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Interactions of Formate Ion with Triplets of Anthraquinone-2-sulfonate, 1,4-Naphthoquinone, Benzophenone-4-carboxylate, and Benzophenone-4-sulfonate

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The interaction of formate with the triplet states of naphthoquinone (NQ), anthraquinone-2-sulfonate (AQS), benzophenone-4-carboxylate (BC), and benzophenone-4-sulfonate (BS) was studied by laser flash photolysis. Rate constants were determined either by direct measurement of triplet lifetimes or by inhibition of product yields by competitive reactants. Radical products are formed in two stages, direct reduction by formate and efficient secondary reduction by initially formed CO$_2^{\bullet-}$ radicals. The quinones react by electron transfer with quenching rate constants $k_q(\mathrm{NQ}) = 3 \times 10^9$ and $k_q(\mathrm{AQS}) = 4 \times 10^8$ M^{-1} s^{-1}, giving anion radicals with primary yields of $\phi_R(\mathrm{NQ}) \sim 0.7$ and $\phi_R(\mathrm{AQS}) \sim 0.3$. Formic acid quenches ^{3}AQS much more slowly. The less strongly oxidizing ketone triplets react by H-atom abstraction, $k_q(\mathrm{BC}) = 1.3 \times 10^7$ and $k_q(\mathrm{BS}) = 5.3 \times 10^7$ M^{-1} s^{-1}, giving protonated ketyl radicals with primary yields $\phi_R \sim 0.7$. Photoreduction of BC exhibits a deuterium isotope effect, $k_H/k_D = 1.6$, whereas AQS shows none. A new, short-lived transient, E, is observed in the ^{3}AQS–formate reaction, which may be an exciplex or adduct. The redox potential, $E^{\circ\prime}(\mathrm{NQ/NQ^{\bullet-}}) = -0.12$ V, and rate constants for radical reactions of NQ and O$_2$ were measured by pulse radiolysis. The results are discussed in terms of pertinent redox potentials, bond strengths, and the nature of the exciplex intermediates.

Introduction

In previous studies, the interactions of various organic triplets with inorganic anions in aqueous solution were found to involve a charge-transfer (CT) mechanism, which may ultimately lead to radical separation.[1-4] The anions studied could be classified into two groups, according to the dependence of primary radical yield, ϕ_R, on anion concentration [X$^-$].[2-4]

Group I (Cl$^-$, Br$^-$, I$^-$, NCS$^-$): At low or moderate concentrations, these anions quench triplets of those aryl ketones or quinones that have been studied, with little or no accompanying formation of radicals. This quenching competes directly with radical or other transient formation arising from possible triplet interactions with the solvent. However, at anion concentrations considerably above those required for complete quenching ([X$^-$] $\gtrsim$ 0.1 M), ϕ_R increases with [X$^-$] up to some limiting value characteristic of each anion, producing equimolar amounts of the reduced species (ketyl or semiquinone) and dianion, X$_2^-$, radicals.[5]

Group II (SO$_3^{2-}$, NO$_2^-$, N$_3^-$): Quenching of the triplet by these anions occurs with accompanying formation of radicals, with yields reaching maximum values at total quenching.[6] With increasing anion concentration, ϕ_R either remains constant or decreases. The only exception observed to date is the azide-benzophenone-4-carboxylate system, in which low yields of ketyl and diazide, N$_6^-$, radicals are formed at high azide concentrations.[4] Thus, N$_3^-$ represents an intermediate case, acting either as a weak group I or group II anion, depending on the nature of the triplet.

