Electron-Transfer Mechanisms with Photoactivated Quinones. The Encounter Complex versus the Rehm−Weller Paradigm

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Abstract: Photoexcited quinones (**Q***) are efficiently quenched by polymethylbenzenes (ArH) via electron transfer (ET). However, the second-order rate constants (k_2) exhibit Rehm−Weller (outer-sphere) dependence on the free energy (ΔG_{ET}), despite our new findings that the quenching occurs via a series of rather strong encounter complexes [**Q***, ArH] with substantial (charge-transfer) bonding. The relatively high formation constants (K_{EC}) of the encounter complexes indicate that any mechanistic interpretation of the driving-force dependence of the observed rate constants is highly ambiguous since k_2 must be a composite of K_{EC} and the intrinsic rate constant (k_{ET}) for electron transfer within the intermediate (inner-sphere) complex. As such, the reorganization energies extracted from Rehm−Weller plots lack thermodynamic significance. On the other hand, the unambiguous driving-force dependence of k_{ET} represents a unique example for the "normal" Marcus behavior of the endergonic electron transfer between the donor/acceptor pair in van der Waals contact as extant in the encounter complex.

Introduction

Fluorescence quenching processes that occur via an electron-transfer mechanism are commonly evaluated using the Rehm−Weller correlation[1,2] which relates the second-order rate constants to the free-energy change (ΔG_{ET}) of the electron-transfer step. Thus, electron-transfer rate constants are frequently calculated for donor/acceptor systems with known redox potentials and excited-state energies,[3] and redox potentials of excited-state and ground-state species are estimated from the rate constants of quenching processes with donors and acceptors with well-known redox potentials.[4] The free-energy correlation introduced by Rehm and Weller[1,2] is an empirical equation to fit the observed driving-force dependence of the fluorescence quenching rate constants. However, the underlying reaction scheme is adopted from the kinetic description of an outer-sphere electron transfer involving purely diffusional encounters between weakly coupled donors and acceptors.[5−7] As such, Rehm and Weller concluded that an intermediate formation of excited complexes[8] must be excluded from the electron-transfer mechanism of the quenching process that follows their correlation.[1]

The question whether excited charge-transfer complexes (or exciplexes) are or are not crucial intermediates in electron-transfer quenching reactions is as old as the Rehm−Weller relationship itself. In particular, the frequent observation of exciplex emissions[8,9] upon photoexcitation of donors and acceptors challenges the general validity of the "outer-sphere" model, and recent fluorescence-quenching studies in acetonitrile even question its suitability in highly polar media.[10] As a result, an alternative mechanism for fluorescence quenching in polar media has been proposed to account for long-lived exciplexes with formation constants that are much greater than those for diffusional encounters.[11] In a recent study,[12] we investigated the quenching reactions of a series of donor/acceptor systems that experience strong complex formation between the excited acceptor and the donor quencher prior to electron transfer. Thus, photoexcited quinones (**Q***) and polymethylbenzene donors (ArH) form encounter complexes[13] with formation constants up to 200 M^{-1} in various solvents of different polarity, as determined by time-resolved absorption measurements on the picosecond/nanosecond time scale. Most importantly, the ab-

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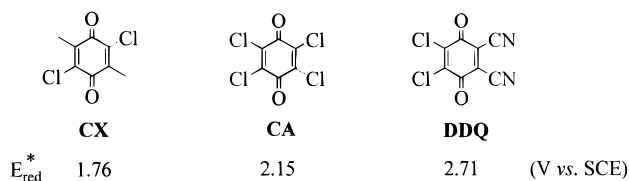
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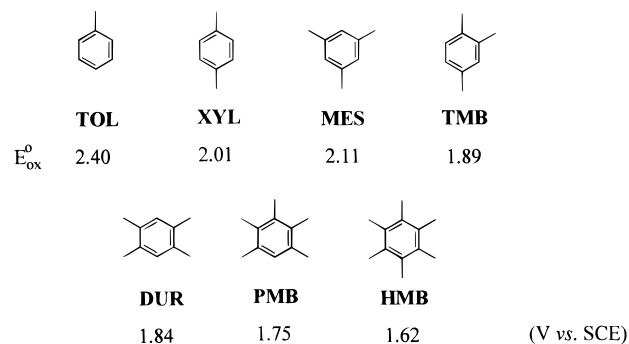
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Chart 1

Quinone Acceptors (Q*)

	CX	**CA**	**DDQ**	
E_{red}^{*}	1.76	2.15	2.71	(V *vs.* SCE)

Polymethylbenzene Donors (ArH)

	TOL	**XYL**	**MES**	**TMB**
E_{ox}^{o}	2.40	2.01	2.11	1.89

	DUR	**PMB**	**HMB**	
	1.84	1.75	1.62	(V *vs.* SCE)

sorption spectra of the intermediate [**Q***, ArH] complexes exhibit characteristic near-IR absorptions, the analysis of which points to high degrees of charge transfer.[14] Thus, these donor/acceptor systems clearly do not meet the criterion set by a weak-coupling limit for outer-sphere electron transfer.[5]

In this study, we now examine an extended series of poly-methylbenzene donors (see Chart 1) to scrutinize the driving-force (ΔG_{ET}) dependence of the electron-transfer quenching of the excited quinone acceptors. We will show that, despite the strong donor/acceptor interactions between photoexcited quinones and polymethylbenzenes,[12] the quenching rate constants can follow a driving-force dependence that is readily fitted to the Rehm−Weller relationship.[1,2] As such, the data presented here will demonstrate that Rehm−Weller-type free-energy relationships cannot provide conclusive evidence for the outer-sphere electron-transfer mechanism. Indeed, we will show that, due to the two-step quenching mechanism, the second-order rate constants are in fact composite quantities. Thus, the ambiguous driving-force dependence raises serious questions about the validity of reorganization energies formally extracted from the Rehm−Weller plots. Since the driving-force dependence of the intrinsic electron transfer within the encounter complex is conjectural, we describe how it may be used to verify electron-transfer theories.

