-hexane (355 nm excitation), 10^{-7} M chloranil in *n*-hexane (355 nm) excitation), and 10^{-6} M C₆₀ (532 nm excitation) in *n*-hexane were used to determine the mobilities of the anions corresponding to these electron acceptors. Except for the chloranil (CA) sample, all of the samples contained 2 $\times 10^{-6}$ M TMPD as the electron photodonor. In the CA case, TMPD interferes because of the formation of a covalent adduct between TMPD and CA (to be treated in a separate publication²²). Thus, with TMPD absent in this case, the unknown intrinsic photodonors, {D_i}, are photoionized by using a much higher excitation intensity. The concentration of the extrinsic



Figure 5. Photocurrent traces for 2×10^{-6} M TMPD and 10^{-5} M octafluoronaphthalene in *n*-hexane with 532 nm excitation. The position of the excitation plane is kept fixed in both of the traces. Trace A is forward-biased; the second break corresponds to the arrival of the cation after traveling the longer distance. Trace B is reverse-biased; the second break corresponds to the arrival of the anion after traveling that same longer distance. The cation is TMPD⁺ (μ + = 10 × 10⁻⁴ cm² V⁻¹ s⁻¹). The anion has a mobility of 9.4 × 10⁻⁴ cm² V⁻¹ s⁻¹.

electron acceptor in these samples is such that the intrinsic electron acceptors are not competitive. The major negative charge carrier in each case is, therefore, the extrinsic electron acceptor. The observed mobilities of these radical anions and their corresponding Stokes radii are presented in Table 1.

Our laboratory previously reported an anionic mobility of 5.1×10^{-4} cm² V⁻¹ s⁻¹ for a solution of 10^{-6} M ZnTPP and 5×10^{-4} M *p*-benzoquinone (PBQ) in *n*-hexane. The anion was thought to be the monomeric PBQ radical anion.⁶ Here we report a concentration study which shows that, at such a high concentration of PBQ, the dimer radical anion dominates the anion population. This study is discussed next where it is shown that the mobility of the monomeric PBQ radical anion is actually 8.0×10^{-4} cm² V⁻¹ s⁻¹.

3.2.2. Dimer Anions. Concentration studies of the anionic mobility of perfluorobenzene (PFB), octafluoronaphthalene (OFN), anthraquinone (ATQ), chloranil (CA), and p-benzoquinone (PBQ) reveal that upon increasing the concentration of the electron acceptor well beyond the threshold value required to overcome the role of the intrinsic acceptors, $\{A_i\}$, a gradual decrease in the anionic mobility is generally observed. This effect is shown for OFN in Figure 6, where the concentration of OFN is varied from 10^{-5} to 0.03 M, while the concentration of the electron photodonor, TMPD, is kept constant at 2×10^{-6} M. The location of the excitation (532 nm) plane is kept fixed for all of the photocurrent traces. The second break in each trace corresponds to the arrival of the anion at the anode. As the OFN concentration is increased, there is an increase in the anionic TOF which, in turn, translates into a decrease in the anionic mobility. Plots of the anionic mobility against acceptor concentration are shown in Figures 7-11. The reduction in the anionic mobility with increasing concentration (once the threshold for overcoming intrinsic competition is surpassed) is evident in these plots. The limited solubility of C_{60} in *n*-hexane prevents its investigation above $\sim 10^{-5}$ M C₆₀, and from 10^{-7} to 10^{-5} M C₆₀, no change in mobility is seen.



Figure 6. Photocurrent traces for 2×10^{-6} M TMPD and octafluoronaphthalene in *n*-hexane with 532 nm excitation. The position of the excitation plane is kept fixed in all of the traces. The concentration of octafluoronaphthalene is (A) 10^{-5} , (B) 10^{-4} , (C) 5×10^{-4} , (D) 10^{-3} , (E) 5×10^{-3} , (F) 0.01, and (G) 0.03 M. Trace G has been magnified by a factor of 3. The first break in each trace corresponds to the arrival of TMPD⁺ ($\mu_{+} = 10 \times 10^{-4}$ cm² V⁻¹ s⁻¹) after traveling the shorter distance. The second break corresponds to the arrival of the anion after traveling the longer distance. The anionic mobility ($\times 10^{-4}$ cm² V⁻¹ s⁻¹) is (A) 9.6, (B) 9.0, (C), 8.7, (D) 8.2, (E) 7.7, (F) 7.2, and (G) 6.5.



Figure 7. Plot of the observed anionic mobility, μ_{eff} , against the prepared concentration of octafluoronaphthalene in *n*-hexane with 532 nm light for excitation. TMPD was used as an electron photodonor in the samples above. The circles are experimental data points. The solid line is a nonlinear least-squares fit of the experimental data to eq 7 with μ_M , μ_D , and K as variables. The fit gives $\mu_M = (9.4 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_D = (6.0 \pm 0.2) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $K = (3.3 \pm 1.0) \times 10^2 \text{ M}^{-1}$.