It was postulated that a triplet CT radical-pair-like exciplex is first formed in these interactions, and ϕ_R is then determined by competition between radical separation and spin reversal (ISC) within the exciplex, leading to deactivation.[2,7] According to the IRSOC model,[2] the rate of spin reversal in these systems is controlled by spin–orbit coupling within the inorganic radical component, which should vanish in radicals with zero orbital momentum (nondegenerate electronic states) such as NO$_2$, SO$_3^-$, and the dianion radicals, X$_2^-$.[8] Quenching by group I anions typically produces X$_2^-$ radicals, which have high formation constants ($K_{eq} \sim 10^5$ M^{-1}) from X$^\bullet$ + X$^-$, and even the much less stable N$_6^-$ is observed.[9] The increase in ϕ_R at high [X$^-$] could thus be explained by assuming that the primary exciplex is intercepted by another X$^-$ ion to form a trimolecular exciplex, with loss of SO coupling. In all these cases, the reduction of the triplets could proceed only by electron transfer. However, with anions containing hydrogen there is also the possibility of H-atom abstraction. We present now our studies of the interaction of formate, HCO$_2^-$, with triplets of anthraquinone-2-sulfonate (AQS), 1,4-naphthoquinone (NQ), benzophenone-4-carboxylate (BC), and benzophenone-4-sulfonate (BS). The role of electron vs hydrogen transfer in these systems and the factors determining radical yields are discussed. Evidence is also given for the production of a short-lived primary transient species in the ^{3}AQS–HCO$_2^-$ system.

Experimental Section

Materials. AQS (sodium salt), NQ, sodium formate, and the inorganic materials were Analar, puriss, or analytical grade and were used as received. DCO$_2$K (99% D) was obtained from Aldrich. Benzophenone-4-carboxylic acid (Aldrich) was recrystallized three times from ethanol. Sodium benzophenone-4-sulfonate was prepared by the method of Ramsey and Cohen[10] and recrystallized three times from ethanol. Water was purified by a Millipore-Q System.

Solutions were deaerated by N$_2$ bubbling. The AQS and NQ solutions were unbuffered; in the presence of sodium formate, their pH was about 8. Some experiments with AQS were conducted in solutions acidified with HClO$_4$. Unless stated otherwise, studies

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(1) Treinin, A.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 3884.

(2) Treinin, A.; Loeff, I.; Hurley, J. K.; Linschitz, H. *Chem. Phys. Lett.* **1983**, *95*, 333.

(3) Loeff, I.; Treinin, A.; Linschitz, H. *J. Phys. Chem.* **1984**, *88*, 4931.

(4) Hurley, J. K.; Linschitz, H.; Treinin, A. *J. Phys. Chem.* **1988**, *92*, 5151.

(5) Besides anthraquinone-2-sulfonate[3] and benzophenone-4-carboxylate,[4] the following triplets showed similar behavior with group I anions: xanthone; 1,4-naphthoquinone; anthraquinone-1-sulfonate; iridium(III) bipyridine complexes (for the latter, see: Salma-Schwok, A.; et al. *J. Phys. Chem.* **1985**, *89*, 2460).

(6) For examples of group II action, see ref 3 and references therein. We have also extended group II studies to triplets of benzophenone-4-carboxylate and anthraquinone-1-sulfonate (unpublished). In the case of NO$_2^-$, quenching by energy transfer from the organic triplet to nitrite may occur if energetically possible, instead of CT quenching.[2]

(7) Winter, G.; Shioyama, H.; Steiner, U. *Chem. Phys. Lett.* **1981**, *81*, 547.

(8) In solution, the degeneracies may be lifted to some extent since the symmetry of the solvent shell is probably lower than that of the inorganic radical. Fluctuations in the solvation shell structure together with SO coupling may still induce spin flips.[7]

(9) Butler, J.; Land, E. J.; Swallow, A. *J. Radiat. Phys. Chem.* **1984**, *23*, 265.

(10) Ramsey, G. C.; Cohen, S. G. *J. Am. Chem. Soc.* **1971**, *93*, 1166. We thank Dr. Y. Naguib for this synthesis.

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on BC and BS were carried out at pH 11.2 (adjusted by NaOH) as in earlier work,[4] to put ketyl radicals completely into the anionic form (pK_a of BCH$^\bullet$ = 8.2). To study these systems at pHs closer to neutrality (but not less than pH 6.0) a phosphate buffer was used (pK_a of BC and formic acid are 4.5[4] and 3.75, respectively). Quinone solutions were prepared freshly for each set of measurements to minimize thermal reactions, and samples were changed after each flash exposure to avoid accumulation of photochemical products. Such instabilities were less marked in the presence of O_2. Absorption spectrum measurements gave no indication of ground-state interactions between HCO_2^- and any of the carbonyl compounds studied in this work.

Apparatus and Procedure. Flash Photolysis: These experiments utilized an Avco-Everett nitrogen laser (337.1 nm, 10 ns, 0.5 mJ), with kinetic traces digitized (Biomation 8100) and averaged (Minta Computer). The other components were conventional, including a pulsed xenon lamp, monochromator, and fast photomultiplier, with collinear measuring and excitation beams.