Results

I. Electron-Transfer Quenching of Photoexcited Quinones by Polymethylbenzene Donors.
Photoexcitation of the quinones (**Q** in Chart 1) with a 10-ns laser pulse at 355 nm generated the

quinones in their excited triplet states (**Q***) with unit efficiency in acetonitrile solution.[12,16] The characteristic absorption spectrum of **Q***[17] decayed to the spectral baseline on the microsecond time scale with rate constants of $k_d < 5 \times 10^4$ s^{-1}.[18] However, in the presence of the aromatic donors (ArH in Chart 1), **Q*** decayed significantly faster, and the concomitant formation of the quinone anion radical (**Q**$^{•-}$)[19] and the arene cation radical (ArH$^{•+}$)[20] was observed with identical (first-order) rate constants for **Q*** decay and ion formation. Quantitative analysis of the time-resolved absorption spectra established the formation of the ion radicals **Q**$^{•-}$ and ArH$^{•+}$ to occur in a 1:1 ratio with unit efficiency,[12] *i.e.*

$$\mathbf{Q^*} + \text{ArH} \xrightarrow[\text{(CH}_3\text{CN)}]{k_2} \mathbf{Q^{\bullet-}} + \text{ArH}^{\bullet+} \qquad (1)$$
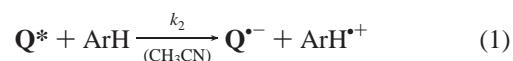
A. Kinetic Evaluation Using the Pseudo-First-Order Approximation. The kinetics of the electron-transfer quenching of **Q*** in eq 1 was examined by monitoring the decay of **Q*** (or the simultaneous growth of **Q**$^{•-}$ and ArH$^{•+}$) as a function of added arene. Figure 1A shows a typical plot of the observed (first-order) rate constant (k_{obs}) for the decay of **Q*** versus [ArH] as exemplified by the electron-transfer quenching of photoexcited dichloroxyloquinone (**CX***) by 1,2,4-trimethylbenzene (**TMB**) in acetonitrile. Thus, for concentrations [**TMB**] < 0.02 M, a linear dependence of k_{obs} on the arene concentration was obtained, and the slope of the pseudo-first-order plot yielded the second-order rate constant $k_2 = 4 \times 10^7$ M^{-1} s^{-1} for the electron transfer from **TMB** to **CX*** (compare eq 1). A slightly lower value of $k_2 = 1.5 \times 10^7$ M^{-1} s^{-1} was obtained for the same quenching reaction in dichloromethane,[21] and the k_2 values for the other quinone/arene combinations in acetonitrile and dichloromethane solution are compiled in Table 1.

B. Kinetics Evaluation Including the Preequilibrium Step. At higher (>0.02 M) arene concentrations, k_{obs} did not increase linearly with [ArH], but approached a plateau value for [**TMB**] > 0.6 M (see Figure 1A). Such a saturation (asymptotic) behavior of k_{obs} was symptomatic of a preequilibrium intermediate[22] between the excited quinone and the aromatic donor, which

(13) (a) Complexes between excited acceptors and donors (in the ground state) are also termed "exciplexes".[8−11] Since the term exciplex is frequently used in a wider, but rather ambiguous way that includes both charge-transfer complexes in the excited state (as defined here) as well as ion−radical pairs,[13b,c] we avoid this terminology to minimize confusion. (b) Levin, P. P.; Kuzmin, V. A. *Russ. Chem. Rev.* **1987**, *56*, 307. (c) Tahara, T.; Hamaguchi, H.-O. *J. Phys. Chem.* **1992**, *96*, 8252. See also ref 30.

(14) On the basis of Mulliken theory,[15] the degree of charge transfer can be estimated from the formation enthalpy (ΔH_f) and the absorption maximum ($h\nu_{CT}$) of the charge-transfer complex as $(b/a)^2 \cong -\Delta H_f/(h\nu_{CT})$. See: (a) Ketalaar, J. A. A. *J. Phys. Radium* **1954**, *15*, 197. (b) Tamres, M.; Brandon, M. *J. Am. Chem. Soc.* **1960**, *82*, 2134. (c) See also Rathore et al. in ref 12.

(15) Mulliken theory describes the wave function (Ψ_{AD}) of a charge-transfer complex primarily as the sum of the dative (bonding) function (ψ_1) and the "no-bond" function (ψ_0), *i.e.*, $\Psi_{AD} = a\ \psi_0(\text{A,D}) + b\ \psi_1(\text{A}^-,\text{D}^+) + ...$ See: (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600. (b) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (c) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(16) (a) Gschwind, R.; Haselbach, E. *Helv. Chim. Acta* **1979**, *62*, 941. (b) Kemp, D. R.; Porter, G. *J. Chem. Soc. (D)* **1969**, 1029. (c) Porter, G.; Topp, M. R. *Proc R. Soc. London* **1970**, *A315*, 163. (d) Kobashi, H.; Gyoda, H.; Morita, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1731.