We propose that the decrease in anionic mobility with increasing electron acceptor concentration is due to the formation of dimer radical anions. Evidence for the existence of dimer radical anions is available in the literature. Williams et al.²³ observed the ESR spectra of dimer anions of several organic nitriles in γ -irradiated matrices (77 K). Shida and Iwata²⁴ detected the absorption spectrum of the anthracene dimer anion in γ -irradiated matrices (77 K) containing dianthracene as a precursor. Homodimer and heterodimer radical anions have been observed in gas-phase electron-transfer reactions^{19,25,26} and in supersonic jets.²⁷ Recently, a study of electron attachment



Figure 8. Plot of the observed anionic mobility, μ_{eff} , against the prepared concentration of *p*-benzoquinone in *n*-hexane with 355 nm light for excitation. TMPD was used as an electron photodonor in the samples above. The circles are experimental data points. The solid line is a nonlinear least-squares fit of the experimental data to eq 7 with μ_{M} , μ_{D} , and *K* as variables. The fit gives $\mu_{\text{M}} = (8.0 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{\text{D}} = (5.4 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $K = (1.1 \pm 0.22) \times 10^4 \text{ M}^{-1}$.



Figure 9. Plot of the observed anionic mobility, μ_{eff} , against the prepared concentration of anthraquinone in *n*-hexane with 532 nm light for excitation. TMPD was used as an electron photodonor in the samples above. The circles are experimental data points. The solid line is a nonlinear least-squares fit of the experimental data to eq 7 with μ_{M} , μ_{D} , and *K* as variables. The fit gives $\mu_{M} = (8.7 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{D} = (5.7 \pm 0.7) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $K = (1.9 \pm 1.5) \times 10^4 \text{ M}^{-1}$.

to toluene in 2,2-dimethylbutane (DMB) (0.11-0.72 m toluene in DMB) at high pressures by a TOF technique was reported by Holroyd et al.²⁸ This work indicates that electron attachment to neutral toluene dimers occurs, producing the toluene dimer radical anion. Arai et al.29 have observed dimer anions of olefin derivatives in low-temperature pulse radiolysis (113 K) and γ -irradiated matrix (77 K) studies. The growth of the dimer anions, monitored by transient IR absorption, was accompanied by a parallel decay of the monomeric radical anion, suggesting that dimer anion formation might be due to the reaction of the neutral parent molecule with its radical anion. This study also suggests that dimer anion formation may be dependent on the electron affinity of the olefin. Kira et al.³⁰ have observed dimer anions of acrylonitrile by monitoring the absorption spectra of γ -irradiated methyltetrahydrofuran glasses (77 K) containing acrylonitrile. Dimer radical anions have also been observed by Werst³¹ in time-resolved fluorescence-detected magnetic resonance (FDMR) experiments on octafluoronaphthalene and 1,2,4,5-tetrafluorobenzene in n-hexane at 190 K. These dimer radical anions are formed when sufficiently high concentrations of the solutes are present. The observed concentration depen-



Figure 10. Plot of the observed anionic mobility, μ_{eff} , against the prepared concentration of perfluorobenzene in *n*-hexane with 355 nm light for excitation. TMPD was used as an electron photodonor in the samples above. The circles are experimental data points. The solid line is a nonlinear least-squares fit of the experimental data to eq 7 with μ_{M} , μ_{D} , and *K* as variables. The fit gives $\mu_{\text{M}} = (8.9 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{\text{D}} = (7.4 \pm 0.3) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $K = 63 \pm 39 \text{ M}^{-1}$.



Figure 11. Plot of the observed anionic mobility, μ_{eff} , against the prepared concentration of chloranil in *n*-hexane with 355 nm light for excitation. TMPD was not present in the samples above. The circles are experimental data points. The solid line is a nonlinear least-squares fit of the experimental data to eq 7 with μ_{M} , μ_{D} , and K as variables. The fit gives $\mu_{M} = (9.3 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{D} = (7.6 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $K = (3.0 \pm 1.0) \times 10^{5} \text{ M}^{-1}$.

dence and kinetics indicate that the monomer radical anion reacts with the neutral parent molecule to form a dimer radical anion. The FDMR spectrum of the octafluoronaphthalene dimer radical anion suggests that this anion might have a "sandwich" structure. The FDMR spectrum of the 1,2,4,5-tetrafluorobenzene dimer radical anion, on the other hand, is not resolvable so no structural information can be deduced from it.

There are two obvious mechanisms for the formation of dimer radical anions, A_D^- . In one, neutral dimers, A_D , are formed first and compete with the monomer acceptor, A_M , for the photoelectrons:

$$2A_{M} \rightleftharpoons A_{D}$$
 (2)

$$A_{M}^{-} + A_{D} \rightleftharpoons A_{M} + A_{D}^{-}$$
(3)

Equation 3 is just a special case of eq 1b. In combination eqs 2 and 3 give

$$A_{M}^{-} + A_{M} \rightleftharpoons A_{D}^{-}$$
(4)

This is the relevant equation for a second mechanism, one

proposed by Arai et al.²⁹ and Werst,³¹ in which the neutral dimer need not exist. Here the monomer radical anion, A_M⁻, directly associates with the neutral monomer, A_M, forming the dimer radical anion, A_D⁻. We are not aware of evidence that supports the existence of neutral homodimers of p-benzoquinone, anthraquinone, chloranil, octafluoronaphthalene, or perfluorobenzene in nonpolar solvents. At least the absorption spectra of these compounds at various concentrations reveal neither shifts in their maxima nor deviations from Beer's law. The low time resolution of the present TOF experiments makes them incapable of distinguishing between the two mechanisms, which, in any case, share the same net charge exchange reaction (eq 4). These studies of the anionic mobility as a function of the electron acceptor concentration can, however, yield a standard Gibbs free energy change, ΔG° , for the appropriate charge exchange reaction—either eq 3 or eq 4. We choose to interpret our results in terms of the latter.