Second-order rate constants, k_q, for quenching of triplets by HCO_2^- were obtained from the observed linear dependence of pseudo-first-order triplet decay constants, k_d, on formate concentration, except for AQS. In this case, the kinetics were more complex, and a competition method had to be employed to obtain k_q (see Results).

Quantum yields of semiquinone or ketyl radicals were measured by using the AQS/Cl$^-$, 2M actinometer.[3] The quantum yield of this actinometer was recalibrated against the benzophenone-in-benzene actinometer,[11] and found to be 0.51 ± 0.04. This value is half of that previously reported,[3] and quantum yields given earlier in ref 3 should be corrected by that factor.[12] All data given in this present paper are so corrected. To measure ϕ_R, the time evolution of transient absorption was recorded at λ_{max} of the respective radicals and extrapolated to zero time. Extinction coefficients ($M^{-1}\ cm^{-1}$) of the radical species were taken as follows: AQS, 8200 at 500 nm;[13] NQ$^-$, 12 500 at 390 nm;[14] BC$^{\bullet-}$, 7660 at 650 nm;[15] BCH$^\bullet$, 5100 at 570 nm;[15] ϵ_{max} of BS$^{\bullet-}$ was assumed to equal that of BC$^{\bullet-}$ at 650 nm. In runs at low formate concentrations, corrections were made for transient absorbances by products of competing reactions of the triplets with water, including anion radicals from the triplet ketones, water adducts (transients B and C) from ^{3}AQS,[16,17] and products of ^{3}NQ–water reactions, absorbing around 390 nm, which have not yet been identified. These were measured at appropriate wavelengths in blank experiments without formate, and their fractional contribution was taken to be in the ratio of quenched to unquenched triplet lifetimes. For AQS, these corrections were obtained in presence of formate, using oxygen to eliminate the semiquinone and isolate absorption of the water adducts[16] (see Results, quenching rates). While the corrections are relatively large in dilute formate solutions, the principal conclusions of this work are based on measurements under conditions of essentially complete quenching by formate, in which competing side reactions play no role.

Steady-state photolysis was conducted using 365-nm light from a medium-pressure Hg lamp (Thorn Lighting, 125 W) and Corning N64 filter. Yields of H_2O_2 were determined colorimetrically by the well-known TiO_2 method and converted to quantum yields by using uranyl oxalate actinometry and the initial slopes of product yield vs time curves.

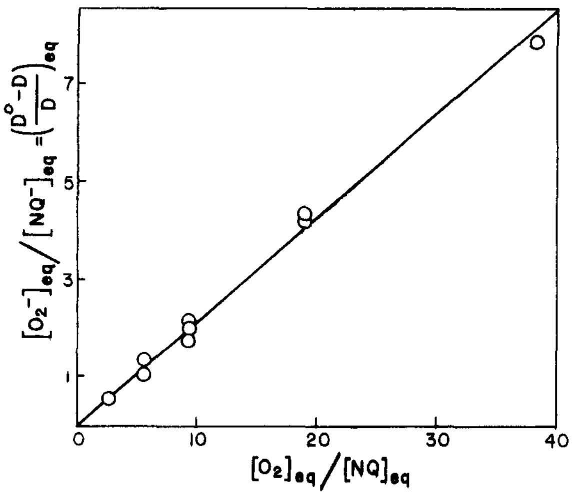

Figure 1. Determination of K_{eq} for the reaction $NQ^- + O_2 = NQ + O_2^-$, by pulse radiolysis. Plot of $[O_2^-]/[NQ^-]$ vs $[O_2]/[NQ]$ at equilibrium. See text for experimental conditions.