(17) The transient spectrum of the triplet excited states of **CA** and **CX** exhibit double maxima at 380 and 510 nm and at 370 and 500 nm, respectively.[12,16] The transient absorption spectrum obtained upon 10-ns laser excitation (at 355 nm) of **DDQ** in acetonitrile exhibits a single absorption band centered at 640 nm.
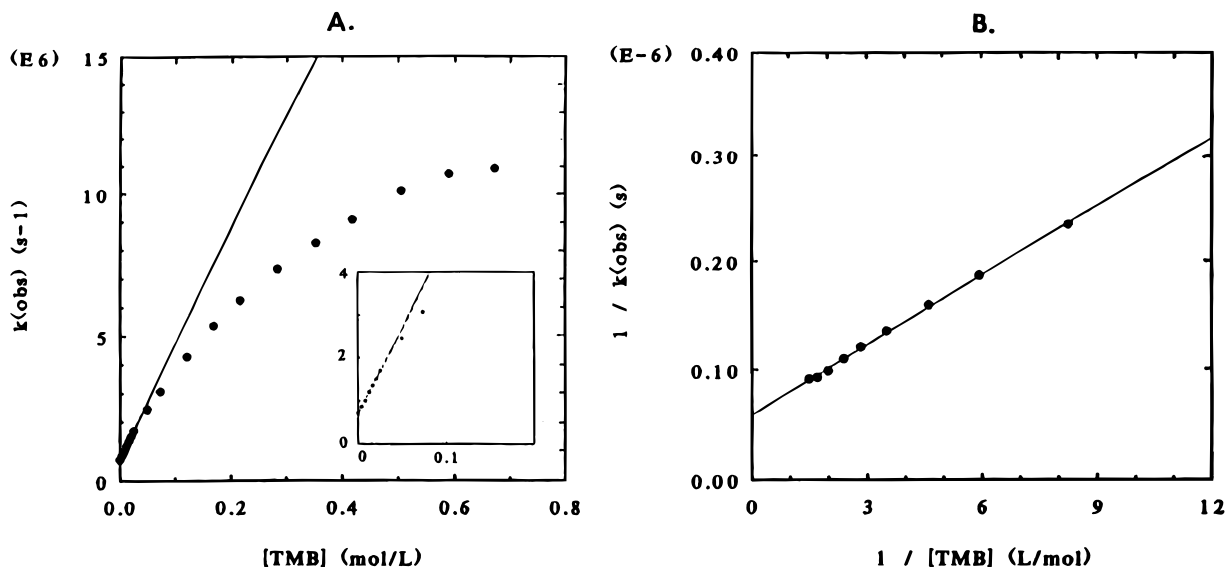
(18) Hubig, S. M. Unpublished results. See also ref 16a.

(19) (a) The anion radicals of **CA**, **CX**, and **DDQ** absorb at 450 nm,[19b] 430 nm,[12] and 440/600 nm,[19c] respectively. (b) André, J. J.; Weill, G. *Mol. Phys.* **1968**, *15*, 97. (c) Desbène-Monvernay, A.; Lacaze, P. C.; Cherigui, A. *J. Electroanal. Chem.* **1989**, *260*, 75.

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(21) In dichloromethane solution, the quenching of **Q*** by polymethylbenzenes (ArCH$_3$) results in the formation of semiquinone (**QH**$^•$) and benzyl (ArCH$_2$$^•$) radicals. However, salt-effect studies unambiguously show that the hydrogen transfer occurs via (rate-determining) electron transfer followed by fast proton transfer. See: Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 2826.

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Figure 1. (A) Saturation (asymptotic) behavior of the observed (first-order) rate constants for the electron-transfer quenching of **CX*** by 1,2,4-trimethylbenzene (**TMB**) in acetonitrile and (B) its double-reciprocal evaluation according to eq 3. The inset in (A) magnifies the linear portion of the plot for [**TMB**] < 0.02 M.

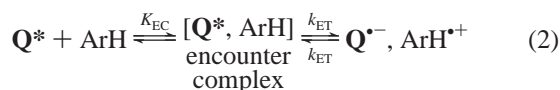**Table 1.**   Kinetic Parameters for the Electron-Transfer Quenching of Photoexcited Quinones by Polymethylbenzene Donors

Q*/ArH[a]	ΔG_{ET}[b] [eV]	solvent[c]	k_2[d] [10^6 M^{-1} s^{-1}]	K_{EC}[e] [M^{-1}]	k_{ET}[f] [10^6 s^{-1}]	$K_{EC}k_{ET}$[g] [10^6 M^{-1} s^{-1}]
CX*/MES	+0.49	A	4.0	1.7	2.3	3.9
		D	5.3	4.0	2.1	8.4
CX*/XYL	+0.44	A	6.3	4.3	2.4	10.3
		D	2.2	2.4	1.9	4.6
CX*/TMB	+0.27	A	40	2.7	17	46
		D	15	4.0	4.5	18
CA*/TOL	+0.25	A	7.0	0.9	11	10
		D	15	8.7	2	17
CX*/DUR	+0.21	A	2600	15	170	2550
		D	300	14	27	378
CX*/PMB	+0.13	D	1500	39	55	2145
CX*/HMB	±0	A	5140	h	h	h
		D	5500	67	110	7370
CA*/MES	−0.04	A	4400	h	h	h
		D	1150	30	36	1080
CA*/XYL	−0.09	A	5400	h	h	h
		D	1200	<10	120	1200
CA*/DUR	−0.32	D	12000	h	h	h
CA*/HMB	−0.53	A	8000	h	h	h
		D	12000	h	h	h
DDQ*/HMB	−1.02	A	21000	h	h	h

[a] See Chart 1. *[b]* Free energy of the electron-transfer reaction as calculated using eq 5. *[c]* A = acetonitrile, D = dichloromethane. *[d]* Rate constant for bimolecular electron transfer as determined from the slope of the initial linear portion of the kinetics plots such as in Figure 1A. *[e]* Equilibrium constant (±10−20%) for encounter-complex formation as determined using eq 3. *[f]* Intrinsic (first-order) rate constant (±10−20%) for electron transfer within the encounter complex as determined using eq 3. *[g]* As determined from the slope of the double-reciprocal plot such as in Figure 1B (see eq 3). *[h]* Not determined owing to insufficient curvature in the kinetics plots (see text).

was previously identified as the encounter complex [**Q***, ArH],[12,13] *i.e.*

Scheme 1

$$\mathbf{Q^*} + \mathrm{ArH} \underset{}{\overset{K_{EC}}{\rightleftharpoons}} \underset{\substack{\text{encounter}\\\text{complex}}}{[\mathbf{Q^*}, \mathrm{ArH}]} \underset{k_{ET}}{\overset{k_{ET}}{\rightleftharpoons}} \mathbf{Q^{\bullet-}}, \mathrm{ArH}^{\bullet+} \qquad (2)$$

Thus, the limiting value of k_{obs} at high donor concentrations

corresponded to the intrinsic rate constant (k_{ET}) of the electron transfer within the encounter complex. [Note that we find that back electron transfer (k_{-ET}) in Scheme 1 is negligible for the donor/acceptor couples in Chart 1 owing to the high ion−radical yields (ϕ_{ion} > 0.9).[41]] Accordingly, the curved kinetics plots such as in Figure 1A were evaluated in a double-reciprocal (linearized) representation[12] (see Figure 1B), from which the preequilibrium constant (K_{EC}) and the intrinsic electron-transfer rate constant (k_{ET}) were extracted (see eq 3[23]). [Note that the direct relationship in eq 3 is valid under the conditions in which (i) the natural decay (k_0) of **Q*** (in the absence of donors) is negligibly slow as compared to the electron-transfer step (k_{ET})[12,18] and (ii) the preequilibrium step (K_{EC}) in eq 2 is established much faster than the follow-up electron transfer.[23]] Thus, the double-reciprocal plot in Figure 1B yielded K_{EC} = 2.7 M^{-1} and k_{ET} = 1.7 × 10^7 s^{-1} for the electron transfer from **TMB** to **CX*** in acetonitrile. The same kinetic evaluation in dichloromethane solution yielded K_{EC} = 4.0 M^{-1} and k_{ET} = 4.5 × 10^6 s^{-1}, and the K_{EC} and k_{ET} values for the other quinone/arene combinations in acetonitrile and dichloromethane solutions are listed in Table 1. The most striking result of this kinetic evaluation was that the K_{EC} values in Table 1 deviated substantially from the unit value[24] calculated for purely diffusional encounters (see the Discussion).
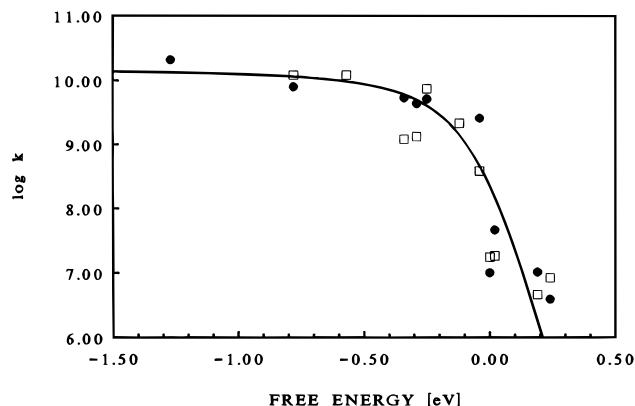
(23) (a) The following double-reciprocal relationship between the observed rate constant (k_{obs}) and the arene concentration ([ArH]) was applied:[12]

$$\frac{1}{k_{obs}} = \frac{1}{k_{ET}} + \frac{1}{K_{EC}k_{ET}}\frac{1}{[\mathrm{ArH}]} \qquad (3)$$

(b) For the general kinetics basis of eq 3, see: Espenson, J. D. *Chemical Kinetics and Reaction mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; p 89f. (c) For the decay kinetics of photoexcited quinones, see: Kobashi, H.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1975. (d) Equation 3 is based on the assumptions that $k_{-d} \gg k_{ET}$ and $k_{-d} + k_d$ [ArH] > $2k_{ET}(k_{-d} − k_d$[ArH]), with k_d and k_{-d} being the rate constants for diffusional formation and dissociation of the encounter complex, respectively.[23e] Both conditions are met even for the fastest electron transfers ($k_{ET} \cong 10^8$ s^{-1}). (e) Ware, W. R.; Watt, D.; Holmes, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 7853.

(24) The equilibrium constant K depends on the effective encounter distance R between the donor and the acceptor. For the encounter complex between uncharged species with distance R = 7 Å, the formation constant is estimated to be K = 0.9 M^{-1}. See: Eigen, M. *Z. Phys. Chem. N. F. (Frankfurt am Main)* **1954**, *1*, 176.

Figure 2. Rehm−Weller treatment of the free-energy (ΔG_{ET}) dependence of the second-order quenching rate constants (k_2) in acetonitrile (●) and dichloromethane (□) solution. The solid line represents the best fit of the data points according to eqs 6 and 7 with $\Delta G^{\ddagger}_{ET}(0) = 0.15$ eV.

C. Interdependence of k_2, K_{EC}, and k_{ET}. At low arene concentrations, eq 3[23] simplified to a linear correlation between k_{obs} and [ArH] to reveal the direct relationship between k_2 (in eq 1) and K_{EC} and k_{ET} (in eq 2), *i.e.*

$$k_{obs} = K_{EC}k_{ET}[\text{ArH}] = k_2[\text{ArH}] \qquad (4)$$

Thus, the second-order rate constants k_2 for electron transfer from ArH to **Q*** could be obtained from either the initial slope of the pseudo-first-order plot (see inset to Figure 1A) or the slope of the double-reciprocal plot (see Figure 1B) as the product $K_{EC}k_{ET}$ (compare columns 4 and 7 in Table 1). In other words, the second-order rate constant k_2 in eq 2 represented a composite quantity, the components of which we examined independently in terms of their driving-force dependence as follows.

II. Driving-Force (ΔG_{ET}) Dependence of k_2, K_{EC}, and k_{ET} for the Electron-Transfer Quenching of Photoexcited Quinones by Polymethylbenzenes. To study the driving-force dependence of the electron-transfer quenching of **Q*** by ArH in eqs 1 and 2, the free-energy change (ΔG_{ET}) was calculated according to eq 5, where E^0_{ox} is the oxidation potential of the
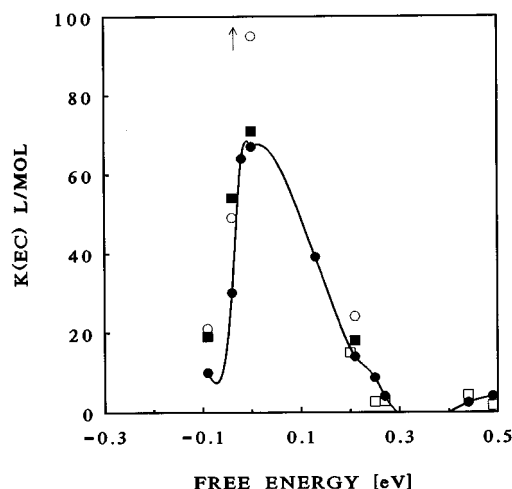
$$\Delta G_{ET} = E^0_{ox} - E^*_{red} + \text{constant} \qquad (5)$$

polymethylbenzene donor (ArH) and E^*_{red} is the reduction potential of the photoactivated quinone (**Q***) in Chart 1.[25]

A. Driving-Force Dependence of the Rate Constant k_2. The second-order rate constants k_2 in Table 1 varied over 4 orders of magnitude from the most endergonic electron-transfer couple (**CX*/MES**) to the most exergonic couple (**DDQ*/HMB**). Figure 2 demonstrates that the rate constants did not increase linearly with the exergonicity of the electron transfer, but a sharp increase over more than 3 orders of magnitude was observed in the endergonic region (0 eV < ΔG_{ET} < 0.5 eV) followed by

(25) (a) The reduction potential of the photoactivated quinones (E^*_{red}) is calculated as the sum of the triplet energy of the quinone ($E_T \cong 2.2$ eV)[26] and the reduction potential of the quinone in its ground state.[25b,c] See also ref 2. (b) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Dekker: New York, 1970. (c) Peover, J. E. *J. Chem. Soc.* **1962**, 4540. (d) For the oxidation potentials of the polymethylbenzenes in Chart 1, see: Howell, J. O.; Goncalvez, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968. (e) The Coulombic work term ($e^2/\epsilon R$) is assumed to be constant for all donor/acceptor combinations employed in this study.

(26) (a) Shcheglova, N. A.; Shigorin, D. N.; Yakobson, G. G. Y.; Tushishvili, L. Sh. *Russ. J. Phys. Chem.* **1969**, *43*, 1112. (b) Trommsdorff, H. P.; Sahy, P.; Kahane-Paillous, J. *Spectrochim. Acta* **1970**, *26A*, 1135. (c) Herre, W.; Weis, P. *Spectrochim. Acta* **1973**, *29A*, 203.

Figure 3. Bell-shaped free-energy (ΔG_{ET}) dependence of the formation constant K_{EC} for the encounter complex [**Q***, ArH] in acetonitrile (□), dichloromethane (●), chloroform (■), and carbon tetrachloride (○), partially based on the data in ref 41.

a mild increase of less than 1 order of magnitude over the entire exergonic region (−1.5 eV < ΔG_{ET} < 0 eV). This driving-force dependence was similar to that observed previously for the electron-transfer quenching of various aromatic donors and acceptors in the excited singlet state.[1−4] Despite the fact that our experimental conditions (*i.e.*, triplet quenching and equilibrium constants $K_{EC} \gg 1$) were significantly different from those for fluorescence-quenching experiments, we arbitrarily fitted our data to eq 6 (as illustrated in Figure 2), to probe the

$$k_2 = (2 \times 10^{10})/\{1 + 0.25[\exp(\Delta G_{ET}/RT) + \exp(\Delta G^{\ddagger}_{ET}/RT)]\} \text{ M}^{-1} \text{ s}^{-1} \quad (6)$$

general applicability of the Rehm−Weller relationship.[1,2] In eq 6, k_2 is the second-order (electron-transfer) rate constant and ΔG_{ET} and $\Delta G^{\ddagger}_{ET}$ are the free-energy change and the activation enthalpy of the electron transfer, respectively. The activation enthalpy $\Delta G^{\ddagger}_{ET}$ was taken as a monotonic function of ΔG_{ET} according to the standard Rehm−Weller formulation,[1,2] *i.e.*

$$\Delta G^{\ddagger}_{ET} = \{(\Delta G_{ET}/2)^2 + (\Delta G^{\ddagger}_{ET}(0))^2\}^{1/2} + \Delta G_{ET}/2 \quad (7)$$

where $\Delta G^{\ddagger}_{ET}(0)$ is the activation enthalpy at $\Delta G_{ET} = 0$. Since there was no substantial difference in the absolute values of k_2 and its driving-force dependence for the two solvents in Table 1, all the experimental data could be simulated with a single Rehm−Weller parameter, $\Delta G^{\ddagger}_{ET}(0) = 0.15$ eV (see the solid line in Figure 2).[27]

B. Driving-Force Dependence of K_{EC}. Figure 3 illustrates the driving-force dependence of the formation constant K_{EC} for the encounter complexes [**Q***, ArH] in eq 2. Thus, a bell-shaped correlation between K_{EC} and ΔG_{ET} was obtained in dichloromethane (filled circles) with a maximum value of $K_{EC} = 67$ M^{-1} at $\Delta G_{ET} = 0$ eV. Importantly, K_{EC} values close to unity were obtained in the endergonic free-energy region ($\Delta G_{ET} > 0.3$ eV) and in the exergonic region ($\Delta G_{ET} < -0.1$ eV). A similar bell-shaped correlation was observed previously in chloroform (filled squares) and carbon tetrachloride (open

(27) To achieve a satisfactory overlap between the experimental data and the Rehm−Weller simulations, all the experimental ΔG_{ET} values of Table 1 are shifted by $\alpha = -0.25$ eV. For a theoretical explanation of the shift parameter α in triplet-quenching experiments, see: Tamura, S.-I.; Kikuchi, K.; Kokubun, H.; Usui, Y. *Z. Phys. Chem. N. F. (Wiesbaden)* **1978**, *111*, 7.
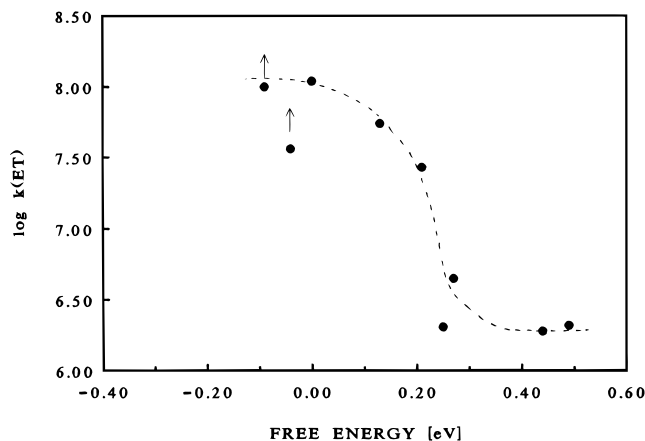
Figure 4. Normal free-energy (ΔG_{ET}) dependence of the intrinsic rate constant (k_{ET}) for electron transfer within the encounter complex in dichloromethane.

circles),[12] and the data points obtainable in acetonitrile[28] seem to follow the same trend (open squares).

C. Driving-Force Dependence of k_{ET}. Figure 4 shows the driving-force (ΔG_{ET}) dependence of the intrinsic rate constant k_{ET} for the electron transfer within the encounter complex of polymethylbenzenes and photoexcited quinones in dichloromethane. The k_{ET} values increased over 2 orders of magnitude in a sigmoidal function from the most endergonic electron-transfer couple (**CX*/MES**) with $\Delta G_{ET} = 0.49$ eV to the isergonic couple (**CX*/HMB**) with $\Delta G_{ET} = 0$ eV. In the exergonic region ($\Delta G_{ET} < 0$), the k_{ET} values were somewhat scattered around an (apparent) plateau value of $k_{max} \cong 10^8$ s^{-1}.[29]

Discussion

The interaction of photoexcited quinones (**Q***) with polymethylbenzenes (**ArH**) in acetonitrile leads to the formation of quinone anion radicals (**Q$^{\bullet-}$**) and polymethylbenzene cation radicals (**ArH$^{\bullet+}$**) with unit efficiency (see eq 1),[12] and thus represents a typical bimolecular electron-transfer quenching process.[21] Accordingly, current electron-transfer theories[1,2,5-7] predict the second-order rate constant (k_2) in eq 1 to show a characteristic dependence on the free-energy change (ΔG_{ET}) associated with the electron transfer from ArH to **Q***. On the other hand, time-resolved spectroscopic studies[12] reveal the electron transfer from the polymethylbenzene to the photoexcited quinone to proceed via an encounter complex[13] with a rather high formation constant K_{EC}. As a result, the kinetics of this electron-transfer quenching is more adequately described by a two-step mechanism as depicted in eq 2, which implies three parameters, viz., K_{EC} and the intrinsic rate constants k_{ET} and k_{-ET} of the electron transfer within the intermediate complex. This electron-transfer mechanism differs significantly from that of Rehm and Weller[1,2] and from that of Kuzmin[11] in the

description of the intermediate donor/acceptor complex. Thus, neither the purely diffusional encounters prior to electron transfer as implied by Rehm and Weller[1,2] nor the alternative exciplex formation by "gradual electron shift" as invoked by Kuzmin *et al.*[11] matches *our description of the encounter complex, which is best described as the excited-state counterpart of (ground-state) electron donor−acceptor (or charge-transfer) complexes.*[30] This encounter complex is the critical intermediate prior to electron transfer. Accordingly, any free-energy (or driving-force) consideration of the resulting two-step electron transfer (see eq 2) must include three kinetics parameters, viz., k_2, K_{EC}, and k_{ET}. As such, we now analyze their mechanistic relevance as follows.

I. Driving-Force Dependence of k_2 and Mechanistic Significance of the Rehm−Weller Correlation. First, we note that the driving-force dependence of the second-order rate constant (k_2) for electron-transfer quenching of photoexcited quinones by polymethylbenzenes can be satisfactorily accommodated by the Rehm−Weller correlation in Figure 2.[1,2] Furthermore, the only parameter that defines the shape of the driving-force dependence of k_2 in the Rehm−Weller formulation (see eqs 6 and 7) is the activation enthalpy $\Delta G^{\ddagger}_{ET}(0)$, which establishes both the position and the steepness of the falloff of k_2 in the endergonic region, whereas the plateau of $k_{2,max} \cong 2 \times 10^{10}$ M^{-1} s^{-1} in the exergonic region corresponds to the diffusional limit of the rate constant in bimolecular reactions.[31] For the electron-transfer quenching of photoexcited quinones, the best fit of the steep falloff of k_2 in the endergonic ΔG_{ET} range yields a reasonable value for the activation enthalpy of $\Delta G^{\ddagger}_{ET}(0) = 0.15$ eV.[1-4]

According to Rehm and Weller, a good agreement between the experimental quenching data and the free-energy correlation in eq 6 points to an outer-sphere electron-transfer mechanism, which must not involve the intermediate formation of excited charge-transfer complexes.[1] However, such a mechanistic conclusion applied to the quenching of the excited quinones is in striking contrast to the experimental findings in this study, viz., the observation of strong encounter complexes which exhibit substantial (charge-transfer) bonding between the polymethylbenzene donor and the quinone acceptor moieties.[12] In

(28) In acetonitrile, significant curvature in the kinetics plot such as that in Figure 1A is only obtained for $\Delta G_{ET} > 0.2$ eV, which allowed us to reliably extract values for K_{EC} and k_{ET} using the reciprocal evaluation in eq 3. The lack of sufficient curvature in the kinetics plots for $\Delta G_{ET} < 0.2$ eV is not likely to be caused by low K_{EC} values since no strong solvent dependence of K_{EC} is evident in Table 1 (see also ref 12), but it arises from the plateau values of k_{obs} which severely exceeded the time resolution of the 10-ns laser pulse ($k_{ET} \gg 10^8$ s^{-1}). See also ref 12.

(29) Since in the driving-force region of the plateau (-0.1 eV $< \Delta G_{ET}$ < 0 eV) the electron-transfer quenching rate constants ($k_2 \approx 10^9$ M^{-1} s^{-1}; see Table 1) are clearly below the diffusion limits, the value of $k_{ET} \cong 10^8$ s^{-1} is most likely not the fastest intrinsic electron-transfer rate constant and may be exceeded substantially in diffusion-controlled electron transfers at highly exergonic driving forces.

(30) (a) Our definition more closely matches Mataga's and Turro's description of an exciplex (see ref 23c and Figure 2 in ref 3f, respectively). Unfortunately, the clear picture of excited charge-transfer complexes has been "blurred" over the years,[13] and we thus prefer the less ambiguous term "encounter complex", which is experimentally characterizable by its intrinsic absorption band ascribed to charge-transfer transitions.[8,12] Similar to ground-state EDA complexes, the formation constants and the degree of charge transfer may vary dramatically with the donor/acceptor properties, the solvent, and also steric effects.[12,41] Whether or not they can be observed spectroscopically will mainly depend on their lifetimes and thus on the rate of the subsequent electron transfer. Thus, for diffusion-controlled electron transfers in the highly exergonic free-energy region, encounter complexes with very short lifetimes (*i.e.*, $K_{EC} \ll 1$) comparable to contact charge-transfer complexes (Tamres; et al. In *Molecular Complexes*; Foster, R. F., Ed.; Academic Press: New York, 1979; Vol. 2, p 352) are expected. As such, our operational definition of the encounter complex can be directly verified by experiment (such as time-resolved absorption spectroscopy) and has theoretical underpinnings based on Mulliken theory.[15] (b) As a consequence of this description of the encounter complex, its decay pathway by electron transfer is straightforwardly given by a simple mechanism in Scheme 1 (eq 2) and the kinetics readily described by three parameters, K_{EC}, k_{ET}, and k_{-ET}. [Note that $k_{-ET} \cong 0$ is omitted in eq 3.] By contrast, the fate of the long-lived exciplex according to Kuzmin[11] is related to the experimental observation of ion radicals. When ion radicals are not observed, the exciplex decays directly to the ground state (without the completion of the electron transfer and the intervention of ion radicals). Alternatively, the observation of ion radicals is attributed to ionic dissociation of the exciplex which necessitates complete electron transfer similar to that in Scheme 1.

(31) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism,* 2nd ed.; Wiley: New York, 1981; p 239f.

fact, the presence of such charge-transfer complexes as excited intermediates implies that the concept of outer-sphere electron transfer is *not* applicable to the quenching reactions of quinones. Thus, the above-delineated (contradictory) conclusions on the electron-transfer mechanism demonstrate that free-energy correlations of quenching rate constants that are arbitrarily fitted to the Rehm−Weller equation do not provide any evidence to either rule out the formation of intermediate excited complexes or to draw any other conclusions about the degree of bonding in the electron-transfer transition state.

II. Driving-Force Dependence of K_{EC} and Its Consequences for the Rehm−Weller Correlation. We now turn to the free-energy dependence of the formation constants K_{EC} in Figure 3, which follows a bell-shaped function with a maximum at $\Delta G_{ET} = 0$. This remarkable driving-force dependence of K_{EC} can be readily explained on the basis of the electronic (charge-transfer) description of the encounter complexes [**Q***, ArH].[32] Thus, the stability of the complex between photoexcited quinone (**Q***) and polymethylbenzene (ArH) depends on the degree of mixing between the "local" excited state and the charge-transfer excited state of the complex, viz., {**Q***, ArH} ↔ {**Q**•−, ArH•+}, which is optimized when the two states are at equal energy levels. In fact, this condition is met for the [**CX***/HMB] couple since the energy of the charge-transfer state, viz., $E_{CT} = E^0_{ox}(\mathbf{HMB}) - E^0_{red}(\mathbf{CX}) = 2.13$ eV,[33] closely matches the energy of the photoexcited quinone, viz., $E_T(\mathbf{CX}) \cong 2.2$ eV,[26] and consequently $\Delta G_{ET} = E^0_{ox} - E^0_{red} - E_T \cong 0$. Accordingly, the formation of strong encounter complexes is particularly important for bimolecular electron-transfer reactions with free energies close to zero (-0.1 eV $< \Delta G_{ET} < 0.3$ eV), and K_{EC} values as high as 200 M^{-1} are in fact found in this free-energy region.[12] This finding has two important consequences for the mechanistic basis of the Rehm−Weller formulation as follows.

First, the Rehm−Weller correlation is based on an outer-sphere reaction scheme in which electron transfer occurs upon a purely diffusive encounter between the donor and the acceptor.[1,2,5] Thus, for any donor/acceptor combination, the equilibrium constant for the formation of the encounter complex is assumed to be close to unity,[24] which implies lifetimes of the diffusive encounters of less than 100 ps.[34a] The data on K_{EC} and k_{ET} reported here (see Table 1) prove both assumptions in their general form to be incorrect. Thus, the free-energy correlation as formulated in eq 6 is not generally applicable since it is not valid for strongly bound (long-lived) encounter complexes.[34b]

Second, we note that the second-order quenching rate constant (k_2) is a composite of K_{EC} and k_{ET} as described in eq 4. Since K_{EC} deviates substantially from unity and both K_{EC} and k_{ET}

exhibit independent and different driving-force dependencies (see Figures 3 and 4), the interpretation of the driving-force dependence of k_2 must be highly ambiguous, particularly in the endergonic region. The endergonic and slightly exergonic regions, however, are the most relevant free-energy regions since they cover the significant changes in k_2 which are simulated by the Rehm−Weller formulation. As a consequence, $\Delta G^{\ddagger}_{ET}(0)$ values or the related reorganization energies that are formally extracted from Rehm−Weller simulations lose thermodynamic significance.