As long as the charge exchange equilibrates on a time scale that is short compared to the time resolution of the TOF experiment (~ 0.01 s), the anionic sheet containing the two distinct anions will move as a single anionic sheet having an average mobility given by¹³

$$\mu_{\rm eff} = \mu_{\rm M} x_{\rm M} + \mu_{\rm D} x_{\rm D} \tag{5}$$

where μ_M and μ_D are the mobilities and x_M and x_D are the anionic mole fractions of the monomer anion and the dimer anion, respectively, with $x_M = 1 - x_D = [A_M^-]/([A_M^-] + [A_D^-])$. The equilibrium constant, K, for the charge exchange reaction (eq 4) is given by

$$K = \frac{[A_{\rm D}^{-}]}{[A_{\rm M}][A_{\rm M}^{-}]} = e^{-\Delta G^{\circ}/RT}$$
(6)

Substituting $[A_D^-]/[A_M^-] = K[A_M]$ in eq 5, we obtain

$$\mu_{\rm eff} = \frac{\mu_{\rm M} + \mu_{\rm D} K[{\rm A}_{\rm M}]}{1 + K[{\rm A}_{\rm M}]} \tag{7}$$

We typically create $\sim 10^{-11}$ C of charge or $\sim 10^8$ photoelectrons in the TOF experiments. These photocharges are created in a sheet with approximate dimensions $0.3 \times 0.01 \times 3 \text{ cm}^3$ and, therefore, with a volume of about 10^{-5} L. The concentration of the photocharges in the sheet is, therefore, about 10^{-11} M, always very much smaller than the concentration of the electron acceptor. Therefore, the equilibrium concentration of the neutral monomer, A_M , is essentially $[A_M]_0$, the molarity defined by preparing the solution. Figures 7-11 show nonlinear least-squares fits of the experimental data to eq 7 with $[A_M] \approx$ $[A_M]_0$. The mobilities of the dimer radical anions obtained from the fits of eq 7 are displayed in Table 1. The fits also give the standard Gibbs free energy change, ΔG° , for the association reaction (eq 4): ΔG° (octafluoronaphthalene) = -0.15 ± 0.01 eV, $\Delta G^{\circ}(p\text{-benzoquinone}) = -0.24 \pm 0.01 \text{ eV}, \Delta G^{\circ}(\text{anthra-}$ quinone) = $-0.25 \pm 0.04 \text{ eV}$, ΔG° (perfluorobenzene) = -0.11 \pm 0.02 eV, and ΔG° (chloranil) = -0.32 \pm 0.01 eV. The equilibrium constant for the association reaction appears to increase with increasing electron affinity of the acceptor. A similar trend in the dimerization of olefins has been noted by Arai et al.²⁹ The results of Kebarle and Chowdhury¹⁹ suggest that in the case of polar electron acceptors the dipole moment of the acceptor is a better predictor of anionic dimerization than electron affinity. However, since the acceptors that we have studied are all nonpolar, these findings are not directly applicable to our work.



Figure 12. Born-Haber cycle for the association between the monomer radical anion, A_M^- , and the neutral molecule, A_M , to form the dimer radical anion, A_D^- . $X = G^\circ$, H° , and S° . Here "(sol)" refers to the solvated state and "(g)" to the gaseous state.

Estimate of the Gas-Phase A_M/A_D Electron Affinity Differences. We can introduce the above Gibbs free energy change, ΔG° , for the association reaction (eq 4) into a Born-Haber cycle (Figure 12) to obtain an estimate of the difference between the gas-phase electron affinities, ΔEA , of the monomer and the homodimer molecules. This Born-Haber cycle includes formation of the neutral dimer, $A_D(g)$, in the gas phase. In fact, numerous organic van der Waals dimers and higher order clusters have been prepared in supersonic jets.^{32,33} The Born-Haber cycle allows us to write for the condensed-phase association reaction (eq 4)

$$\Delta X = -\Delta X_{sol}(A_{M}) - \Delta X_{sol}(A_{M}) + \Delta X_{sol}(A_{D}) - \Delta X_{M} + \Delta X_{D} + \Delta X_{dim} \quad (X = G^{\circ}, H^{\circ}, \text{ and } S^{\circ}) \quad (8)$$