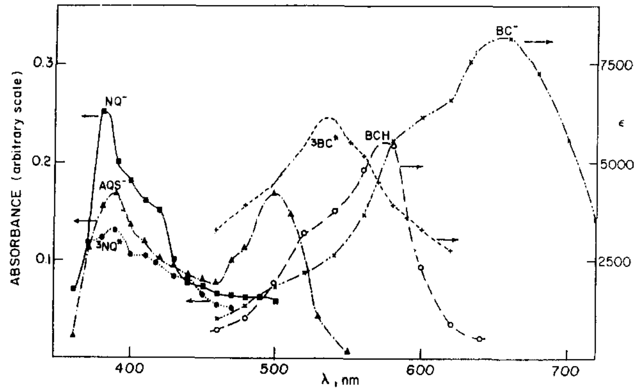

Figure 2. Absorption spectra of triplets and one-electron reduced species. AQS$^{\bullet-}$: from ref 3, laser photolysis of 6 × 10^{-4} M AQS + 6 × 10^{-3} M NO_2^-. BC: from ref 15. NQ: laser photolysis of 7 × 10^{-4} M NQ + 2.5 × 10^{-2} M NO_2^-; see ref 16, Figure 2 for ^{3}AQS spectrum.

Pulse radiolysis (PR) experiments were performed with a Varian 7715 linear accelerator and measuring system utilizing a 150-W xenon lamp, Bausch and Lomb grating monochromator, and IP28 photomultiplier. The signal was digitized (Biomation 8100) and sent to a Nova minicomputer that controlled the system. Rate constants for the reactions of $CO_2^{\bullet-}$ with NQ and BC were determined by PR of a solution containing various concentrations of the carbonyl compound, 0.1 M HCO_2^-, and saturated with N_2O as described by Hulme et al.[13] In the case of BC, relatively low-dose pulses were used, since the rate constant of its reaction with $CO_2^{\bullet-}$ (k = 3.6 × 10^7 $M^{-1}\ s^{-1}$) is low compared with that for self-annihilation of $CO_2^{\bullet-}$.[18a]

To avoid uncertainties arising from electrochemical irreversibilities, a PR technique was also used to determine the one-electron reduction potential of NQ.[19] The equilibrium constant of the reaction $NQ^{\bullet-} + O_2 = NQ + O_2^-$ was obtained by pulsing solutions containing air (2.4 × 10^{-4} M O_2), 0.1 M HCO_2^- (to convert all OH$^\bullet$ and H$^\bullet$ radicals to reducing $CO_2^{\bullet-}$ radicals), 10^{-3} M phosphate buffer, pH 7.5, and variable concentrations of NQ. In absence of oxygen, at ~10^{-4} M NQ, all reducing species including e(aq) are captured by the quinone. Thus, the absorbance, D^0, of $NQ^{\bullet-}$ in such a pulsed He-bubbled solution measures the total amount of radicals, O_2^- and $NQ^{\bullet-}$, produced in a test solution

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[11] Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

[12] In our previous work on the reaction between ^{3}AQS and NO_2^- and SO_3^{2-}, we pointed out a puzzling discrepancy between radical yields measured directly and those calculated from kinetic data (ref 3, p 4935). This discrepancy is now removed by the actinometric correction.

[13] Hulme, B. E.; Land, E. J.; Phillips, G. O. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1992.

[14] Patel, K. B.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 814.

[15] With the ratio of BCH/BC$^-$ absorbance = 0.67 at respective λ_{max}, from: Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 7323.

[16] Loeff, I.; Treinin, A.; Linschitz, H. *J. Phys. Chem.* **1983**, *87*, 2536.

[17] Moore, J. N.; Phillips, D.; Nakashima, N.; Yoshihara, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 745.

[18] (a) At ionic strengths used in this work, 2k ~ (1.3 ± 0.4) × 10^9 $M^{-1}\ s^{-1}$. Buxton, G. V.; Sellers, R. M. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 555. (b) Ilan, Y.; Rabani, J. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 609.

[19] For a simple review, see: Neta, P. *J. Chem. Educ.* **1981**, *58*, 110. See also ref 14.

TABLE I: Second-Order Rate Constants (k, 10^8 M^{-1} s^{-1}) for Elementary Reactions from Flash Photolysis (FP) and Pulse Radiolysis (PR) of M/HCO_2^- and M/Cl^- Systems[a,b]

			quenching const		$k(CO_2^{\bullet-} + M)$		
triplet, M	$E°$, V vs NHE	$E° + E_T$,[c] eV	$k_q(HCO_2^-)$	$k_q(Cl^-)$	FP	PR	$k(M^{\bullet-} + O_2)$
NQ	−0.12	2.36	30	17[f]	40	32	0.37[i]
AQS	−0.38[d]	2.30	4	5[g]	21	31[h]	5
AQS			3.5[b]				
BC	−1.13[e]	1.83	0.13	0.0008	0.32	0.36	
BC			0.085[b]				
BS			0.53				

