Photoreduction of Chloranil by Benzhydrol and Related Compounds. Hydrogen Atom Abstraction vs Sequential Electron−Proton Transfer via Quinone Triplet Radical Ion−Pairs

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Received January 27, 1997⊗

Abstract: The photoreduction of chloranil (Q) to the hydroquinone (QH_2) in benzene by benzhydrols and by related arylmethanols has been investigated. The products of photooxidation of the benzhydrols are benzophenones, in lieu of formation of benzpinacols. Three distinct mechanisms of oxidation−reduction have been identified from quantum yield determinations and laser flash photolysis experiments, including quinone triplet quenching via H-atom and electron transfer paths. Direct excitation of ground state quinone complexes has also been investigated. The quenching of the triplet state of the quinone by benzhydrol proceeds normally ($k_q = 1.3 \times 10^6$ M^{-1} s^{-1}) and gives semiquinone radical ($QH^\bullet$, $\lambda_{max} = 435$ nm) and the benzhydryl radical ($\lambda_{max} = 535$ nm). The latter intermediate decays by pseudo-first-order kinetics through hydrogen atom transfer with ground state quinone (Q). Triplet quenching by bis(4-methoxyphenyl)methanol proceeds at a more rapid rate ($k_q = 5.5 \times 10^9$ M^{-1} s^{-1}) leading to an intermediate that is identified as the chloranil radical anion ($\lambda_{max} = 450$ nm). A similar intermediate is observed on Q quenching by 1-naphthylmethanol and acenapthenol with the appearance of an accompanying naphthalene radical cation absorption (ca. 670 nm). The radical ion transients, which are assigned to contact ion-pairs (triplet excited complexes) of the quinone and the various electron donors, decay to semiquinone radicals ($QH^\bullet$) by first-order processes occurring in the 100 ns time regime. The transient behavior is interpreted in terms of a hydrogen atom transfer mechanism for photoreduction with benzhydrol and, for the more robust electron donors, a mechanism involving electron transfer followed by proton transfer between geminate radical ions. For the electron transfer donors, ground state charge-transfer (CT) complexes can be observed (λ_{max} ca. 500 nm). Selective CT excitation leads to quinone photoreduction with reduced quantum yield. The results are discussed in terms of the time resolution of sequential electron/proton transfer steps for photogenerated ion-pairs, the occurrence of one photon−two electron transfer photoredox mechanisms, and the kinetically distinct pathways for decay of singlet and triplet intimate radical ion-pairs.

The photoreduction of carbonyl compounds ranks among the best known of organic photochemical processes.[1] The focus of early mechanistic studies was the photoreduction of benzophenone by benzhydrol,[2] for which a mechanism involving hydrogen atom transfer to the triplet state of the ketone, followed by the coupling or disproportionation of resulting radicals was readily discerned.[3] Many variations on this theme have now appeared, usually involving the carbonyl compound participating as an electron acceptor and various reducing agents leading to charge transfer in a primary quenching step. For example, in an extensive series of studies, Wagner and his co-workers,[4] using quantum yield, product, and substituent effect probes have distinguished the differing paths of photoreduction for acetophenones and benzophenones by arenes (e.g., toluenes) and identified structural features that dictate the changeover from H-atom abstraction to electron transfer for these systems. CIDNP, CIDEP, and flash photolysis techniques have also been applied to the problem of atom vs electron transfer mechanisms in the photoreduction of carbonyl compounds.[5,6] Coupled electron/proton transfer sequences have played a role as well in the transformation of other functional groups (e.g., photochemical addition or substitution involving stilbene[7] or iminium functional groups).[8] Only rarely has it been possible to observe directly sequential steps of electron and proton transfer that appear to be important to these carbonyl photoreduction mechanisms. For example, Manring and Peters[9a] and Mataga et al.[9b] using picosecond pulsed laser techniques observed the evolution of ion-pairs into radical pairs on photolysis of benzophenone and *N*,*N*-dialkylanilines.

Adding to studies of the electron transfer photochemistry of the high potential quinone chloranil (Q) with cyclopolyenes,[10] arenes,[11] and pinacols[12] we have investigated quinone reactions

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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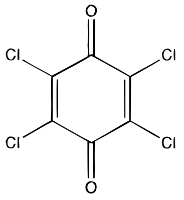
S0002-7863(97)00271-0 CCC: $14.00 © 1997 American Chemical Society

with benzhydrol and related arylmethanols with the objective of relating the mechanism of formal two-electron reduction of the quinone ($Q \rightarrow QH_2$) to the classic example of benzophenone photoreduction. The strongly oxidizing properties of chloranil and its spectral features are uniquely suited for examination of photoredox processes under several modes of photoexcitation. For example, using nanosecond laser flash photolysis methods, we can observe ion-pairs derived from Q and simple arenes (e.g., 1,4-dimethylnaphthalene and related donors, represented schematically as DH_2) in a nonpolar solvent (benzene).[11] Thus, for these systems that show a ground state interaction (for high concentrations of quinone and electron donor), the lowest triplet of the charge-transfer (CT) complex is accessible through quenching of free triplet chloranil (eq 1).

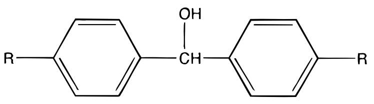
$$^{3}Q + DH_2 \rightarrow \underset{\text{triplet excited complex (TEC)}}{^{3}(Q^{\bullet -}, DH_2^{\bullet +})} \qquad (1)$$

$$^{3}(Q^{\bullet -}, DH_2^{\bullet +}) \rightarrow {}^{3}(QH^{\bullet}, DH^{\bullet}) \qquad (2)$$

Several unusual and noteworthy features emerge from laser flash photolysis experiments on this system. Electron transfer intermediates (radical ion spectra) that result from the quenching of quinone triplets (eq 1) can be observer directly in the convenient time domain of 50−500 ns following the laser pulse. These species *which can be generated in a nonpolar solvent* (typically benzene) are shown to evolve subsequently into radical species, the result of intra-ion-pair proton transfer (eq 2). Using straightforward photokinetic techniques, it is possible to extract rate constants for intrapair proton transfer and for back electron transfer with the ion pair and to establish structure−reactivity relationships for radical ion reactivity with various Q/donor combinations.[11] The observation of triplet excited complexes (TEC) on laser photolysis of Q/arenes is important and not an isolated incident, as suggested by the identification of similar long-lived ion-pair intermediates for several quinones with a variety of electron donors (other arenes, anilines, and nitrogen heterocycles[13,14]). These triplet excited complexes have been structurally characterized by resonance Raman spectroscopy which reveals a highly radical ionic character.[14]

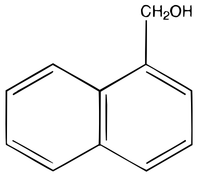


Q

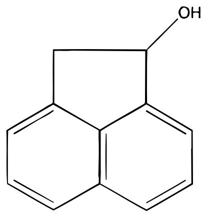


Ph_2CHOH, R=H

An_2CHOH, R=OCH_3



NCH_2OH



ANOH

There is a long standing interest in the steps involved in a net two-electron reduction of quinones, in part due to their importance in biological redox processes.[16,17] The issue of hydrogen atom vs electron transfer (or hydride) as a primary step in quinone reductions was raised some years ago,[18] and many studies have been directed to differentiating these mechanisms for biological systems.[19,20] For special consideration is a class of photoredox reactions that involve a net two electron reduction−oxidation per initiating photon (e.g., reduction of indigo dyes or flavins by amines).[21]

In the present work we report the photoreduction of chloranil in the presence of benzhydrols of variable oxidation potential with other arylmethanols substituted with naphthalene moieties (NCH_2OH and ANOH). Of particular interest is the observation of ion-pair intermediates and the direct measurement of intrapair proton transfer rate constants including kinetic isotope effects. The results also provide a comparison of the behavior of triplet and singlet excited complexes (radical ion-pairs) and further reveal mechanistic steps for a one photon−two electron redox system.

Results

Chloranil (Q) Photoreduction by Hydrogen Atom Donors. On irradiation of 5.0 mM 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione (Q) and 500 mM Ph_2CHOH in benzene at 366 nm,[22] benzophenone and tetrachlorohydroquinone (QH_2) were obtained as the exclusive products (HPLC). These products were identified by comparison with authentic samples; the routine oxidation product, benzpinacol,[3] was unobserved. The quantum yields for steady irradiation at 366 nm (low conversion) were benzophenone, 0.24, QH_2, 0.31, and benzpinacol, < 0.01. Apparent quantum yields were diminished at higher degrees of conversion ($>10\%$) due to the known tendency of QH_2 to act as an inhibitor and unproductive quencher of quinone excited states.[16]

Laser flash photolysis of the Q/benzhydrol system was carried out using the frequency tripled output of a Nd/YAG laser (355 nm, typically 80 mJ/per 7 ns pulse) and the detection system previously described.[23] In Figure 1 the absorption due to phototransients is depicted for several time intervals following the laser pulse. The triplet state of the quinone ($\lambda_{max} = 510$ nm), apparent in early times, was replaced by the superimposed absorptions of the semiquinone radical ($QH^{\bullet}$, $\lambda_{max} = 435$ nm)[24] and the benzophenone ketyl ($\lambda_{max} = 535$ nm).[26] Apparent in Figure 1 also is the dramatic difference in rate of disappearance of the two radical species suggesting a rapid decay path for the ketyl that competes with conventional radical recombination.

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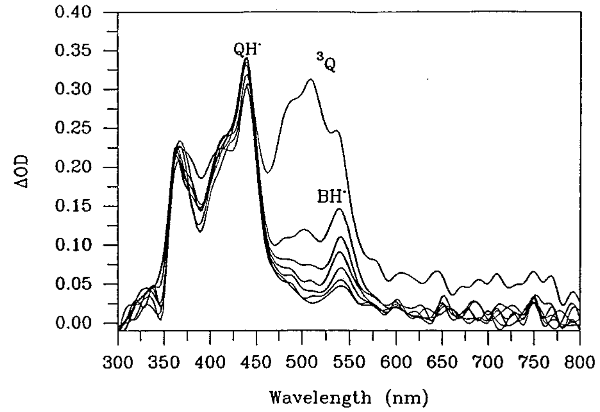

Figure 1. Transient spectra resulting from flash photolysis of 0.5 mM chloranil (Q) and 0.6 M benzhydrol (Ph_2CHOH) in benzene. Peak maxima are associated with the intermediate triplet quinone, the semiquinone radical ($QH^\bullet$), and the benzhydryl radical, $Ph_2C^\bullet(OH)$. Delay times are 0.25−3.85 μs following a 355 excitation pulse (descending curves at 500−550 nm, 600 ns intervals).

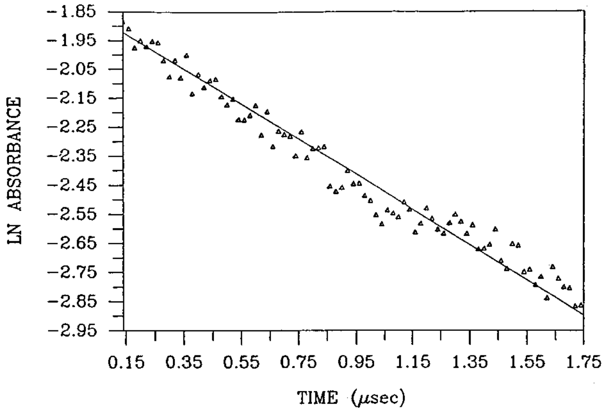

Figure 2. Decay kinetics for the 535 nm transient (benzhydryl radical) resulting from flash photolysis of 0.5 mM chloranil and 0.6 M benzhydrol in benzene (λ_{exc} = 355 nm).

Scheme 1

$^3Q + Ph_2CHOH \rightarrow QH\bullet + Ph_2C\bullet(OH)$ atom transfer quenching

$Ph_2C\bullet(OH) + Q \rightarrow QH\bullet + Ph_2C{=}O$ radical trapping by quinone

$QH\bullet + QH\bullet \rightarrow Q + QH_2$ semiquinone disproportionation

Notably, the disappearance of the ketyl transient followed first-order kinetics (Figure 2, correlation coefficient = 0.98); the decay rates for the 535 nm transient were also dependent on the concentration of ground state Q. Thus, the lifetimes of the decay monitored at 535 nm were obtained for concentrations of Q = 0.25−1.5 mM, and from a plot of $1/\tau = 1/\tau_o + k_q[Q]$, the value of the rate constant for presumed bimolecular trapping of the ketyl by Q was calculated ($k = 1.1 \times 10^9$ M^{-1} s^{-1}. Other reactions of ketyls with ketones have been measured to be 3.6 × 10^5 M^{-1} s^{-1}).[27] The decay of the transient absorbing at 435 nm ($QH^\bullet$) followed second-order kinetics. From a plot of the data (r = 0.984), $k/\epsilon = 2.1 \times 10^6$ cm s^{-1} could be calculated, and using ϵ = 7300 M^{-1} cm^{-1} for the semiquinone radical,[24] the rate constant for bimolecular reaction of $QH^\bullet$ was obtained (1.5 × 10^9 M^{-1} s^{-1}). The mechanism proposed for Q photoreduction−benzhydrol oxidation is shown in Scheme 1.

Rate constants for the quenching of quinone triplet with various donors including benzhydrol and a prototype hydrogen donor alcohol, isopropyl alcohol, are shown in Table 1. For these measurements, the transient at 510 nm was monitored as a function of donor concentration and lifetime quenching plots obtained. Preparation of deuterated benzhydrol (Ph_2CDOH) allowed determination of the isotope effect on bimolecular quenching (k_H/k_D = 2.0 ± 0.2).

Table 1. Rate Constants for Quenching of Triplet Chloranil by Hydrol Donors, Absorption Data, and Formation Constants for Ground State Q/Donor Complexes in Benzene Solution

	$k_q{}^a$ (M^{-1} s^{-1})	λ_{max} (CT) (nm)	K_{CT}, M^{-1}	ϵ_{CT}
$(CH_3)_2CHOH$	6.6 × 10^6			
Ph_2CHOH	1.3 × 10^7			
Ph_2CDOH	0.70 × 10^7			
An_2CHOH	5.5 × 10^9	470	3.6	200
NCH_2OH	4.0 × 10^9	500	0.52	665
ANOH	8.1 × 10^9	510		

[a] Obtained from 0.5 mM Q in benzene. Values are ±15%.

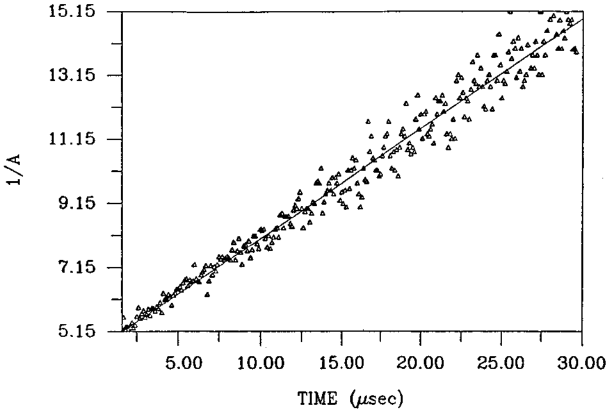

Figure 3. Decay kinetics for the $QH^\bullet$ transient resulting from flash photolysis of 0.5 mM chloranil and 0.6 M benzhydrol in benzene.

Chloranil Photoreduction with Electron Donors. Chloranil also could be photoreduced with the benzhydrol donor substituted with electron donating groups, [(p-$MeOC_6H_4)_2CHOH$ (dianisylmethanol or An_2CHOH)]. Again, hydroquinone (QH_2) and substituted benzophenone $An_2C{=}O$ were the exclusive products; the quantum yields for photolysis of a benzene solution with 5.0 mM Q and 10 mM An_2CHOH at 366 nm were 0.063 ($An_2C{=}O$) and 0.051 (QH_2). Flash photolysis experiments revealed that although there were apparent similarities in the overall photoreduction, the mechanism in fact involved a different path. The triplet state of Q was quenched at a very high rate by An_2CHOH (Table 1). Notably also, triplet quenching now results in a phototransient at 450 nm (Figure 4), characteristic of the quinone radical-anion.[11,13a,24] The corresponding anisole-type radical cation would be expected to absorb in the same region, about 440 nm.[25] These absorptions are diminished rapidly to give a weakly absorbing transient at 435 nm ($QH^\bullet$), which persists well into the 10 ms regime. Although the overlapping absorptions are difficult to distinguish, the single exponential decay profile for absorption at 450 nm (Figure 5) is fully consistent with the assignment of the radical ion intermediates $Q^{\bullet-}$ and $An_2CHOH^{\bullet+}$ decaying as a bound pair. The radical species, $An_2C^\bullet OH$, which would result (along with $QH^\bullet$) from proton transfer between primary electron transfer products ($Q^{\bullet-}$, $An_2CHOH^{\bullet+}$) is observed at several hundred ns following the laser flash but is rapidly depleted (or absent), depending on quinone concentration, due to reaction with ground state Q (vide supra).

The replacement of substituted benzhydrol by arylmethanols having naphthalene moieties led to a somewhat different display of the ion-pair structures. A broad featureless component of the phototransient spectra was introduced suggesting the

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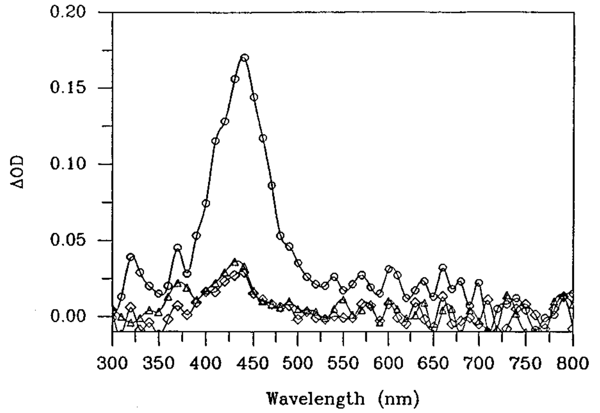

Figure 4. Transient spectrum from 355 nm laser flash of 0.5 mM chloranil and 5.0 mM An_2CHOH in benzene. The curves are recorded 180 ns, 2.65 μs, and 3.85 μs after the flash in descending order.

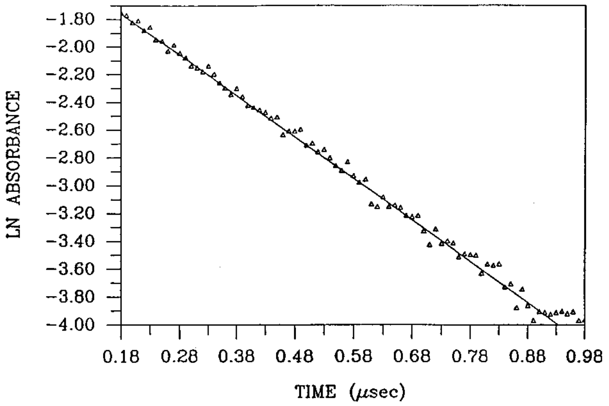

Figure 5. Decay of the 450 nm transient ($Q^{\bullet -}$) on flash photolysis of 0.5 mM chloranil and 5.0 mM An_2CHOH in benzene.

characteristic appearance of naphthalene radical cations (λ_{max} = 650−690 nm[11,24]). This feature decays rapidly along with $Q^{\bullet -}$ and is shown in Figure 6 for Q triplet quenching by 1-naphthylmethanol (NCH_2OH). The first-order decays found for radical ion transients (monitored at 670 nm for the naphthalenes and at 450 nm for the benzhydrols) are shown in the Figure 6 inset and in Table 2. Data at both wavelengths fit first-order decay curves, and the resulting rate constants, 1.1×10^7 and 3.1×10^7 s^{-1}, are the same within experimental error, consistent with the decay of a bound pair of ions.

It was possible to monitor conveniently the growth and decay of the radical species resulting from electron/proton transfer (note transients at longer time scales in Figure 7). Thus, the species $NCH^{\bullet}OH$ was observed to grow in at 370 nm; inspection of the early time domain revealed a first-order growth of this transient (Figure 7, insert) with a $\tau = 120$ ns. This mirrored the corresponding decay of the radical ion (670 nm). Concomitant with the formation of the donor-derived radical was a shift in the $Q^{\bullet -}$ absorption at 450 to 435 nm, characteristic of the radical, $QH^{\bullet}$. This later radical transient disappeared at a rate that depended on Q concentration (most noticeably at [Q] > 1.0 mM). Monitoring the 370 nm transient ([Q] = 0.5 mM) fit second-order decay, consistent with a recombination process of $NCH^{\bullet}OH$ and $QH^{\bullet}$ with a rate constant of 1.3×10^9 M^{-1} s^{-1}. The radical species observed for acenapthenol (ANOH) (390 nm) was also shown to appear ($\tau = 95$ ns) concomitant with decay of the TEC intermediate.

Kinetics of Intra-Ion-Pair Proton Transfer for Chloranil Complexes. The alternative mechanism for quinone triplet quenching via electron transfer with arylmethanols is shown in Scheme 2. The key steps involve the formation and decay of the intimate radical ion-pair of presumed triplet multiplicity.[28] According to the scheme, the rate constant for decay and the lifetime for the triplet ion-pair are related as $k_d = 1/\tau = k_H + k_{isc}$, involving the separate steps of intra-ion-pair proton transfer and decay to the ground state, respectively. Rate constants can therefore be calculated as follows

$$k_H = \Phi(QH^{\bullet})/\tau \qquad (3)$$

$$k_{isc} = [1 - \Phi(QH^{\bullet})]/\tau \qquad (4)$$

where $\Phi(QH^{\bullet})$ is the quantum yield for the conversion of triplet ion-pairs to radical pairs, computed as previously described for Q complexes of substituted naphthalene (hydrocarbon) donors.[11] For this measurement the decay of species at 450 nm was monitored following a 355 nm laser pulse as shown in Figure 5. Transient absorbances associated with quinone anion (*ca.* 100 ns decay time) and radical (*ca.* 50 ms decay) were extrapolated to zero time, and the ratio of transients taken, assuming extinction coefficients for $Q^{\bullet -}$ (ϵ_{450} = 9300 M^{-1} cm^{-1})[24] and $QH^{\bullet}$ (ϵ_{435} = 6600 M^{-1} cm^{-1})[12b]. The data including the lifetimes of the ion-pair intermediates, the quantum efficiencies for radical formation, and the derived rate constants are shown in Table 2. For the deuterated dianisylmethanol, An_2CDOH, an isotope effect on the intra-ion-pair proton transfer was obtained: $k_H/k_D = 1.37 \pm 0.24$.

Quinone Photoreduction on Direct Irradiation of Ground State Complexes. An additional distinguishing feature for the arylmethanols that are better electron donors is the observation of ground state complexes with Q and charge-transfer (CT) absorption bands.[28] The intervention of complexes is illustrated for the dianisylmethanol donor in Figure 7 and other absorption data with computed complexation constants provided in Table 1. With the combination of Q and concentrations of donor sufficiently high for ground state interaction, another option for photoexcitation of the pair was available. Under conditions in which benzene solutions were nearly saturated with An_2CHOH (0.3 M) and [Q] = 2.5 mM, samples were irradiated at 436 nm (Hg lamp), a wavelength where free quinone absorbs poorly. From the equilibrium and absorptivity data, it was possible to estimate that virtually all the light under these conditions was absorbed by the complex. Redox products, hydroquinone and benzophenone, were again obtained, but quantum yields were significantly reduced: $An_2C{=}O$, 0.029; QH_2, 0.036. Also, laser photolysis at 355 nm resulted in negligible transient absorption at >20 ns time delays consistent with excitation of quinone complexes and rapid decay of the resultant singlet radical ion-pairs (eq 5).[28]

$$^1[Q^{\bullet -}, ArCH(OH)R^{\bullet +}] \rightarrow [Q, ArCH(OH)R] \qquad (5)$$

Discussion

The photolysis of chloranil in the presence of the benzhydrols (arylmethanols) takes a course that differs from the conventional route to benzpinacol for carbonyl compounds and alcohols.[3] The photoredox products (hydroquinone and ketone) are, however, those that have been observed in many cases of quinone photoreduction by alcohols.[16] The reaction is facilitated by the interception of radicals by ground state quinone, according to the mechanism of Scheme 1. This step can proceed in one of several ways including H-atom or electron transfer.[29] The

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[28] Singlet excited CT complexes exhibit lifetimes generally in the 0.1−1.0 ns range. For a review of time resolved measurements, see: Jones, II, G. In *Photoinduced Electron Transfer* Fox, M. A., Chanon, M., Eds.; Elsevier Science Publishers: Amsterdam, 1989; Vol. A.

[29] Reaction of Q and benzhydryl radicals leading to hemiacetal adducts is a possibility which has some precedence in thermal quinone oxidations (ref 30).

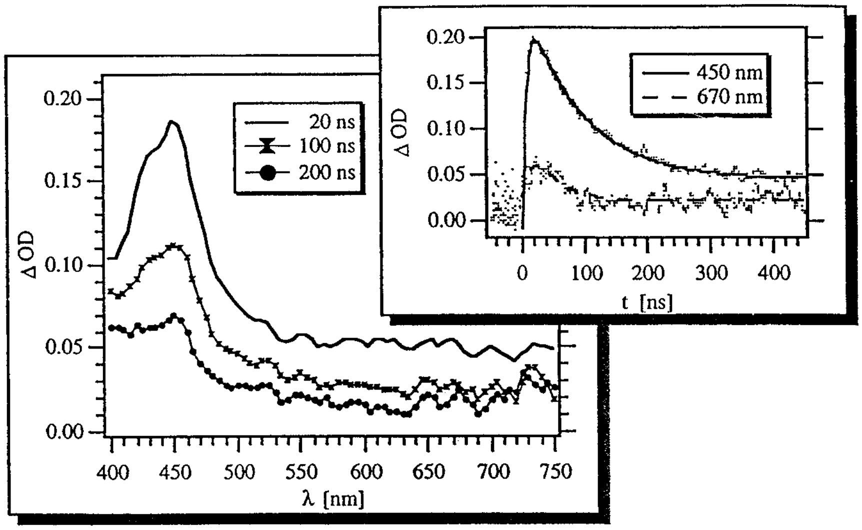

Figure 6. Absorption spectra of transients obtained from flashing 0.59 mM chloranil and 56.7 mM naphthylmethanol in benzene at delay times 20, 100, and 200 ns. Insets are the decay curves monitored at 450 and 670 nm. Data points have been fit to exponential decay curves.

Table 2. Lifetimes of Radical Ion-Pair Intermediates (TEC), Quantum Yields, and Rate Constants for Intra-Ion-Pair Proton Transfer for Excited Complexes of Chloranil and Hydrol Donors[a]

	τ, ns	$\Phi(QH^\bullet)$	$10^{-6}\, k_H$, s^{-1}	$10^{-6}\, k_{isc}$, s^{-1}
An_2CHOH	130	0.15	1.3	6.4
An_2CDOH	120	0.12	0.91	7.4
NCH_2OH	110	0.34	2.5	6.6
ANOH	95	0.11	1.1	9.9

[a] Obtained from 0.5 mM solutions of Q in benzene. Values are ±15%.

mechanism of hydrogen atom transfer has been proposed previously,[31] based on pulse radiolysis and flash photolysis experiments in which hydroxyalkyl radicals react with ground state (benzo)quinone. Alternatively, electron transfer trapping of the arylmethanol radicals appears feasible (eq 6) and would be appropriately fast ($k_{obd} > 10^9$ M^{-1} s^{-1}).

$$Q + ArC^\bullet(OH)R \rightarrow [Q^{\bullet -}, ArC^+(OH)R] \qquad (6)$$

Formation of an ion-pair in benzene solvent (followed by a final proton transfer step or ionic addition[29]) thus would be attractive, given the oxidative properties of chloranil[32] and the strongly reducing characteristics of (OH)- and (OR)-substituted carbon radicals.[33] The other prominent examples of sequential two-electron reduction (reduction with amines[21]) require also reducing (aminoalkyl) radicals.[33] In the present case the interception of $ArC^\bullet(OH)R$ radicals in the follow up step for reduction of the quinone can be directly observed. The primary step of H-atom transfer for Q and benzhydrol (Scheme 1) proceeds for benzhydrol (and isopropyl alcohol) at a normal (although fast) rate for hydrogen abstraction,[1,3] consistent with an accessible n,π^* triplet for chloranil.[34]

The significant aspects of the present work concern the observation of ion-pair intermediates for quinone reduction in benzene and the temporal resolution in the 100 ns regime for the critical intra-ion-pair proton transfer step. The high rate of triplet quenching (near the diffusion limit of ca. 5 × 10^9 M^{-1} s^{-1} for benzene, 25 °C) for the hydrols that are more effective electron donors[36] signals the change in mechanism. The appearance of transients that are assigned to the chloranil radical anion ($\lambda_{max} = 450$ nm) and the naphthalene radical cation ($\lambda_{max} = 650-690$ nm) is consistent only with a mechanism for photoreduction which employs electron transfer as a primary step. The first-order decay in the 100 ns regime for the radical ion species followed by the appearance of a second longer lived intermediate (435 nm, $QH^\bullet$) further confirms the mechanism (Scheme 2).

A feature that confers stability on the ion-pair transients is the large charge-transfer component between donor and acceptor moieties. That is, these intermediates are true Mulliken ion-pairs,[37] a characteristic that is not necessarily shared by other triplet "exciplexes" that have larger contributions from electronic configurations that are local in character.[38] Chloranil-alkylbenzene triplet excited complexes show a substantial radical ion character as shown by transient resonance Raman spectroscopy.[14] The absence of local excited state character, the Coulombic stabilization of an electrostricted pair (in nonpolar solvent), and the imposition of a somewhat larger S_1-T_1 singlet-triplet splitting may contribute to the stability of the quinone triplet excited complexes (TECs).[11b]

The TEC species participate in proton transfer within the solvent cage yielding a radical pair that dissociates readily. The lower magnitude of the quantum yield for photoreduction and the modest quantum yields of radicals on adoption of the electron transfer mechanism show that intrapair proton transfer is a modest competitor for intersystem crossing (note k_H and K_{isc} values in Table 2). Comparison of kinetic acidities for several radical-cation systems is warranted. The proton transfer step proceeds somewhat more slowly (from 3 × 10^2 to 2 × 10^7 M^{-1} s^{-1}) for bimolecular transfer to pyridine bases from arene radical cations in acetonitrile.[39] Faster proton transfers have

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(30) (a) Walling, C.; Zhao, C.; El-Taliawi, G. M. *J. Org. Chem.* **1983**, 48, 4919. (b) Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607.

(31) (a) Land, E. J.; Swallow, A. J. *J. Biol. Chem.* **1970**, *245*, 1890. (b) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904.

(32) The reduction potential for Q in acetonitrile solvent is 0.01 V vs SCE: Mann, C. K. Barnes, K. K. *Electrochemical Reactions in Non-aqueous Systems*; Marcell Dekker, Inc.: New York, 1970.

(33) (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988,** *110*, 132. (b) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, 103, 1586.

(34) The assignment of the configuration of the chloranil triplet has varied but most evidence favors a low lying π,π^* triplet state.[35] Consistent with the notion of a close lying, accessible and a reactive n,π^* triplet are the various observations of Paterno−Buchi cycloadditions of Q (for a review of the observations, see: Jones, II, G. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1982; Vol. 5).

(35) Bunce, N. J.; Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *45*, 283.

(36) Oxidation potentials for model compounds are as follows: for benzyl alcohol, 1-methylnaphthalene, acenaphthene, and anisole, >2.3, 1.53, 1.36, and 1.65 V vs SCE, acetonitrile (ref 32).

(37) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969.

(38) O'Connor, D. V.; Ware, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 121.

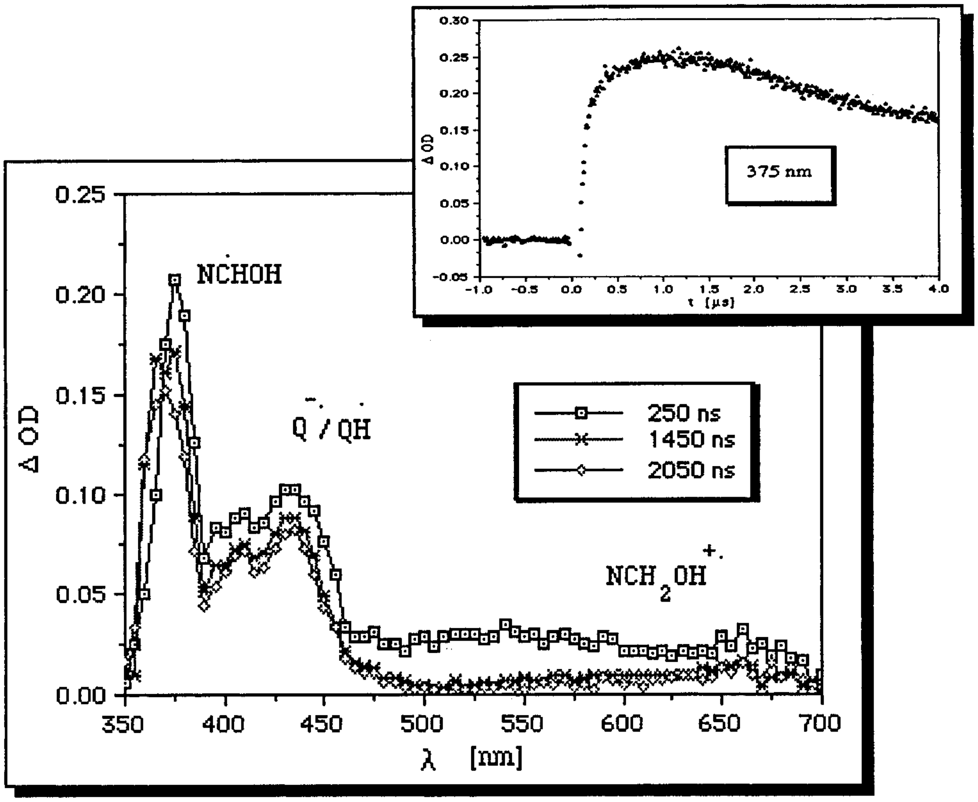

Figure 7. Absorption spectra of transients obtained from flashing 1.0 mM chloranil and 25 mM naphthylmethanol in benzene. The inset represents the time evolution of the decay monitored at 375 nm.

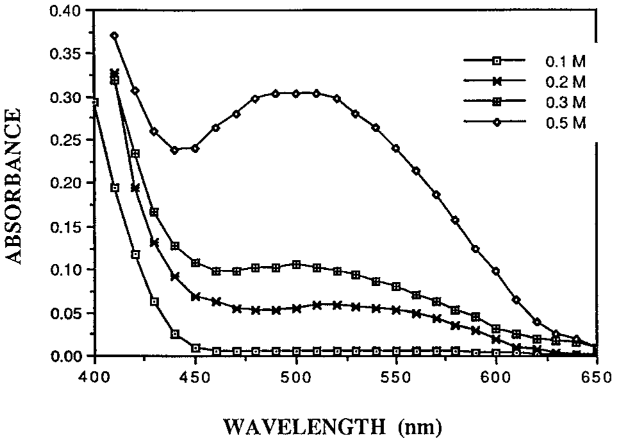

Figure 8. Development of charge-transfer absorption on addition of An_2CHOH to chloranil (1.0 mM) in benzene.

been observed sometimes ($k = 1.5 \times 10^9$ s^{-1} for intra-ion-pair transfer from diphenylmethylamine to benzophenone[9a] and $k = 5.4 \times 10^9$ s^{-1} for intra-ion-pair transfer from benzophenone and alkylanilines).[9b] In related experiments on chloranil in combination with arenes (e.g., 1-methylnaphthalene), k_H values ranging from 0.4×10^6 to 4.2×10^6 correlated with the charge density associated with the aromatic ring position next to the acidic (CH_3) site.

The kinetic isotope effect for quenching of Q triplets, $k_q(H)/k_q(D) = 1.9 \pm 0.20$, shows C−H bond breaking and therefore H-atom abstraction for Ph_2CHOH. On the other hand, the value of $k_q(H)/k_q(D) = 1.1 \pm 0.10$ for An_2CHOH indicates that H transfer is not the rate-determining step. Wagner[4] similarly found negligible isotope effects on triplet quenching when electron transfer was involved. On the other hand, the kinetic isotope effect for the proton transfer step, $k_H/k_D = 1.4 \pm 0.24$ measured for An_2CHOH, can be compared with that determined for Q and 1-methylnaphthalene system ($k_H/k_D = 3.4$).[11b] Maximum kinetic isotope effects have been obtained for systems with symmetrical transition states.[40] The smaller magnitude found for intrapair proton transfer in An_2CHOH suggests that proton transfer in the triplet ion-pair of proceeds via an earlier, less symmetrical transition state. This is consistent with the enhanced stability associated with benzhydryl radical relative to the naphthylmethyl. Another isotope-lowering effect in this system may be the enforced nonlinearity of the transition state for proton transfer associated with a sandwich-like arrangement in the contact ion-pair. (For an earlier depiction see Scheme 5 in ref 11a.) Manring and Peters[9a] also obtained a value of 1.4 for the isotope effect for the proton transfer within the radical ion-pair for benzophenone and dimethylaniline.

Of interest also is the contrasting behavior of the CT complex of Q and An_2CHOH. Under "CT irradiation" conditions, a

Scheme 2

$^3Q + ArCH(OH)R \rightarrow {}^3[Q^{-\bullet}, ArCH(OH)R^{+\bullet}]$ TEC (ion pair) formation

$^3[Q^{-\bullet}, ArCH(OH)R^{+\bullet}] \rightarrow [QH\bullet, ArC\bullet(OH)R]$ intra-pair proton transfer

$^3[Q^{-\bullet}, ArCH(OH)R^{+\bullet}] \rightarrow Q + ArCH(OH)R$ radical ion-pair decay (k_{isc})

$[QH\bullet, ArC\bullet(OH)R] \rightarrow QH\bullet + ArC\bullet(OH)R$ radical pair dissociation

$ArC\bullet(OH)R + Q \rightarrow QH\bullet + ArCOR$ radical trapping by quinone

$QH\bullet + QH\bullet \rightarrow Q + QH_2$ semiquinone disproportionation

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(39) Schlesener, C. J., Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.

(40) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987; pp 236−238.

radical ion species of singlet multiplicity is expected.[28] The diminution of quantum yield for photoreduction under these conditions is consistent with the exceedingly rapid back electron transfer step for the singlet ion-pair (ps) that has been observed in the recent study of Q and durene that included a picosecond time resolved measurement.[41] Photoreduction based on the electron transfer mode therefore depends on a moderate rate of intra-ion-pair proton transfer that successfully competes with a (back) electron transfer for radical ion-pairs generated on Q triplet bimolecular quenching. The back electron transfer step is prohibitively fast for singlet ion-pairs produced on direct excitation of the Q/arylmethanol CT complex.

In the present example of a two electron reduction−oxidation that is apparently driven by excitation by a single photon, the circumstances are dictated by the secondary reaction of a reducing radical derived from the benzhydrols with the ground state of chloranil. This pattern of reactivity is now familiar for photoreductions that employ amines[21] but is less well understood for simple alcohols that are themselves less readily oxidized. We are continuing studies directed to a better understanding of redox photoprocesses that employ sequential steps of electron and proton transfer.

Experimental Section

Benzhydrol and benzpinacol (Aldrich) were purified by recrystallization from ethanol. Benzophenone and 4,4′-dimethoxybenzophenone were recrystallized from methanol and petroleum ether. Tetrachlorohydroquinone (Aldrich) was purified by recrystallization from glacial acetic acid, followed by washing with distilled water, drying under vacuum, and then vacuum sublimation. Baker HPLC grade benzene was purified by fractional distillation from P_2O_5 and then stored over molecular sieves. Chloranil (Q) purchased from Aldrich was further purified by recrystallization from purified benzene (vide supra) followed by vacuum sublimation at 2.5 T (ca. 135 °C). The purified quinone gave rise to the characteristic shoulder in benzene ($\epsilon_{330} = 2200$ M^{-1} cm^{-1}).[11a] Acenapthenol (ANOH) (mp 147−148 °C) and 1-naphthylmethanol (mp 61−62 °C) (Aldrich) were recrystallized from hexanes. Spectrograde isopropyl alcohol was fractionally distilled.

Benzhydrol-*d* and Bis(4-methoxyphenyl)methanol-*d*. Specifically monodeutereated samples of the title alcohols were obtained by hydride reduction of benzophenone and 4,4′-dimethoxybenzophenone following procedures for reduction leading to undeuterated benzhydrols.[42] Benzophenone (0.02 mol) was allowed to react with 0.44 g (0.01 mol) of $LiAlD_4$ in dry ether. The mixture was refluxed for 10 min and poured onto a mixture of 1 mL concentrated sulfuric acid and 20 g of crushed ice. The ether layer was separated, washed, dried, and evaporated to give white crystals which were recrystallized from ethanol/water, yielding 2.0 and 2.7 g of Ph_2CDOH and An_2CDOH, respectively. NMR spectra confirmed the position of the deuterium label (absence of peak at 4.5 δ, $CDCl_3$) and showed >95% deuterium incorporation.

Laser Flash Photolysis. The apparatus described elsewhere in detail[23] is comprised of a Quantel YG-581 Nd:YAG laser (with frequency doubling and tripling capability) interfaced with a LeCroy Tr8818 100-megasample/s digitizer with an Apple Macintosh IIci computer. Other components include an Oriel 150-W xenon monitoring lamp, Instruments SA H-20 monochromator with attached Kinetic Systems stepping-motor controller for microcomputer controlled wavelength selection from 200−800 nm, and an RCA 4840 photomultiplier tube. Monitoring and laser beams were configured perpendicularly with a cell path length for the monitoring beam of 2 cm and that for the laser beam of 1 cm.

Transient spectra were obtained using one to five laser pulses for sampling at each monitoring wavelength (typically increments of 2−5 nm). Decay curves were obtained from a collection of data points generated via many laser pulses (usually from 10 to 100) and plotted either as ln ΔOD vs time or 1/ΔOD vs time (linear least squares analysis). All samples were photolyzed at room temperature using purified anhydrous benzene as solvent with argon sparging (usually 5 min/mL). Photoexcitation was carried out by irradiation into the chloranil absorption (330 nm) using the third harmonic of the Nd:YAG laser (355 nm). Rates of quenching of the Q triplet were determined by measurement of the pseudo-first-order decay of the triplet transient at 515 nm with varying concentrations of hydrol donors. Lifetimes were determined from 400 digitized signal averaged data points (> 3 decades, $r > 0.990$) and plotted: $\tau_o/\tau = 1 + k_q\tau_o$[donor] ($\tau_o = 5.7$ ms for Q in benzene). At least three separate determinations were averaged with a variance of 15%. Decay of the QH$^\bullet$ radical was fit to second-order plots, the slopes of which yielded $k/\epsilon = 2.1 \times 10^6$ cm s^{-1} for flash photolysis of 0.5 mM Q and 0.6 M benzhydrol.

Steady State Photolysis. For determination of product quantum yields previously described an apparatus was used, the essential components of which are an Oriel 500 W lamp, a B and L monochromator (9.6 nm bandpass), and a rhodamine B quantum counter.[43] Ferrioxalate actinometry was used for calibration of the apparatus.[44] Typically a 2 mL solution of the sample was placed in a quartz cuvette with magnetic stir bar, sealed with a septum, and then sparged with argon before irradiation in the monochromator apparatus with magnetic stirring. The products were analyzed (an average of three runs) by HPLC with reference to a calibration curve of integrated area versus concentration determined for the pure substance (authentic samples of benzophenones and hydroquinone, QH_2).

The HPLC system used was a Rainin/Gilson HP/HPX instrument with binary solvent delivery system with a Rainin Microsorb high performance C_{18} reversed phase column and a microprocessor. Sample injections were made via a Rheodyne 725 injector; a KRATOS 757 variable wavelength UV−vis detector was used. The HPLC solvent system was 100% Baker HPLC grade methanol vs a mixture of 90% Millipore water (MilliQ system with ion and carbon filters) and 10% methanol. The solvents were sparged with argon and maintained under argon throughout the analytical runs. Column operating conditions were 1.2 mL/min at 3500 psi, while the detector was set at a wavelength of 330 nm and a sensitivity of 0.05 absorbance units full scale. Retention times in minutes were benzophenone, 12.5; tetrachlorohydroquinone, 5.2; chloranil, 9.5; and 4,4′-dimethoxybenzophenone, 11.5. An HP 3380A plotting integrator was used for recording sample absorbances and retention times as well as quantifying peaks through their integrated areas relative to an internal standard or with respect to a calibration curve of integrated area versus concentration. Irradiation times were generally 10−60 min. The reported quantum yields are an average of duplicate independent measurements and were reproducible to within ±15%.

Formation Constants for Charge-Transfer Complexes. For three hydrol donors ground state association with chloranil was detected in terms of long wavelength absorption bands that were not ascribable to the sum of spectra for Q and donor (Figure 8). Association constants, K_{ct}, and extinction coefficients for the complexes, ϵ_{ct}, could be obtained using the Benesi−Hildebrand spectrophotometric method.[45] The change in optical density (OD) was recorded for dilute Q solutions with added excess hydrol donor. Analysis of the slopes and intercepts of plots of [Q]/ΔOD vs 1/[hydrol] ($r > 0.995$) gave values of K_{ct} and ϵ_{ct}, the data shown in Table 1 with CT absorption band maxima (analysis wavelengths).

Acknowledgment. The authors thank the Office of Basic Energy Sciences of the Department of Energy for support of this work. We thank also Valentine Vullev, Mohammad Farahat, and William Petit for technical assistance.

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