The standard Gibbs free energy of solvation, ΔG°_{sol} , of A_{M}^{-} and A_D^- consists of an electrostatic part, $\Delta G^\circ_{s,e}$, and another part, $\Delta G^{\circ}_{s,m}$, due to "mixing", which takes the solute from the gaseous standard state at 1 atm to the standard state in solution at 1 M. $\Delta G^{\circ}_{s,m}$ is usually small compared with $\Delta G^{\circ}_{s,e}$, which can be estimated by the Born relation³⁴ (eq A.2), in which r is the radius of the anion. Since we know of no alternative measurements of the effective radii of these dimers, we choose to use Stokes radii as an estimate in the Born equation for both monomer and dimer anions. Furthermore, we are encouraged that our choice of radius is reasonable because of our successful calculation of the IP of TMPD (Appendix A) from liquid-phase photoconductivity data by using its Stokes radius in the Born equation. For the neutral solute, A_M , ΔG°_{sol} consists only of $\Delta G^{\circ}_{s,m}$. We will assume that A_M , A_M^- , and A_D^- have comparable $\Delta G^{\circ}_{s,m}$'s: $\Delta G^{\circ}_{sol}(A_M) = \Delta G^{\circ}_{s,m}(A_M) = \Delta G^{\circ}_{s,m} \approx$ $\Delta G^{\circ}_{s,m}(A_{M}^{-}) \approx \Delta G^{\circ}_{s,m}(A_{D}^{-})$. (See Appendix B for estimates of $\Delta G^{\circ}_{s.m.}$) Equation 8 (for $X = G^{\circ}$) then becomes

$$\Delta G^{\circ} = -\Delta G^{\circ}_{s,e}(A_{M}^{-}) - \Delta G^{\circ}_{s,m} + \Delta G^{\circ}_{s,e}(A_{D}^{-}) - \Delta G^{\circ}_{M} + \Delta G^{\circ}_{D} + \Delta G^{\circ}_{dim}$$
(9)

Next, if we assume that the standard changes in entropy of the gas-phase ionization of $A_M^-(g)$ and $A_D^-(g)$ are nearly the same, then $\Delta S^\circ_D - \Delta S^\circ_M \approx 0$, and we have

$$\Delta G^{\circ}_{D} - \Delta G^{\circ}_{M} \approx \Delta H^{\circ}_{D} - \Delta H^{\circ}_{M} = \Delta E^{\circ}_{D} - \Delta E^{\circ}_{M} = EA(A_{M}) - EA(A_{D})$$
(10)

At this point the only unknown term in eq 9 is $\Delta G^{\circ}_{\text{dim}}$, the standard Gibbs free energy change for the formation of neutral

dimers from neutral molecules in the gas phase. Ideal gas behavior gives for the dimerization

$$\Delta H^{\circ}_{dim} = \Delta E^{\circ}_{dim} + RT\Delta n$$
$$= \Delta E^{\circ}_{dim} - RT \qquad (11)$$

The translational and rotational contributions to the internal energy change, ΔE°_{dim} , can be treated classically. Upon dimerization there is a loss of three translational and three rotational degrees of freedom. Assuming that the thermalizable intramolecular vibrations of the monomer, A_M, change little upon dimerization, the principal vibrational contribution to ΔE°_{dim} is due to a gain of six intermolecular vibrational degrees of freedom in the dimer: one stretch, two bends, and three torsional modes. These are expected to be low-frequency modes. Vibrational spectroscopy of mixed dimers of benzene with methane, ammonia, and water in supersonic jets³⁵ indicates that the intermolecular vibrational modes of the dimers have low frequencies of the order of $10-100 \text{ cm}^{-1}$. Treating these contributions classically and taking the (unknown) electronic contribution to be ΔE°_{e} , the principle of equipartition gives altogether

$$\Delta E^{\circ}_{dim} = 3RT + \Delta E^{\circ}_{e} \tag{12}$$

So eq 11 becomes

$$\Delta H^{\circ}_{dim} = 2RT + \Delta E^{\circ}_{e} \tag{13}$$

Similarly, the entropy change, ΔS°_{dim} , of the dimerization reaction has translational, rotational, and vibrational contributions. The translational contribution due to the loss of three translational degrees of freedom upon dimerization is largely responsible for the overall negative value of ΔS°_{dim} . The rotational and vibrational contributions reflect details of the (unknown) structure of the dimer molecule. In the absence of a structure and force field, let us realistically neglect the entropy change due to the loss of three rotational degrees of freedom and the gain of six vibrational degrees of freedom. This is expected to be quite small compared to the translational contribution to the entropy change. Consequently, for the ideal gas, we have³⁶

$$\Delta S^{\circ}_{dim} = S^{\circ}(A_{\rm D}) - 2S^{\circ}(A_{\rm M})$$
$$\approx -R \ln \left[\left(\frac{\pi m kT}{h^2} \right)^{3/2} \frac{kT}{P} e^{5/2} \right] \qquad (14)$$

where *m* is the molecular mass of A_M and P = 1 atm under standard conditions. Equations 13 and 14 should provide reasonable estimates of ΔH°_{dim} and ΔS°_{dim} , respectively, which can be used to calculate ΔG°_{dim} .

Now one can estimate the difference between the gas-phase EA's of the monomer and dimer:

$$\Delta EA = EA(A_{D}) - EA(A_{M}) \approx \Delta G^{\circ}_{s,e}(A_{D}^{-}) - \Delta G^{\circ}_{s,e}(A_{M}^{-}) - \Delta G^{\circ}_{s,m} + \Delta G^{\circ}_{dim} - \Delta G^{\circ}$$
(15)

The calculated ($\Delta EA - \Delta E^{\circ}_{e}$)'s are displayed in Table 2. Their accuracy is limited principally by use of the Born equation for $\Delta G^{\circ}_{s,e}$, the assumptions involved in estimating $\Delta G^{\circ}_{s,m}$, and the assumption that the standard entropy change upon dimerization in the gas phase is only that due to the loss of three translational degrees of freedom.

Though not known for our systems, the ΔE°_{e} 's are expected to be small. Menapace and Berstein³⁵ have calculated the binding energies (BE) of mixed dimers such as benzene-

TABLE 2: Standard Gibbs Free Energy Change for the Monomer/Monomer Anion Association Reaction in n-Hexane and the Upper Limit for the Difference Between the Gas-Phase Electron Affinities of the Monomer and Dimer Molecules at Room Temperature

electron acceptor (A _M)	ΔG° (eV)	$\frac{\Delta EA - \Delta E^{\circ}{}_{e}{}^{a}}{(eV)}$	$\begin{array}{c} EA\left(A_{M}\right)\\ (eV) \end{array}$	$\frac{\text{EA} (\text{A}_{\text{D}}) - \Delta E^{\circ} e^{a}}{(\text{eV})}$
octafluoronaphthalene	-0.15	1.3		
p-benzoquinone	-0.24	1.2	1.91 ¹⁹	3.1
anthraquinone	-0.25	1.6	1.59 ¹⁹	3.2
chloranil	-0.32	1.4	2.78 ¹⁹	4.2
perfluorobenzene	-0.11	1.0	0.8620	1.9

^{*a*} We estimate that $-\Delta E^{\circ}_{e} \leq 10\%$ of ΔEA .

methane (BE = 540 cm⁻¹ = 0.067 eV), benzene-water (BE = 504 cm⁻¹ = 0.063 eV), and benzene-ammonia (BE = 711 cm⁻¹ = 0.088 eV assuming C_{3v} symmetry or BE = 608 cm⁻¹ = 0.076 eV assuming C_s symmetry). We expect that, for the gas-phase dimerization of the monomers used in our work, the $\Delta E^{\circ}e's$ are probably exoergic by no more than 0.1 eV. This would mean that columns 3 and 5 in Table 2 represent upper limits to the actual ΔEA and $EA(A_D)$, respectively. At worst, they represent overestimates by less than 10% of the actual relative EA and by less than 5% of the gas-phase EA of the neutral dimer, $A_D(g)$.

4. Conclusion

This work has extended the thin-sheet TOF technique to carry out mobility measurements of the cations of several extrinsic photoelectron donors (TMPD, ZnTPP, and pyrene) and the anions of various extrinsic electron acceptors (PFB, PBQ, ATQ, CA, OFN, and C₆₀) in *n*-hexane at room temperature. The effective spherical radii of the ions are then obtained from their ionic mobilities via Stokes' law. The Stokes radius of TMPD⁺ is an excellent estimate of its effective spherical radius in the Born equation, since the calculated IP of TMPD in *n*-hexane agrees exactly with the experimental value. The Stokes radii of ZnTPP⁺ and pyrene⁺ are used to estimate the IPs of ZnTPP and pyrene in *n*-hexane, respectively.

The observed anionic mobility as a function of extrinsic electron acceptor concentration reveals that (1) at low extrinsic electron acceptor concentrations, competition for the photoelectrons occurs between (unknown) intrinsic and (known) extrinsic electron acceptors; (2) beyond a threshold extrinsic electron acceptor concentration, the extrinsic acceptor becomes the dominant photoelectron scavenger, overwhelming the scavenging role of (unknown) intrinsic electron acceptors; and (3) at sufficiently high extrinsic electron acceptor (PFB, PBQ, ATQ, CA, and OFN) concentrations, dimer radical anions of the extrinsic electron acceptor are formed. Charge exchange with the monomer acceptors occurs on a time scale that is faster than the time resolution of the TOF experiment, and consequently, the anions move as a single thin sheet. The mobility of this sheet is just the anionic number average of the monomer and dimer mobilities. From these concentration studies, we have obtained the mobility of the dimer anion, the standard Gibbs free energy change, ΔG° , for the association reaction between the neutral electron acceptor and its monomer anion, and an estimate of the difference between the gas-phase EA's of the electron acceptor and its neutral dimer molecule.

We still do not fully understand the charge-transfer reactions occurring in some TOF experiments, especially those involving mixtures of p-benzoquinone and perfluorobenzene (see Appendix C). We believe that the increase in anionic mobility seen upon addition of perfluorobenzene to a sample of pbenzoquinone may be due to the formation of mixed dimer anions between perfluorobenzene and monomer anions of *p*-benzoquinone. Currently, additional studies seek further examples of the $A_M + A_M^-$ association. We also hope to examine simpler cases of A_1/A_2^- electron exchange competition in which A_1 and A_2 are not related by a second equilibrium (eq 2), as they could be in the present study. Finally, for a given A_1/A_2 system, one can attempt to create a double anionic break (one for each anion, A_1^- and A_2^-) in the TOF signal by using sufficiently dilute solutions so that the time required for bimolecular charge equilibrium (eq 1b) exceeds the TOF time scale. This would open up the technique to chemical kinetic studies.

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Appendix A: The IPs of the Electron Photodonors in *n*-Hexane

The IP of TMPD in *n*-hexane has been experimentally determined by a liquid-phase pump-probe photoconductivity method to be 5.0 eV.^{37,38} The threshold IPs (or I_c's) of ZnTPP and pyrene in *n*-hexane are not known. However, the threshold IP of a solute in a nonpolar solvent, I_c , is related to the gas-phase IP, I_g , by the familiar relation

$$I_{\rm c} = I_{\rm g} + V_0 + P^+ \tag{A.1}$$

where V_0 is the electron affinity of the solvent ($V_0 = 0.02 \text{ eV}$ for *n*-hexane³⁹) and P^+ is the polarization energy of the cation. Although we lack a model of solvent polarization that treats an ionic geometry similar to that of the planar ions generated in these experiments, we proceed by estimating the polarization energy, P^+ , by using the Born equation for a spherical charge³⁴

$$P^{+} = \frac{-e^{2}}{2r} \left(1 - \frac{1}{\epsilon}\right) \tag{A.2}$$

where e is the electronic charge, r is the radius of the ion, and ϵ is the dielectric constant of the solvent ($\epsilon = 1.8838$ for *n*-hexane at 24 °C¹⁰).

We will now demonstrate that the treatment above with r in eq A.2 chosen to be the Stokes radius of the cation (as presently determined) works very well for TMPD. The gas-phase IP, I_g , of TMPD has been experimentally determined to be 6.2 eV.^{40,41} Our TOF mobility measurement yields a Stokes radius of 2.8 Å for TMPD⁺. With r = 2.8 Å in eq A.2, we obtain P^+ (TMPD) = -1.2 eV. Equation A.1 therefore gives I_c (TMPD) = 5.0 eV, which agrees exactly with experiment. While acknowledging the full complexity of the problem, this remarkable agreement for TMPD encourages one to take the Stokes radius of the cation as its effective spherical radius in the Born equation when calculating the I_c 's of ZnTPP and pyrene, as we now do.

Using the effective Stokes radii of the ZnTPP and pyrene cations for r in eq A.2, we obtain $P^+(\text{ZnTPP}) = -0.46 \text{ eV}$ and $P^+(\text{pyrene}) = -0.84 \text{ eV}$ in *n*-hexane. The gas-phase IP, I_g , of pyrene is 7.41 eV.¹⁰ The I_g of ZnTPP is not known, but its I_c has been determined by a condensed-phase photoconductivity method,⁴² which yields $I_c(\text{ZnTPP}) = 4.84 \pm 0.10 \text{ eV}$ in isooctane. We can use eqs A.1 and A.2 to estimate the I_g of

ZnTPP. With $\epsilon = 1.934$ for isooctane at 24 °C¹⁰ and r = 7.3Å (Stokes radius of ZnTPP⁺ in *n*-hexane) in eq A.2, we obtain $P^+(ZnTPP) = -0.48$ eV for isooctane. Using $V_0 = -0.17$ eV for isooctane³⁹ in eq A.1, we get $I_g(ZnTPP) \approx 5.5$ eV. Therefore, in *n*-hexane, $I_c(ZnTPP) \approx 5.1$ eV and $I_c(pyrene) \approx$ 6.6 eV, both below 7 eV.

Appendix B: Estimates of the Standard Gibbs Free Energies of Mixing, $\Delta G^{\circ}_{s,m}$

 $\Delta G^{\circ}_{s,m}(A)$ is the standard Gibbs free energy change involved in taking the solute, A, from its standard state in the gas phase (1 atm, 298 K) to the solution-phase standard state (1 M (Henry's law), 1 atm, 298 K). This free energy change for a switch in standard states can be estimated by first considering the condensation of gaseous A to give pure liquid or pure solid A (as convenient) and then considering the dissolution of A (solid or liquid) in the solvent (*n*-hexane in this work), according to Henry's law, up to the mole fraction, x°_{A} , that corresponds to 1 M.

The "mixing" process can be written as a sum of two steps (eqs B.1a and B.1b)

$$A(g) \xrightarrow{-\Delta G^{\circ}_{\text{phase}}} A(\alpha)$$
 (B.1a)

$$A(\alpha) \xrightarrow{\Delta G^{\circ}_{\text{solution}}} A(\text{sol}; x^{\circ}_{A})$$
(B.1b)

where $\alpha = l$ refers to pure liquid A and $\alpha = s$ to pure solid A. Thus,

$$\Delta G^{\circ}_{s,m} = \Delta G^{\circ}_{solution} - \Delta G^{\circ}_{phase}$$
(B.2)

In a saturated solution, we have

$$\mu_{A}^{*}(\alpha) = \mu_{A}(\operatorname{sol}; x_{A}^{s}) \tag{B.3}$$

where $\mu^*_A(\alpha)$ is the chemical potential of pure A in the α -phase and $\mu_A(\text{sol}; x^s_A)$ is the chemical potential of A in the saturated solution with x^s_A as the mole fraction of A in the saturated solution. If Henry's law holds up to the saturation limit of A, then we can write

$$\mu_{A}(\text{sol};x_{A}^{s}) = \mu^{\dagger}_{A}(\text{sol};x_{A}=1) + RT \ln x_{A}^{s}$$
 (B.4)

Equations B.3 and B.4 then allow us to express the chemical potential of the solution-phase standard state, $\mu^{\circ}_{A}(sol;x^{\circ}_{A})$, as

$$\mu^{\circ}{}_{A}(\operatorname{sol};x^{\circ}{}_{A}) = \mu^{\ddagger}{}_{A}(\operatorname{sol};x_{A}=1) + RT \ln x^{\circ}{}_{A}$$
$$= \mu_{A}(\operatorname{sol};x^{s}{}_{A}) + RT \ln \left(\frac{x^{\circ}{}_{A}}{x^{s}{}_{A}}\right)$$
$$= \mu^{\ast}{}_{A}(\alpha) + RT \ln \left(\frac{x^{\circ}{}_{A}}{x^{s}{}_{A}}\right)$$
(B.5)

We therefore obtain

$$\Delta G^{\circ}_{\text{solution}} = \mu^{\circ}_{A}(\text{sol}; x^{\circ}_{A}) - \mu^{*}_{A}(\alpha)$$
$$= RT \ln \left(\frac{x^{\circ}_{A}}{x^{\circ}_{A}}\right)$$
(B.6)

Liquid A, A(l), as Intermediate. For solutes such as perfluorobenzene (PFB), the pure liquid intermediate ($\alpha = 1$) is suitable. If we assume that no change in volume occurs upon



Figure 13. Photocurrent traces of 2×10^{-6} M TMPD, 8×10^{-5} M *p*-benzoquinone, and perfluorobenzene in *n*-hexane with 532 nm excitation. The position of the excitation plane is kept fixed in all of the traces. The concentration of perfluorobenzene is (A) 0, (B) 8×10^{-7} , (C) 8×10^{-6} , and (D) 8×10^{-4} M. The first break in each trace is due to the arrival of TMPD⁺ at the negative electrode while the second break corresponds to the arrival of the anion at the positive electrode after traveling the longer distance. The anionic mobility ($\times 10^{-4}$ cm² V⁻¹ s⁻¹) is (A) 6.8, (B) 7.8, (C) 7.8, and (D) 7.6.

mixing PFB (d = 1.612 g/cm³ (Aldrich Chemical)) and *n*-hexane (d = 0.6603 g/cm^{3 10}), then $x^{\circ}_{A} = 0.13$. For PFB we estimate that $x^{s}_{A} \approx 1$. For PFB $\Delta H^{\circ}_{vap}(25 \text{ °C}) = 35.71$ kJ/mol, $\Delta H^{\circ}_{vap}(T_{vap}) = 31.66$ kJ/mol, and $T_{vap} = 80.1 \text{ °C}.^{10}$ Assuming $\Delta S^{\circ}_{vap}(25 \text{ °C}) \approx \Delta S^{\circ}_{vap}(T_{vap}) = 83.7$ J/(mol K), we find $\Delta G^{\circ}_{s,m}(25 \text{ °C}) \approx -0.1$ eV for PFB.

Solid A, A(s), as Intermediate. On the other hand, for solutes such as *p*-benzoquinone (PBQ), chloranil (CA), anthraquinone (ATQ), and octafluoronaphthalene (OFN), it is more suitable to introduce the solid phase ($\alpha = s$) as the intermediate.

To obtain $\Delta G^{\circ}_{\text{sublim}}$, we have the standard enthalpies and entropies of sublimation: PBQ ($\Delta H^{\circ}_{\text{sublim}} = 62.8 \text{ kJ/mol}$; $\Delta S^{\circ}_{\text{sublim}} = 0.136 \text{ kJ/(K mol)}$),¹⁰ CA ($\Delta H^{\circ}_{\text{sublim}} = 99.0 \text{ kJ/mol}$; $\Delta S^{\circ}_{\text{sublim}} = 0.176 \text{ kJ/(K mol)}$),¹⁰ ATQ ($\Delta H^{\circ}_{\text{sublim}} = 110.0 \text{ kJ/}$ mol; $\Delta S^{\circ}_{\text{sublim}} = 0.180 \text{ kJ/(K mol)}$),¹⁰ and OFN ($\Delta H^{\circ}_{\text{sublim}} =$ 79.4 kJ/mol; $\Delta S^{\circ}_{\text{sublim}} = 0.189 \text{ kJ/(K mol)}$).⁴³

To calculate $\Delta G_{\text{solution}}$, we require the solubilities of the various solutes in *n*-hexane at room temperature. We did not determine these solubilities accurately because $\Delta G^{\circ}_{\text{s,m}}$ can tolerate an error as large as a factor of ~5 in the estimated solubilities. We estimate that the solubilities of PBQ, CA, ATQ, and OFN in *n*-hexane at room temperature are ~5 × 10⁻³, ~4 × 10⁻⁴, ~4 × 10⁻⁴, and ~0.1 M, respectively. We will assume that 1 L of solution ≈ 1 L of *n*-hexane. With the density of *n*-hexane as 0.6603 g/cm³ at 20 °C,¹⁰ we obtain $x^{\circ}_{A} = 0.12$ for a solution that is 1 M in A. We therefore estimate that $\Delta G^{\circ}_{\text{s,m}}(\text{PBQ}) = -0.1 \text{ eV}$, $\Delta G^{\circ}_{\text{s,m}}(\text{CA}) = -0.3 \text{ eV}$, $\Delta G^{\circ}_{\text{s,m}}(\text{ATQ}) = -0.4 \text{ eV}$, and $\Delta G^{\circ}_{\text{s,m}}(\text{OFN}) = -0.2 \text{ eV}$.

Appendix C: Formation of Mixed Dimer Anions in the Perfluorobenzene/p-Benzoquinone System

Surprisingly, the addition of perfluorobenzene (PFB) to a solution containing *p*-benzoquinone (PBQ) (and TMPD as the photodonor) causes an increase in the anionic mobility, provided that the PBQ concentration is in the intermediate region where both PBQ⁻ and (PBQ)₂⁻ are present. Figure 13 shows four photocurrent traces (at a fixed position of the 532 nm excitation

plane) for *n*-hexane solutions of 2×10^{-6} M TMPD and $8 \times$ 10^{-5} M PBQ at four concentrations of PFB from 0 to 8×10^{-4} M. At 8×10^{-5} M PBQ we have the intermediate concentration region where the PBQ dimer anion becomes significant (see Figure 8). Even up to 10^{-3} M PFB, PFB dimer anions themselves are unimportant (see Figure 10) so the interfering role of only the PFB monomer anion need be considered. In the complete absence of PFB (trace A of Figure 13), the anions consist of a rapidly equilibrated mixture of monomer (μ_{-} = $8.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and dimer ($\mu_{-} = 5.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ s^{-1}) anions of PBQ, which gives a single sheet anionic mobility of 6.8 \times 10^{-4} cm^2 V^{-1} s^{-1}. In the presence of 8 \times 10^{-7} to 8 \times 10⁻⁴ M PFB (traces B, C, and D), the anionic mobility increases to $\sim 7.8 \times 10^{-4}$ cm² V⁻¹ s⁻¹. However, at a higher PBQ concentration $(5 \times 10^{-4} \text{ M})$ where the PBQ dimer anion normally dominates, the presence of 10⁻⁴ M PFB causes little change in the anionic mobility.

One possible source of the PFB effect might have been an electron exchange reaction with PBQ⁻ (i.e., PFB + PBQ⁻ \Rightarrow PFB⁻ + PBQ), causing the position of equilibrium of the association reaction, PBQ + PBQ⁻ \Rightarrow (PBQ)₂⁻, to shift to the left. Since the mobility of PFB⁻ (μ - = 8.9 × 10⁻⁴ cm² V⁻¹ s⁻¹) is larger than that of (PBQ)₂⁻ (μ - = 5.4 × 10⁻⁴ cm² V⁻¹ s⁻¹), this would lead to an increase in the observed anionic mobility. However, the EA of PFB is too small (EA(PFB) = 0.86 eV, EA(PBQ) = 1.91 eV) for any significant charge exchange competition to occur.

Octafluoronaphthalene and 1,2,4,5-tetrafluorobenzene were found not to form dimer anions in toluene.³¹ It has been suggested³¹ that the absence of dimer anions may be principally a rate issue in that solvation of the monomer anions by toluene may prevent close encounter between the electron acceptor and its monomer anion. Like toluene, PFB might be hindering the formation of $(PBQ)_2^-$ by (1) associating with PBQ to form a ground state charge-transfer complex, (PBQ-PFB), which could compete with PBQ⁻ for the negative charge

$$(PFB-PBQ) + PBQ^{-} \rightleftharpoons (PFB-PBQ)^{-} + PBQ \qquad (C.1)$$

and/or (2) associating directly with PBQ^{-} also to form a mixed dimer anion, $(PBQ-PFB)^{-}$

$$PFB + PBQ^{-} \rightleftharpoons (PFB - PBQ)^{-} \qquad (C.2)$$

Our TOF studies indicate that $(PBQ)_2^-$ has a Stokes radius of 5.2 Å and $(PFB)_2^-$ has a Stokes radius of 3.8 Å. We expect the mixed dimer anion, $(PFB-PBQ)^-$, to be larger than $(PFB)_2^-$ but smaller than $(PBQ)_2^-$. If the additivity rule holds with regard to the Stokes radii, then the mixed dimer anion would have a Stokes radius of 4.5 Å, which corresponds to an ionic mobility of $6.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, about 15% greater than $(PBQ)_2^-$. A mixed dimer anion that is faster than $(PBQ)_2^-$ would qualitatively explain the observed increase in anionic mobility upon addition of PFB to the PBQ solution.

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(11) Although Stokes' law is an ideal not perfectly followed by every solute in every solvent, we nevertheless use it because of its simple form. We have also examined a simple semiempirical equation developed by Luthjens et al.¹² that relates the diffusion coefficient, $D (\text{cm}^2/\text{s})$, to the mass of the solute, m (amu) and the viscosity of the solvent, η (cP): $D = 22 \times 10^{-5}\eta^{-0.62}m^{-0.5}$. This equation succeeds in predicting the observed diffusion coefficients of certain gaseous electron acceptors in several nonpolar hydrocarbons. However, when applied to the diffusion in *n*-hexane of the solutes used in our work, it overestimates the mobilities ($\mu = De/kT$) by factors ranging from 17% (C₆₀) to 113% (PBQ).

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(18) The charge-transfer (CT) method¹⁹ was used to determine the following electron affinities: EA(p-benzoquinone) = 1.91 eV, EA-(anthraquinone) = 1.59 eV, and EA(chloranil) = 2.78 eV. The EA's of perfluorobenzene and C_{60} are 0.86^{20} and $2.7 \pm 0.1 \text{ eV}$,²¹ respectively. The EA of octafluoronaphthalene is not available, but we expect it to be larger than that of perfluorobenzene.

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