[a] Except where noted, data are from present work. [b] For quenching by DCO_2^- in D_2O. [c] For triplet energies, see: NQ, ref 50; AQS, ref 16; BC, ref 4. [d] Meisel, D.; Neta, P. *J. Am. Chem. Soc.* **1975**, *97*, 5198. [e] Reference 4. [f] Unpublished results. [g] Reference 3. [h] Reference 13. [i] The value obtained by flash photolysis agrees well with that found by pulse radiolysis (see Experimental Section).

containing both O_2 and NQ. The ratio $([O_2^-]/[NQ^{\bullet-}])_{eq}$ is then given by $(D° - D_{eq})/D_{eq}$, where D_{eq} is the $NQ^{\bullet-}$ absorbance in a pulsed test solution at equilibrium. The ratio $([NQ]/[O_2])_{eq}$ is obtained by subtracting $[O_2^-]$ and $[NQ^{\bullet-}]$ from the corresponding original concentrations. Since the fractional conversions were small (less than 5% for NQ, 1% for O_2), any uncertainty in the extinction coefficient of $NO^{\bullet-}$ introduces little error. The linear plot of Figure 1 establishes that equilibrium is reached in this system and gives $K_{eq} = 0.21$. Combining this with the known one-electron reduction potential of O_2, $E°' = -0.330$ V at 1 atm or −0.16 V at 1 M, we obtain $E°'(NQ) = -0.12$ V. From the same set of PR experiments, measuring the effective rate constant $(k_+[O_2] + k_-[NQ])$ for equilibration following the pulse, we determine also the rate constants of the two opposing reactions $k(NQ^{\bullet-} + O_2) = 3.7 \times 10^7$ M^{-1} s^{-1}; $k(NQ + O_2^-) = 1.8 \times 10^8$ M^{-1} s^{-1}.

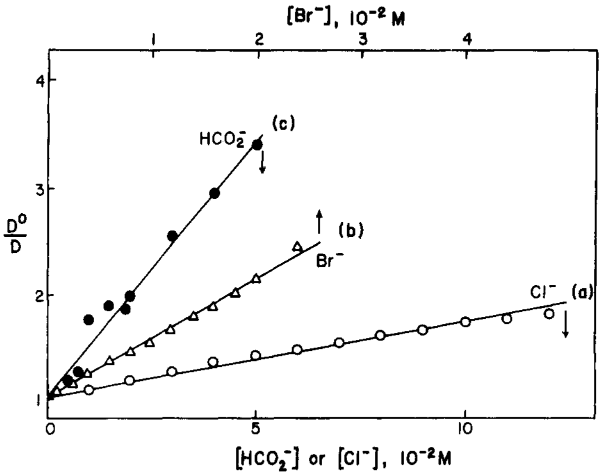

Figure 3. (a, b) Stern-Volmer plots for inhibition of transient E formation by Cl^- (○) and Br^- (△), respectively; 2×10^{-4} M AQS, 0.16 M HCO_2^-, N_2 saturated. (c) Stern–Volmer plot for inhition of transient B formation by HCO_2^-; 2×10^{-4} M AQS, O_2 saturated. $D°$ and D are transient absorptions at $\lambda_E = 500$ nm (a, b) and $\lambda_B = 480$ nm (c) in the absence ($D°$) and presence (D) of inhibitor.

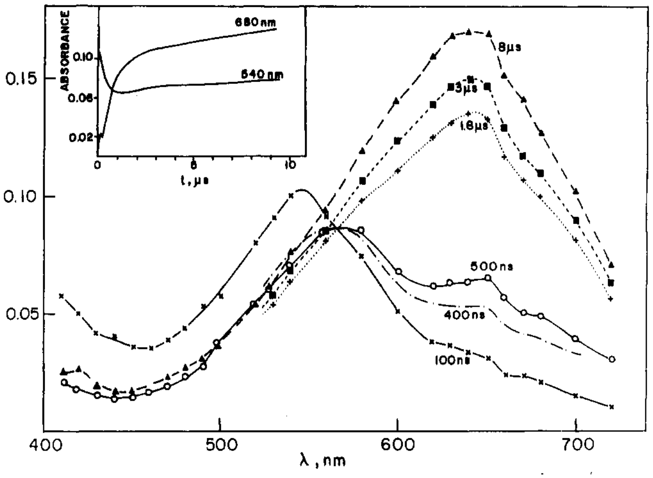

Figure 4. Laser photolysis of 4×10^{-3} M BC + 0.4 M HCO_2^-, pH 11.2, N_2 saturated. Transient spectra at various times after flash. Insert: kinetic traces.

Results

Absorption spectra of the triplets (^3M) and one-electron-reduced species ($M^{\bullet-}$ or $MH^{\bullet}$) are given in Figure 2. The spectra of the BS transients (not shown) closely resemble those of BC, but ^3BS decays somewhat faster ($k = 2.2 \times 10^5$ s^{-1}) than ^3BC. Both ^3NQ and the anion radical $NQ^{\bullet-}$ absorb in the same region ($\lambda_{max} \sim 390$ nm), but the triplet is short-lived, with the decay rate depending on NQ concentration: $k_d = (4.5 \times 10^6 + 4 \times 10^9[NQ])$ s^{-1}. This decay is associated with formation of various intermediates whose identity is still being studied.

Quenching Rates. The rate constants for triplet quenching by HCO_2^-, k_q, are recorded in Table I. These were measured directly (see Experimental Section) except for ^3AQS, where the triplet absorption and decay were overlapped by that of a short-lived intermediate we denote E. This caused deviations from pseudo-first-order kinetics and, depending on wavelength, led to an apparent "halt" in quenching by formate at $[HCO_2^-] \gtrsim 0.1$ M, i.e., the transient decay became almost independent of formate concentration. This effect was least marked in the wavelength range 410–440 nm, where $k_q = (2 \pm 1) \times 10^8$ M^{-1} s^{-1} was measured directly. The fast formate-independent decay may presumably be assigned to a product of triplet–formate interaction, transient E, which survives triplet disappearance and is therefore most evident at high $[HCO_2^-]$. This may be tested, and a more reliable value of k_q also obtained, by measuring the effect of added halide ion, X^-, with known $k_q^{X^-}$, on the yield of E, at constant $[HCO_2^-]$. The halides (group I) at low concentration efficiently quench ^3AQS without producing any observable intermediate (see Introduction). A simple treatment of the competition between HCO_2^- and X^- then leads to the Stern–Volmer relation:

$$D°/D = 1 + \left(k_q^{X^-}/k_q^{HCO_2^-}[HCO_2^-]\right)[X^-]$$

where $D°$ and D are the initial absorbances of E in the absence and presence of $[X^-]$, respectively, and $[HCO_2^-]$ is taken to be high enough so that triplet absorbance is not seen. Figure 3 demonstrates the validity of this relationship for both Cl^- and Br^-. From the slopes of the lines and the known values[3] $k_q^{Cl^-} = 5.0 \times 10^8$ M^{-1} s^{-1} and $k_q^{Br^-} = 3.8 \times 10^9$ M^{-1} s^{-1}, we obtain $k_q^{HCO_2^-}$. Both halides gave almost identical values, $k_q^{HCO_2^-} = 4.2 \times 10^8$ M^{-1} s^{-1}. A closely similar value (4.9×10^8 M^{-1} s^{-1}) was also derived from the competing effect of formate on the yield of the water adduct, transient B ($\lambda_{max} = 480$ nm, $k_d = 3 \times 10^4$ s^{-1}) in presence of O_2 at $t > 5$ μs, a time sufficient for removal of interfering $AQS^{\bullet-}$ absorbance.[16] Kinetic complications arising from overlapping transients were also encountered with the benzophenone derivatives when k_q was measured in alkaline solutions (pH 11.2, see below). The best linear plots of k_d vs $[HCO_2^-]$ were obtained at 410 nm, giving $k_q = 1.3 \times 10^7$ M^{-1} s^{-1}. However, at pH 6 this difficulty disappeared, and a constant value $k_q = (1.3 \pm 0.1) \times 10^7$ M^{-1} s^{-1} was measured for ^3BC at wavelengths extending from 380 to 660 nm. For ^3BS at pH 11.2 a higher value was found for k_q (Table I). