Competitive Consecutive Electron Transfer in Determination of Ionization Potentials: Ketene Derivatives

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Kinetics of competitive consecutive electron transfer was used to determine ionization potentials of transient species. Kinetics of two-stage electron transfer reactions in aprotic solvent was studied using 355 nm laser flash photolysis. The concentrations of transients produced by the laser flash photolysis were monitored by their light absorption. Triplet-excited tetrachloro-*p*-benzo-quinone (*p*-chloranil) generated by a 355 nm laser flash oxidized diethyl ketene, diphenyl ketene, or phenyl ethyl ketene to form radical cations. The ketene radical cations, in turn, oxidized tertiary amine, forming ground state ketene and ammonium radical cation. The kinetics of the disappearance of ketene radical cations (and/or appearance of ammonium radical cations) due to consecutive, competitive electron transfer to ketene and *p*-chloranil radical cations was monitored. By monitoring kinetics in the presence of tertiary amines with different oxidation potentials, it was established that in acetonitrile the oxidation potential of diethyl ketene was 5.4 eV; for phenyl ethyl ketene, it was ≈4.8 eV; and for diphenyl ketene, it was 4.6 eV. The results were in agreement with the oxidation potentials of ketenes computed using published data.

Introduction

Ionization potential (IP) measurements by direct spectroscopic or electrochemical methods are complicated when the molecules are unstable or have poor solubility in particular solvents.[1−3] The direct electrochemical techniques for measuring the potentials of transient species, such as conducting oxidation−reduction reactions on a rotating electrode or using pulsed methods, are not universally applicable.[4,5] Most often, indirect methods based on modeling, compilation of related data, and extrapolation from the known analogues are used.[6,7]

Energy levels of one of the reacting species may be found by comparison with the known energies of the other species involved in the reaction. The relative approach based on the change of reaction kinetics is useful when direct measurements of properties are hindered by low concentrations or instability of the species of interest. For example, the relative approach was used to find vibrational energy distribution of thermally excited molecules.[8−10] Rabinovitch and co-workers extended the idea by using the molecules that yielded different products depending on the excitation level from which these molecules reacted.[9,10] The relative yields of the products forming by the reactions with different threshold energies defined "competitive reactions spectroscopy" that yielded relative energy distributions of the excited reactant molecules.[10] We applied this concept of competitive reactions spectroscopy and used competitive, consecutive oxidation reactions in solutions to estimate oxidation potentials.

In a system consisting of three or more species with different oxidation potentials, electron transfer (ET) occurs in a series of consecutive and parallel ("competitive" as termed by Rabinovitch[9,10]) reactions. Two-step ET initiated by laser flash pho-

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SCHEME 1: Structure of Tetrachloro-*p*-benzoquinone (*p*-Chloranil) Used in Its Excited Triplet State as the Lowest Energy Electron Acceptor in Competitive Consecutive ET
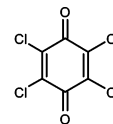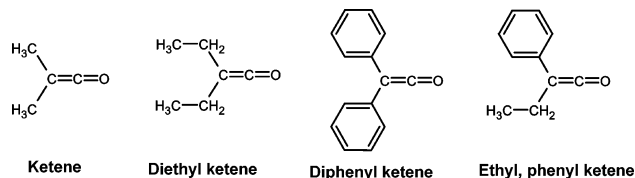

Tetrachloro-p-benzoquinone (p-Chloranil)

tolysis was recently reported.[11] In these studies, radical cations of oxidizing species were formed through the reaction with the triplet excited state of tetrachlo-*p*-benzoquinone (*p*-chloranil) (³Chl) (Scheme 1). The "primary" radical cations could not be detected directly. They were monitored by light absorption of the products of ET from species that formed radical cations with detectable light absorption. The ET was used exclusively for transient species detection ("reporting"). Physical validity of the reporting was not evident.

We used multistep ET to the *p*-chloranil triplet excited state[11] to find IP of ketene derivatives in solution. Photoexcitation kinetics of *p*-chloranil in solution, the oxidation potential of ³Chl, and kinetics of ET from one donor at a time to ³Chl were characterized by Kochi and co-workers.[12] Electron donors were selected on the basis of their photochemical stability and expected oxidation kinetics as further described.[13,14]

Ketenes. Diphenyl ketene (Scheme 2) was first synthesized and studied by Herman Staudinger, who described in 1905 its extreme sensitivity to atmospheric oxygen.[15] The photochemistry of ketene was pioneered by Kistiakowsky and co-workers in the 1930s−1950s.[16,17] This work was followed by the gas-phase studies of Rabinovitch and co-workers[18,19] and Noyes and co-workers[20,21] in the 1950s and 1960s. Chemical properties of ketene and ketene derivatives in solution were studied in detail by Tidwell and co-workers.[22,23] Thermodynamic properties of some ketene derivatives were computed[24] and measured.[25]

Competitive Consecutive Electron Transfer

J. Phys. Chem. A, Vol. 110, No. 51, 2006 **13809**

SCHEME 2: Structures of Ketene and Its Derivatives Used to Verify the Competitive Consecutive ET Approach for Determination of IPs

Scwartz and co-workers found that the ketene radical cation reacts with ammonia through ET.[26] Shaik modeled ET to ketene.[27]

There is a continued interest in ketene chemistry and photochemistry stipulated by the practical importance of ketenes in polyester production and in photoimaging and electronics that utilize diazoquinones that initiate photopolymerization, disputably, through a ketene intermediate.[28] It was suggested that ketene elimination could be a part of biocatalytic processes.[29] Ketene spectroscopy in solution is being extensively studied.[30]

Vertical IPs of several substituted ketenes in a gas phase were found.[2,25] However, electron binding energies of ketenes in solution were not measured. We monitored kinetics of ET from tertiary amines to radical cations of several ketene derivatives (Scheme 2) in acetonitrile solution and used a competitive consecutive ET method to find IPs of these unstable molecules[15−23,28,31−34] in solution. The obtained data, in turn, proved the applicability of the competitive consecutive ET technique.