Conclusions

Driving-Force Dependence of k_{ET} and Its Mechanistic Significance. The intrinsic rate constants k_{ET} in Figure 4 represent the (first-order) rate constants for the electron transfer within the initially formed encounter complex. These electron-transfer rate constants are by definition not affected by the preceding diffusional processes that establish the preequilibrium in eq 2, and thus may be directly compared with rate constants of other diffusion-free electron-transfer processes such as back electron transfer in ion−radical pairs[35,36] or intramolecular electron transfer between a donor and an acceptor molecule linked by a rigid spacer.[37] A variety of such donor/acceptor systems (in particular intramolecular donor−acceptor pairs[37] and solvent-separated ion−radical pairs[36]) have been successfully used to verify the bell-shaped driving-force dependence for electron-transfer rate constants predicted by Marcus theory.[5] Thus, in the "normal" region the rate constants increase with the exergonicity of the electron transfer until $-\Delta G_{ET}$ equals the reorganization energy (λ). Once the electron transfer becomes more exergonic ($-\Delta G_{ET} > \lambda$), the rate constants decrease in the "inverted" region. However, the rates of back electron transfer ($-$ET) in contact ion−radical pairs do not follow these predictions of Marcus theory. Instead, the rate constants (ln k_{-ET}) decrease linearly with decreasing free-energy change over a rather wide exergonic driving-force region (-3.0 eV $< \Delta G_{ET} < -0.5$ eV).[35] Unfortunately, owing to the experimental procedures for the generation of the ion−radical pairs,[38] the back electron transfer in contact ion−radical pairs is restricted to the exergonic free-energy region. In contrast, this study describes *endergonic* electron transfer between a donor and an acceptor molecule which are in close (van der Waals) contact.[39] For such electron-transfer processes, the

(32) Weller, A. Reference 9.

(33) The reduction potential of **CX** is $E^0_{red} = -0.51$ V[12] and the oxidation potential of **HMB** is $E^0_{ox} = 1.62$ V[25d] vs SCE.

(34) (a) For example, a unit equilibrium constant for diffusive association (k_d) and dissociation (k_{-d}), i.e., $K = k_d/k_{-d} = 1$, and a diffusion-controlled rate constant $k_d = 2 \times 10^{10}$ M^{-1} s^{-1} for the association process result in a dissociation constant of $k_{-d} = 2 \times 10^{10}$ s^{-1} which corresponds to a lifetime of 50 ps for the encounter complex. See also: Marcus, R. A. Reference 5a. (b) The high formation constants of the encounter complexes in this study may be related to the long lifetimes of the excited (triplet) quinones which allow multiple collisions with donors during their natural decay. However, high formation constants ($K \approx 40$ M^{-1}) are also found for various excited complexes in the singlet manifold[10c,11a,34c] (where the excited-state lifetimes are orders of magnitude shorter than those of the triplet quinones), and thus the relevance of the lifetimes is questionable. [Note that a direct comparison of encounter complexes with singlet and triplet quinone is not possible owing to the ultrashort lifetime ($\approx$10 ps) of singlet excited quinones. See: Hubig, S. M.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 2926.] (c) Nath, S.; Pal, H.; Palit, D. K.; Sapre, A. V.; Mittal, J. P. *J. Phys. Chem. A* **1998**, *102*, 5822.

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(38) Contact ion−radical pairs are generated by charge-transfer excitation of electron donor/acceptor complexes which effects the spontaneous transfer of an electron from the donor to the acceptor.[35] This photoinduced charge-separation process is strongly endergonic by nature, and thus the corresponding charge recombination or back electron transfer is exergonic.

(39) The charge-transfer transitions in the absorption spectra of the encounter complexes [**Q***, ArH] point to a strong orbital overlap between donor and acceptor molecule, which is achieved by close contact as observed in the analogous ground-state EDA complexes. See: Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393.

driving-force dependence in Figure 4 clearly reveals a normal region; *i.e.*, the rate constants increase with increasing driving force $-\Delta G_{ET}$.[5-7] Thus, we hope that the data presented here will provide a new proving ground (a) to study the direct (diffusion-free) electron transfer between donors and acceptors in van der Waals contact[39] over an endergonic as well as (slightly) exergonic free-energy range and (b) to test recent electron-transfer theories[40] that are not limited to the outer-sphere model, but consider significant bonding in the transition state of bimolecular electron transfer. On the other hand, in a separate study[41] we will demonstrate how the complications in the kinetics evaluation that are caused by the formation of encounter complexes with strong charge-transfer bonding (as described herein) can be circumvented by employing sterically encumbered electron-transfer substrates.

Experimental Section

Materials. Durene, pentamethylbenzene, hexamethylbenzene, chloranil, and dichlorodicyanobenzoquinone were obtained from Aldrich and purified by recrystallization from ethanol.[42] Mesitylene, *p*-xylene, and 1,2,4-trimethylbenzene (Aldrich) were purified by distillation. Toluene (reagent grade) was distilled from sodium and benzophenone under an argon atmosphere. Acetonitrile (reagent grade) was stirred over $KMnO_4$ and subsequently distilled from P_2O_5. Dichloromethane (reagent grade) was stirred over concentrated H_2SO_4, washed with aqueous bicarbonate, and distilled serially from P_2O_5 and from CaH_2 under an argon atmosphere. The synthesis and purification of 2,5-dichloroxyloquinone was described previously.[12]

Kinetic Measurements. The laser flash experiments were carried out using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (10 ns fwhm) and a kinetic spectrometer with a time resolution of less than 10 ns as described earlier.[12,43]

General Procedure. Upon 355-nm laser excitation of the quinone (ca. 5 mM) in acetonitrile or dichloromethane, the decay of the triplet quinone (**Q***) was observed at 500 nm in the presence of varying concentrations (10^{-4} to 10^{-1} M) of polymethylbenzene. The exponential decay was fitted to first-order kinetics, and lifetimes close to the time domain of the laser pulse were corrected by the (pythagorean) approximation $\tau_{corr} = (\tau^2_{meas} - \tau^2_{laser})^{1/2}$. The observed rate constants (k_{obs}) were plotted against the arene concentration. The slope of the linear (initial) portion of the pseudo-first-order plot yielded the bimolecular rate constant k_2 in Table 1 (see eq 1), and the kinetics of the entire (curved) plot is evaluated on the basis of eqs 2, 3, and 4. For the extracted K_{EC} and k_{ET} values (see Table 1), we estimate error limits of $\pm 10-20\%$ considering both the inherent numerical errors of double-reciprocal evaluations and the varying degree of curvature in the kinetics plots such as in Figure 1A. For additional details of the experimental procedures and the kinetics analysis, see Rathore et al. in ref 12.

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