Experimental Section

Apparatus and Run Procedure. A preassembled nanosecond laser photolysis spectrometer, LKS.60, from Applied Photophysics was used. A Surelite SSP (with Surelife Separation Package for clean harmonic separation) NdYAG laser (Continuum Scientific), with selected 355 nm harmonics and a 2−5 ns pulse width at 50−60 mJ/pulse, was used for pulsed excitation. Excitation was conducted at a 90° angle to the analyzing light. Pulsed analyzing light came from a 150 W Xe high-pressure light source (Applied Photophysics). The constant intensity duration of the Xe arc pulse was >2 μs. The analyzing light flash was started prior to a laser flash; thus, transients were created and detected during the time when the intensity of the Xe arc flash was constant. Analyzing light passed through optical filters and two monochromators (4.65 nm/mm gratings, Applied Photophysics) placed along the optical path of analyzing light before and after the sample. The analyzing light absorption was detected using a photomultiplier assembly with R329 or R928 side-on photomultiplier tubes (the choice depended on the species of interest absorption spectra) (Hamamatsu). The signal from the photomultiplier was recorded by a digital oscilloscope, HP 54522A, 2 GSa/s, 500 MHz resolution (Hewlett-Packard). The data were further transferred to a computer system that also controlled the timing of the laser and analyzing light pulses. Monoexponential fitting was used to deduce the kinetic parameters of signal rise and decay. It was verified that the observed kinetics were diffusion controlled in all of the experiments; that is, decay rate constants were of the order of 10^{10} dm^3 mol^{-1} s^{-1}. Kinetics of the triplet *p*-chloranil, ^{3}Chl (Scheme 1), concentration change was detected by 510 nm absorption. Other transient species formation and disappearance were also monitored by light absorption.

The solutions were deoxygenated by purging for 20 min with He, prior to laser flash photolysis. The absence of oxygen effects was verified by radical decay kinetics monitoring. The degassed
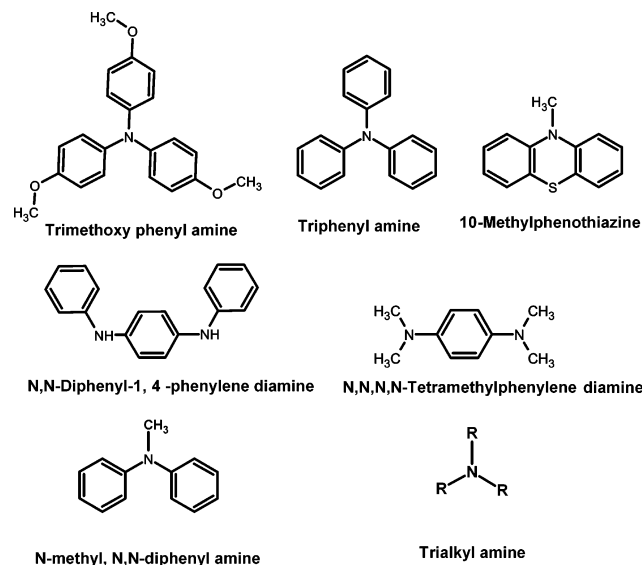
solutions were passed at 5 cm^3/min under He pressure through a 1.0 cm optical path fused silica cell (fluorescence flow cell, Starna Co.). The residence time of the solution in the laser illuminated portion of the beam was ≈2 s, substantially longer than that of the studied ET reactions duration, <10^{-6} s. This precluded a mass transfer-stipulated concentration change in the reaction detection region during the reaction.

Materials. Diethyl ketene and ethyl phenyl ketene (Scheme 2) were synthesized from substituted diethyl malonic acid (Aldrich) and trifluoroacetic anhydride (Aldrich) as described by Duckworth and co-workers.[31] Thus, 2.1 mol equiv of trifluoroacetic anhydride was added dropwise to 3.0 g of diethyl malonic acid dissolved in freshly distilled ethyl ether. After the mixture was kept at room temperature for 30 min, it was further diluted with 80 mL of petroleum ether. Following the addition of 3 mL of pyridine, the mixture was filtered and the filtrate was collected. After solvent removal in a rotary evaporator, the concentrate was pyrolyzed under vacuum.[31] A light yellow liquid was collected. The collected diethyl ketene was placed into −20 °C storage immediately upon collection to delay degradation. Infrared (IR), proton, and ^{13}C NMR spectra showed that it contained ≥90% diethyl ketene. ^{1}H NMR (CDCl$_3$): δ 2.00 (q, 4H, $J = 7.5$, 15 Hz), 1.10 (t, 6H, $J = 7.5$ Hz). ^{13}C NMR (CDCl$_3$): δ 206 (CO), 34 (CCO), 19 (CH$_2$CH$_3$), 13 (CH$_2$CH$_3$). Diethyl ketene in pure form degraded in 2−3 days even at −20 °C; thus, sampling and experimentation in dilute solutions had to be conducted accordingly.

Ethylphenyl malonic acid for ethyl phenyl ketene synthesis was prepared as described elsewhere.[32,33] A 4.5 mL amount of trifluoroacetic anhydride was added slowly, dropwise to 3 g of ethylphenyl malonic acid dissolved in 30 mL of ethyl ether.[31] The reaction continued for 20 min at room temperature; then, the solvent was evaporated at reduced pressure. The remaining liquid was pyrolyzed at 120−130 °C under vacuum. Diethyl ketene was stored at −20 °C to delay degradation, occurring in a pure form.[31] The collected liquid was shown to be ∼90% ethyl phenyl ketene (^{13}C NMR, proton NMR, IR). ^{1}H NMR (CDCl$_3$): δ 7.42−7.40 (m, 2H, *m*-ph), 7.35−7.25 (m, 3H, *o,p*-ph), 2.99 (q, 2H, $J = 7.5$, 15 Hz), 0.80 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR (CDCl$_3$): δ 205 (CO), 132 (ipso-ph), 129 (ph), 124 (ph), 123 (Ph), 41 (CCO), 17 (CH$_2$CH$_3$), 13 (CH$_2$CH$_3$).

Diphenyl ketene (Scheme 2) was synthesized according to the method of Anderson and Broughton.[34] A three-neck flask was equipped with a glass-fritted bubbler, an output valve, and a dripping funnel. The system was airtight. Twenty grams of diphenyl acetyl chloride was placed in 180 mL of freshly distilled ethyl ether and carefully degassed with a flow of dry nitrogen gas for 1 h. Simultaneously, triethyl amine was degassed by nitrogen flow in a dripping funnel attached to the reaction vessel. The triethyl amine was added slowly, dropwise to the solution of diphenyl acetyl chloride cooled in an ice bath. Triethyl amine addition was conducted under continuous flow of dry nitrogen gas through dripping funnel and a three-neck flask. The reaction mixture was then left in an ice bath overnight (≈15 h). The precipitate was filtered under a vacuum through a cannula with a fritted glass end. A reddish-yellow, viscous fluid remained after vacuum evaporation of ether from the collected filtrate. It was identified using ^{13}C NMR as 90% diphenyl ketene. ^{1}H NMR (CDCl$_3$): δ 7.47−7.40 (m, 4H, *m*-ph), 7.23−7.38 (m, 6H, *o,p*-Ph). ^{13}C NMR (CDCl$_3$): δ 201 (CO), 131 (ipso-Ph), 129 (Ph), 128 (Ph), 126 (Ph), 46.7 (CCO).

Diphenyl ketene was relatively stable; however, extreme measures were taken to reduce oxygen and water exposure

SCHEME 3: Structures of High-Energy Electron Donors Used in the Competitive Consecutive ET Approach for Determination of IPs

Trimethoxy phenyl amine

Triphenyl amine

10-Methylphenothiazine

N,N-Diphenyl-1,4-phenylene diamine

N,N,N,N-Tetramethylphenylene diamine

N-methyl, N,N-diphenyl amine

Trialkyl amine

SCHEME 4: Kinetic Model of Competitive Consecutive ET Reactions

$Chl + h\nu \rightarrow {}^3Chl$ photo-generation of lowest energy $\bar{e}$-acceptor

${}^3Chl + D_1 \rightarrow D_1^{\bullet+} + Chl^{\bullet-}$ $\bar{e}$-transfer from $\bar{e}$-donor with unknown ionization potential

${}^3Chl + D_2 \rightarrow D_2^{\bullet+} + Chl^{\bullet-}$ $\bar{e}$-transfer from highest energy $\bar{e}$-donor

$D_1^{\bullet+} + D_2 \rightarrow D_1 + D_2^{\bullet+}$ $\bar{e}$-transfer between the $\bar{e}$-donors of different ionization potentials

${}^3Chl \rightarrow Chl$ decay of lowest energy $\bar{e}$-acceptor without reactions with $\bar{e}$-donors

$Chl^{\bullet-} \rightarrow Chl$ chloranil anion disappearance not involving reactions with $\bar{e}$-donors D_1 and D_2

$D_1^{\bullet+} \rightarrow D_1$ radical cation deactivation by reactions other than with D_2 donor

$D_2^{\bullet+} \rightarrow D_2$ radical cation deactivation by reactions other than with D_1 donor

during the synthesis. Storage at -20 °C was essential for degradation delay.

All of the substituted ketenes described above decayed within a week from purification, despite storage under nitrogen at -20 °C, and had to be synthesized repeatedly. In diluted acetonitrile solutions, ketenes could be stored for longer periods without decomposition at -20 °C and well over a week at room temperature. All ketenes exhibited an IR absorption peak in the $2080-2100$ cm^{-1} region (C=C=O). Degradation of the synthesized ketenes and their solutions was elucidated based on absorption spectra changes over time.

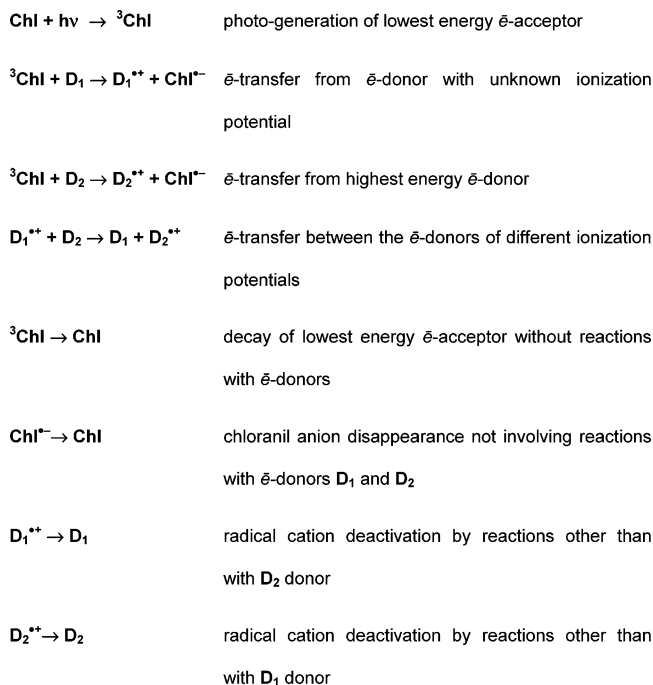Tris(*para*-methoxyphenyl)amine [(*p*-CH$_3$OC$_6$H$_4$)$_3$N] (Scheme 3) was synthesized as described elsewhere.[35] Commercial triphenyl amine [(C$_6$H$_5$)$_3$N], N-methyl, N,N-diphenylamine [(C$_6$H$_5$)$_2$NCH$_3$], 10-methylphenothiazine, N,N-diphenyl-1,4-phenylenediamine, N,N,N,N-tetramethylphenylene diamine, trimethyl amine, triethyl amine, and tripropyl amine (Aldrich and Fisher Scientific) (Scheme 3) were used without further purification.

Acetonitrile (Optima brand, Fisher Scientific, as was) was selected as a solvent since the oxidation potential of acetonitrile is among the highest, 9.19 eV.[36] The possibility of acetonitrile reaction with olefins was insignificant under present conditions.[37]

Solutions. The concentration of tetrachlo-*p*-benzoquinone (*p*-chloranil) (Aldrich) was 10^{-3} M in all of the experiments. The concentration of ketene derivatives varied between 10^{-2} and 10^{-4} M. The second electron donor concentration was 10^{-4} M in all of the experiments.

Ketene derivatives, especially diphenyl ketene, tend to polymerize upon deoxygenation in $>10^{-2}$ M ketene solutions, forming polyester precipitates as was shown by Staudinger and other researchers.[15,38] To avoid polymerization, the consecutive, competitive ET reactions in the presence of ketenes and nitrogen-containing donors were conducted using 10^{-3} M ketene solutions.

Conventional spectrophotometer (8453 UV/visible, Agilent Technology) was used in all measurements. The absorption spectrum of *p*-chloranil exhibits three broad bands, <240, 240−310, and 310−450 nm, with a maximum at 365 nm.[12] Selected ketene and nitrogen-containing electron donors showed no detectable absorption at selected concentrations at the excitation wavelength, 355 nm, and detection wavelengths of 510, 650, and 720 nm.[11] The optical density of 10^{-3} M solution of *p*-chloranil in acetonitrile was 0.7 at 355 nm.

The absorption spectra assignment of radical cations of *p*-chloranil[12a−g] and substituted amines and phenothiozines[11,12h−l] were confirmed by comparison with the published data.

Results and Discussion

Principle of the Method. In a solution of *p*-chloranil (Chl) and two electron donors, D_1 and D_2, prepared to ensure that an optical density of Chl at 355 nm was substantially higher than that of D_1 and D_2, 355 nm (O.D.$_{Chl}$ = 0.7; O.D.$_{donors}$ ≈ 0), the laser pulse would be predominately absorbed by Chl. This would result in a higher concentration of *p*-chloranil triplets, ${}^3Chl$, than other species. Triplet ${}^3Chl$ could react with electron donors, D_1 and D_2, by two parallel (competitive) reactions, producing radical cations $D_1^{\bullet+}$, $D_2^{\bullet+}$, and radical anion ${}^3Chl^{\bullet-}$ (Schemes 4 and 5). The concentration of $\bar{e}$-donor D_1 with a higher electron binding energy (oxidation potential) in solution, B_{1+}, was selected to be 10 times higher than the concentration of donor D_2 with a lower electron binding energy, B_{2+}. In the presence of a higher concentration of D_1, the formation of $D_2^{\bullet+}$ radical cations by the reaction ${}^3Chl + D_2 \rightarrow Chl^{\bullet-} + D_2^{\bullet+}$ would be slower than the formation $D_1^{\bullet+}$ by a *competitive* reaction ${}^3Chl + D_1 \rightarrow Chl^{\bullet-} + D_1^{\bullet+}$ (Figure 1). With a large enough difference $[D_1] \gg [D_2]$, $B_{1+} \geq B_{2+}$, the competitive ET reaction ${}^3Chl + D_2 \rightarrow Chl^{\bullet-} + D_2^{\bullet+}$ would be suppressed and most of the $D_2^{\bullet+}$ radical cations would be produced by *consecutive* ET reaction $D_1^{\bullet+} + D_2 \rightarrow D_1 + D_2^{\bullet+}$. Conducting ET with initial $[D_1] \gg [D_2]$ also substantially simplified the analysis of the experimental data, although kinetic analysis was possible with other initial concentrations. The kinetics of ET could be monitored by light absorption of any of the transients, $D_1^{\bullet+}$, $D_2^{\bullet+}$, ${}^3Chl$, or $Chl^{\bullet-}$, as described above.

When the electron binding energy of one of the molecules D_1 or D_2 is known, the electron binding energy of the other can be approximated, provided that both binding energies are

Competitive Consecutive Electron Transfer

J. Phys. Chem. A, Vol. 110, No. 51, 2006 **13811**

SCHEME 5: Diagram of the Relative Electronic Energy Levels of Acceptor and Two Electron Donors Involved in Competitive Consecutive ET Reactions
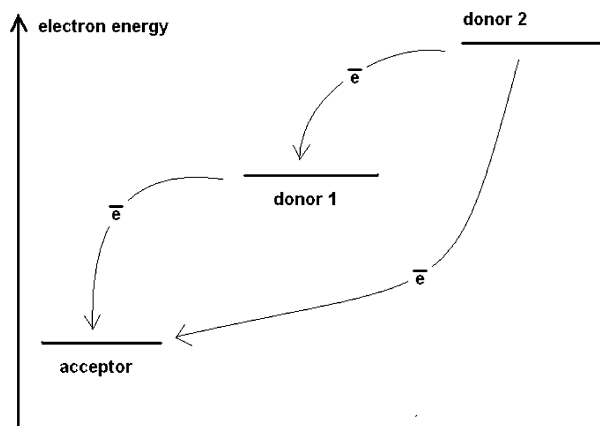
lower than that of *p*-chloranil triplet excited state. Monitoring the kinetics of ET from a series of D_2 with known electron binding energies to the same $D_1^{\bullet+}$ would yield an approximation of the electron binding energy on D_1. In low viscosity solutions, the ET rate increases monotonously with the difference in electron binding energy until it reaches a diffusion-controlled rate constant limit (Rehm−Weller).[1,4,13,14] Therefore, for $B_{1+} \leq B_{2+}$, the ET $D_1^{\bullet+} + D_2 \rightarrow D_1 + D_2^{\bullet+}$ would not occur providing the lower limit for B_{1+}. For $[D_1] \gg [D_2]$ and $B_{1+} \leq B_{2+}$, the reaction $^3Chl + D_2 \rightarrow Chl^{\bullet-} + D_2^{\bullet+}$ would be relatively suppressed as well, due to the concentration difference under diffusion-controlled kinetics (Rehm−Weller).[1,4,13,14] With less

Figure 1. Computed kinetics of triplet chloranil, ^3Chl, and donor radical cation, $D_2^{\bullet+}$, reaction with and without the donor D_1 with a higher electron binding energy than D_2.

or no $D_2^{\bullet+}$ formed by ET to ^3Chl or $D_1^{\bullet+}$, only ET observed would be due to the reaction $^3Chl + D_1 \rightarrow Chl^{\bullet-} + D_1^{\bullet+}$. If $[D_1] \gg [D_2]$ is maintained, while the donors D_2 are selected with the binding energy B_{2+} increasing from $B_{1+} \geq B_{2+}$ to $B_{1+} < B_{2+}$, the decrease in the amount of $D_2^{\bullet+}$ formed will be observed. No $D_2^{\bullet+}$ will form for systems with $B_{1+} \approx B_{2+}$ and above. Under 10-fold differences in $[D_1]$ and $[D_2]$ concentrations of the present work, suppression of $D_2^{\bullet+}$ formation was, indeed, observed experimentally. The electron binding energy of the donor D_1 was deduced accordingly.

The method is symmetric and can yield the electron binding energy of the electron donor D_2 (lower binding energy), if binding energies of a series of D_1 acceptors (higher binding energies) are known.

To illustrate expected results, the differential equations describing the kinetics of the ET reactions (Scheme 4) were solved numerically by Kaps−Rentrop finite difference method for solution of stiff differential equations as implemented by PSI Plot software package (Poly Software International) (Figure 1).

According to Marcus−Levich theory, the rate of ET depends nonlinearly on the difference in donor and acceptor electron binding energies.[13,14] Marcus or Rehm−Weller regions in the nonlinear dependence of the rate of ET kinetics on the electron binding energies difference were not observed since kinetics was diffusion-controlled in low-viscosity acetonitrile solution. The possibility of ET reactions not controlled by diffusion of the components is discussed below.

Computations of IPs (Electron Binding Energies) in Acetonitrile. To ensure validity of the proposed competitive consecutive ET method, IPs of donors and acceptors in solution found by this method were compared with those obtained by established methods. IPs in solution of ketenes and some of the amines used here were not known; therefore, IPs of those molecules in solution were calculated. According to the Jortner and Raz approach,[6,7,39−41] the IP (oxidation potential, electron binding energy) for a molecule in a liquid or solid solution, I_s, can be derived from the expression:

$$I_s = I_g + P_+ + V_o \tag{1}$$

where I_g is the vertical IP in the gas phase, P_+ is the polarization energy of the radical cation (or the solvent positive hole), and V_o is the energy of quasi-free electron in the solvent.[7,36,39−41] The expression for solvent polarization energy was derived based on Fowler's work.[42] Grand and Bernas showed that Born's equation can be used to compute P_+:[7]

$$P_+ = -(e^2/4r\pi\epsilon_o)(1 - 1/\epsilon) \tag{2}$$

where $e = 1.602 \times 10^{-19}$ C is electron charge, $\epsilon_o = 8.85 \times 10^{-12}$ J^{-1} C^2 m^{-1} is the vacuum permittivity, ϵ is the optical dielectric constant, and r is the "effective" radius of the radical cation (solvent positive hole), which can be derived by a variety of methods[7,36,39−44] and depending on an algorithm may be considered as equal approximately to a radius of a neutral molecule[36,41−44] or to solvent atoms spacing.[7,39,40]

Biswas and Bagchi and Faria and Steenken derived IPs and listed parameters for the computation of P_+ of acetonitrile[43,44] and the energy of electron solvation by acetonitrile, $V_o = -1.5$ eV.[44] This value was used in all of the computations below.

The radius of cation radical in acetonitrile was $r \approx 4.48 \times 10^{-10}$ m, $\epsilon = 35.77$;[43] thus, we computed for acetonitrile $P_+ \approx -1.5$ eV (eq 2).
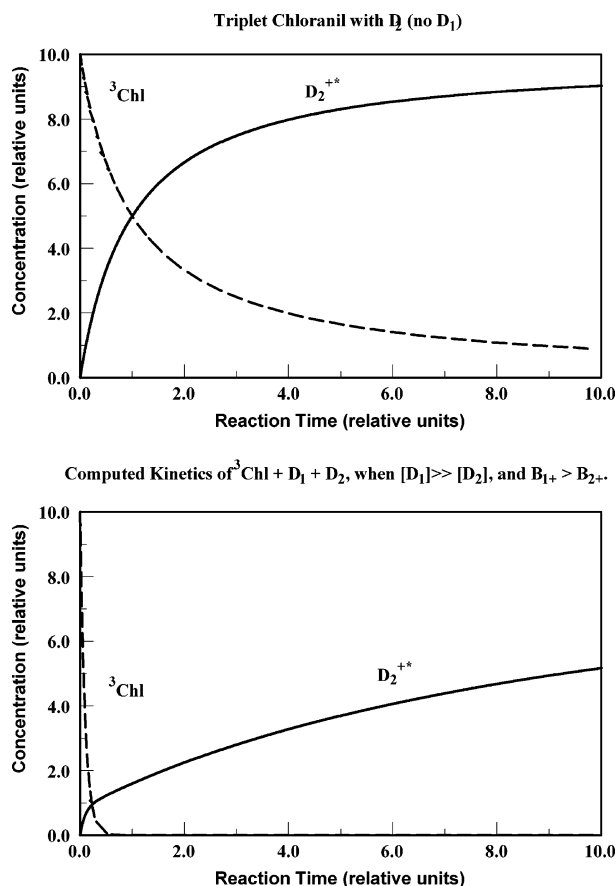
TABLE 1: Computed and Reported IPs

molecule	gas-phase IP I_g (eV)	ref	$E_{1/2}$ vs SCE (eV)	ref	computed IP in acetonitrile I_s (eV)
$H_2C=C=O$	9.64	2	2.19 (pyr)		6.60
	9.60	46			
$CH_3HC=C=O$	8.95	46–48	1.49 (pyr)		5.95
$(p\text{-}CH_3\text{-}C_6H_5)(CH_3)C=C=O$			1.18	55, 56	5.62 (pyr)
$(p\text{-}CH_3O\text{-}C_6H_5)(CH_3)C=C=O$			0.98	55, 56	5.42 (pyr)
$(CH_3)_2C=C=O$	8.38	46	0.93 (pyr)		5.40
	8.45	48			
$(C_6H_5)HC=C=O$	8.17	46	0.72 (pyr)		5.06
	8.06	45			
$(C_6H_5)_2C=C=O$	7.64	45	0.19 (pyr)		4.64
pyridine	9.26	2	1.82	54	6.26
	9.67	50			
$(C_6H_5)_3N$			0.92	50	5.36
$(CH_3OC_6H_4)_3N$			0.52	50	4.96, 4.25
$(C_6H_5)_2NCH_3$	7.44	51	0.71	51	4.44
10-methylphenothiazine			0.40	50	4.84 (pyr)
N,N-diphenyl-1,4-pehnylenediamine			0.335	50	4.76 (pyr)
N,N,N-tetramethyl phenylene diamine			0.15	50	4.59 (pyr)
$(CH_3)_3N$	7.82	50	0.82	52	4.82
$(C_2H_5)_3N$	7.50	50	0.66	52, 53	4.50
$(C_3H_7)_3N$	7.23, 7.18	50	0.64	52, 53	4.23
acetonitrile	12.19	36			9.19

In most computations, we used previously published values of gas-phase IPs of ketene derivatives obtained by photoelectron spectroscopy.[2] When gas-phase photoelectron spectroscopy data were not available for ketenes and tertiary amines, electrochemical potentials measured by other methods were combined with the Jortner–Raz computations[12,45–56] (Table 1).

The gas-phase IP of ketene, $I_{ketene} = 9.64$ eV,[2] therefore in acetonitrile solution at standard conditions $I_{ketene} = 6.64$ eV (eq 1). Experimentally obtained gas-phase IPs of monophenyl ketene is 8.06 eV, and of diphenylketene, 7.64 eV.[45] This yielded for acetonitrile solution $I_{monophenylketene} = 5.06$ eV and $I_{diphenylketene} = 4.64$ eV (eq 1). IPs in acetonitrile of other compounds were similarly computed (Table 1).[40]

The gas-phase IP of pyridine was reported to be 9.26[2] and 9.67 eV.[54] We used the value of 9.26 eV to compute pyridine IP in acetonitrile solutions. The half-wave potential, $E_{1/2}$, of pyridine in acetonitrile measured using dripping mercury electrode relative to saturated calomel electrode (SCE) was reported to be 1.82 eV.[50] The IPs of other stable compounds were computed here as was recommended previously by the difference in their half-wave potentials and that of pyridine.[40]

$$I_{s\ unknown} = I_s (\text{pyridine}) + (E_{1/2\text{pyridine}} - E_{1/2\text{unknown}}) \quad (3)$$

All of the computed oxidation potentials of electron donors were lower than those reported for *p*-chloranil triplet.[12] The precision of our experimental determination of oxidation potentials of ketenes was limited by the available tertiary amines, used as ē-donors, D_2 (Table 1).

Oxidation Potentials of Ketene. To monitor ET kinetics, amines forming radical cations with distinct detectable light absorption, upon ET, to *p*-chloranil triplet or ketene cation radical were selected[11,12] (Scheme 3). It was observed that in the absence of diethyl ketene the rate of ^{3}Chl disappearance (510 nm absorption) due to ET from $(p\text{-}CH_3OC_6H_4)_3N$, $(C_6H_5)_3N$, or other amines was equal to that of the formation of $(p\text{-}CH_3OC_6H_4)_3N^{\bullet+}$, $(C_6H_5)_3N^{\bullet+}$ detected at an appropriate wavelength [720 nm for $(p\text{-}CH_3OC_6H_4)_3N^{\bullet+}$ and 650 nm for $(C_6H_5)_3N^{\bullet+}$] (Figure 2). In the presence of ketenes, the rate of 510 nm ^{3}Chl absorption decay was correspondingly higher. The yield of amine radical cations was lower in the presence of ketene due to the decrease in contribution from the direct amine oxidation

by ^{3}Chl. The decrease in amine radical cation concentration was higher at higher concentrations of ketene (Figure 3 and 4). As expected, when the oxidation potential of the amine was higher than that of ketene, no ammine radical cation formation was detected. The triplet *p*-chloranil//ketene//amine ET kinetics were in a qualitative agreement with the computations based on the expected kinetic scheme (Scheme 4 and Figure 1).

It was found that diethyl ketene radical cation oxidized tris(methoxyphenyl)amine and N-methyl, N,N-diphenylamine, and N,N-diphenyl-1,4-phenylenediamine and 10-methylphenotiazine (Figure 3). Indeed, even when the concentration of ^{3}Chl was reduced to zero by the reactions (Scheme 1), the concentration increase of radical cation of tris(*p*-methoxyphenyl)amine continued, apparently due to ET from amine to diethyl ketene cation radical. Similar behavior was observed with N-methyl, N,N-diphenylamine.

For D_1 and D_2 with similar oxidation potentials, the ET rate by the reaction $D_1^{\bullet+} + D_2 \rightarrow D_1 + D_2^{\bullet+}$ would be at or near zero, and the consecutive competitive ET kinetics would be controlled by ^{3}Chl $+ D_2 \rightarrow$ Chl$^{\bullet-} + D_2^{\bullet+}$ reaction rate. Consequently, after conversion of most ^{3}Chl to Chl$^{\bullet-}$, continued formation of $D_2^{\bullet+}$ would not occur.
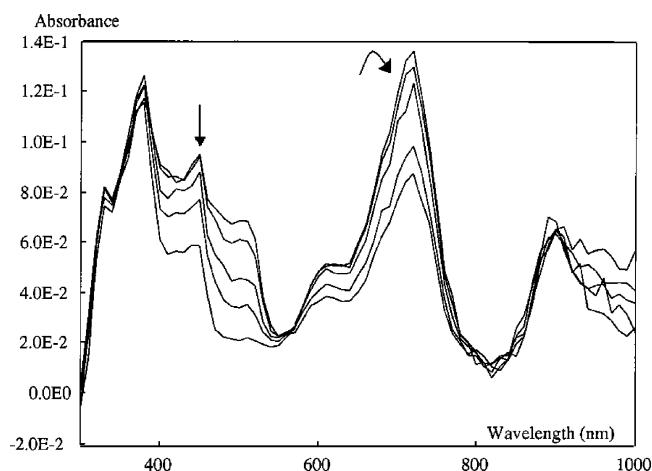

Figure 2. Change in the absorption spectrum of solution of 10^{-3} M *p*-chloranil, 10^{-3} M diethyl ketene, and 10^{-4} M tris(methoxyphenyl)-amine, following laser pulse irradiation at 355 nm.
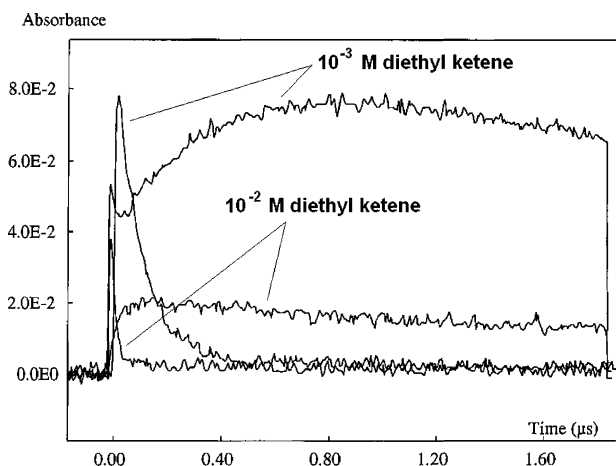
Competitive Consecutive Electron Transfer

J. Phys. Chem. A, Vol. 110, No. 51, 2006 **13813**

Figure 3. Kinetics of (p-CH$_3$OC$_6$H$_4$)$_3$N$^{\bullet+}$ radical cation formation and ^{3}Chl decay as a function of diethyl ketene concentration. The detection was conducted at the absorption maximum of ^{3}Chl, 510 nm, and tris-(methoxyphenyl)amine cation radical, 720 nm.
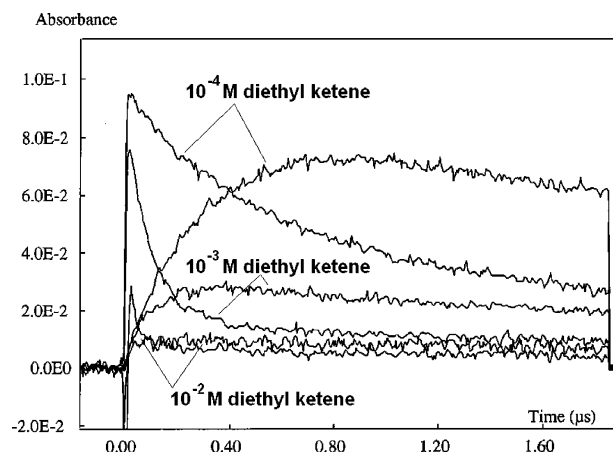

Figure 4. Kinetics of (C$_6$H$_5$)$_3$N$^{\bullet+}$ radical cation formation and ^{3}Chl decay as a function of diethyl ketene concentration. The detection was conducted at the absorption maximum of ^{3}Chl, 510 nm, and triphenyl amine radical cation, 650 nm. Initial, almost vertical, portion of ^{3}Chl absorption decay curve in the presence of 10^{-3} and 10^{-2} M was not recorded due to scope trace response peculiarity.

This type of kinetics was observed for diethyl ketene and triphenyl amine system indicating similar oxidation potentials (Figure 4). The oxidation potential of triphenyl amine in acetonitrile was computed according to eq 3 to be ≈5.36 eV. Thus, diethyl ketene oxidation potential should be around 5.36−≈5.4 eV. The oxidation potential of dimethyl ketene based on earlier reports was around 5.40 eV (Table 1). The change from methyl to ethyl substituents on ketene was not expected to significantly alter the oxidation potential, confirming the validity of the determination. It appears that the competitive consecutive ET approach yields results consistent with those obtained by other methods.

Ethyl phenyl ketene and diphenyl ketene and their radical cations were detected by well-resolved absorption spectra directly, and kinetics of ET involving these molecules were monitored by absorption of ketenes, not amine radical cations (Figure 5 and 6). It was found that neither ethyl phenyl ketene nor diphenyl ketene oxidized either (C$_6$H$_5$)$_3$N or (p-CH$_3$-OC$_6$H$_4$)$_3$N. Phenyl ethyl ketene and diphenyl ketene radical cations did not oxidize amines with even lower oxidation potentials, such as 10-methylphenothiazine (I_s = 4.84 eV). These results agree with the data calculated using published gas-phase data (eqs 1−3). Indeed, the calculated oxidation potential of
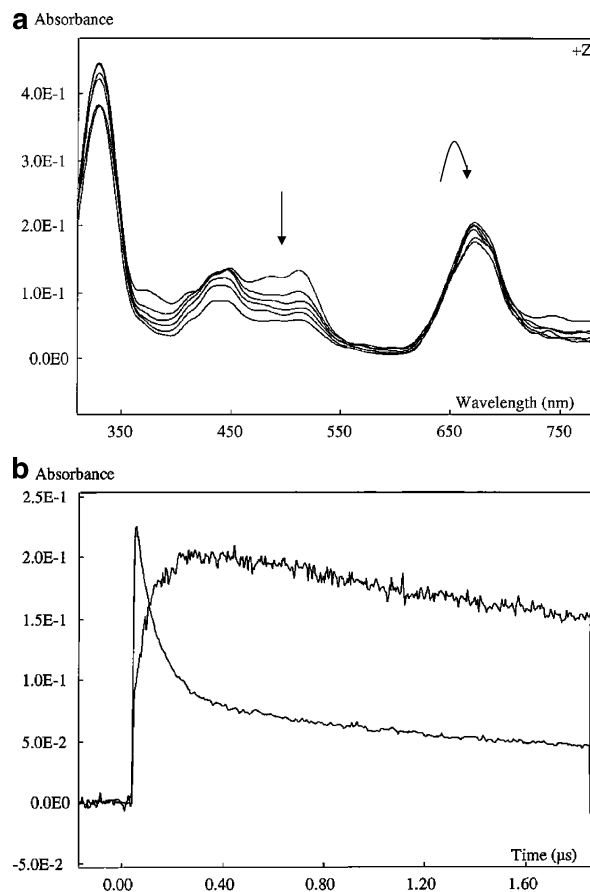

Figure 5. (a) Change in the absorption spectra of solution of 10^{-3} M p-chloranil and 10^{-3} M diphenyl ketene, following laser pulse irradiation at 355 nm. (b) Kinetics of ^{3}Chl decay (detected at 510 nm) and diphenyl ketene radical cation formation (detected at 650 nm) following 355 nm laser pulse irradiation.

diphenyl ketene in acetonitrile solution was 4.64 eV (Table 1), lower than 4.84 eV reported for 10-methylphenothiazine.

The reported difference between oxidation potentials of ketene and methyl ketene was 0.65 ≈0.6 eV,[46] while the reported difference between methyl ketene and dimethyl ketene was 0.57 ≈0.6 eV.[46] Similarly, our computations based on published data indicated that methyl group substitution in ketene and methyl ketene decreased their oxidation potentials by ≈0.6 eV (Table 1). It can be expected that electron donation by ethyl group would be less or equal to that from the methyl group. Indeed, the oxidation potential of diethyl ketene was computed to be 5.36 eV while that of dimethyl ketene was 5.40 eV (Table 1). The oxidation potential of phenyl ketene was computed based on gas-phase oxidation potential to be 5.10 eV; thus, one may expect the oxidation potential for phenyl ethyl ketene to be ≈4.5 eV (5.10−0.6 eV). The oxidation potential of diphenyl ketene was derived to be 4.64 eV (Table 1). The experimentally observed oxidation kinetics apparently reflected a slightly higher oxidation potential of diphenyl ketene, relative to that of phenyl ethyl ketene. Indeed, the experimentally detected rate of diphenyl ketene oxidation by ^{3}Chl (Figure 5b) is lower than the rate of diphenyl ethyl ketene oxidation by ^{3}Chl (Figure 6b). These low oxidation potentials are responsible for the absence of consecutive ET from the selected amine donors to diphenyl ketene and phenyl ethyl ketene. These data confirmed a validity of the consecutive ET approach.

Schmittel and Seggern reported values of cyclic voltammetry peak current, E_p, measured relative to SCE electrode for p-methoxyphenyl methyl ketene E_p = 0.91 eV and for p-
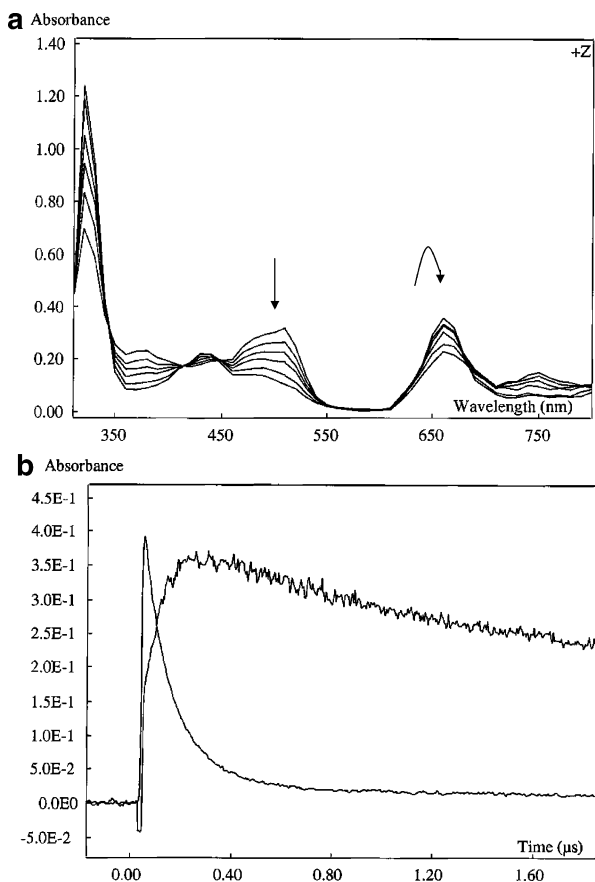
Figure 6. (a) Change in the absorption spectra of solution of 10^{-3} M *p*-chloranil and 10^{-3} M phenyl ethyl ketene, following laser pulse irradiation at 355 nm. (b) Kinetics of ^{3}Chl decay (detected at 510 nm) and phenyl ethyl ketene radical cation formation (detected at 650 nm) following 355 nm laser pulse irradiation.

methylphenyl methyl ketene, $E_p = 1.11$ eV.[55,56] Considering that for equilibrium processes $E_{1/2} = E_p + 1.1(RT/nF) = E_p + 1.1 \times 0.0592$,[50] the Schmittel and Seggern results would yield for *p*-methoxyphenyl methyl ketene $E_{1/2} = 0.98$ eV, and for *p*-methylphenyl methyl ketene, $E_{1/2} = 1.18$ eV. These values are of the same order of magnitude as the values of Table 1. Indeed, our calculations yield for dimethyl ketene $E_{1/2} = 0.94$ eV, for methyl ketene $E_{1/2} = 1.49$ eV, and for phenyl ketene $E_{1/2} = 0.72$ eV relative to SCE, based on difference with pyridine values (Table 1).

Consecutive ET kinetics results outlined above suggested that the diethyl ketene oxidation potential was higher than that of tris(methoxyphenyl)amine and likely close to that of triphenyl amine. These results were in agreement with those of Table 1.

Attempts to use nitrogen-containing electron donors with lower oxidation potentials, such as N,N,N,N-tetramethylphenylenediamine, were complicated by the formation of strong ground-state charge transfer complexes with *p*-chloranil and consequent charge transfer-initiated polymerization of diphenyl ketene and ethyl phenyl ketene, resulting in precipitation of polyester.[57]

Conclusions

We devised and used a method of deduction of IPs of unstable species based on the observation of the kinetics of competitive and consecutive ET from several species. The method was based on finding a series of competitive, consecutive ET reactions for oxidation and reduction of an unstable molecule with unknown IP. In this technique, transient species with higher

electron affinity than unknown are created by laser flash photolysis (pulsed radiolysis can be used as well[40]) and are reduced by the ET from the unknown molecule. The unknown is, in turn, reduced by ET from the species with known oxidation potential. Oxidation potentials of unknown species are found by matching with known oxidation potentials of ē-donor and ē-acceptor (Scheme 5). The method is particularly useful for finding IPs of unstable species in nonaqueous solutions.

Observed consecutive competitive ET kinetics are in qualitative agreement with those obtained by numerical solution of differential equations describing kinetics of consecutive parallel reactions. Agreement between the values obtained by consecutive competitive ET kinetics method, computed values, and reported experimental results suggested a validity of our approach to measuring oxidation potentials of unstable species in solution. Naturally, the same approach can be applied to any species that can enter into a series of competitive consecutive ET reactions.

The technique can be reversed, to determine the IPs of the electron donors, by oxidation potential of the molecules forming cation radical. Indeed, the method of consecutive ET can be considered as a competitive ET spectroscopy, where the energy levels of reactive transients are marked by the IPs of other molecules (Scheme 5). Consecutive competitive ET may be modified to study the solvent contribution to ET as well.

While applying the technique, one must keep in mind that the low rate of ET may be due to small or large differences in oxidation potentials of reagents (Marcus[13,58] or Rehm–Weller[58,59] portions of falloff curve). Considering the difficulties in achieving the conditions under which one could reach a large energy difference portion of the falloff,[1,40] the consecutive competitive ET method is rather safely applicable. Because of a fast increase in the rate of ET with the difference in IPs of the donor and acceptor,[1,13,14,58,59] one may expect an error of 0.2 eV in application of the consecutive ET method.

The application of the method to the determination of the IPs of substituted ketenes in acetonitrile solutions yielded the values consistent to those determined by other techniques or deduced by calculations. Thus, it was found that the IP of diethyl ketene in acetonitrile solution was 5.4 eV, and ethyl phenyl ketene was ≤4.8 eV. The results for diphenyl ketene are consistent with the value of IP in acetonitrile, of 4.6 eV, that we computed.

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Competitive Consecutive Electron Transfer

J. Phys. Chem. A, Vol. 110, No. 51, 2006 **13815**

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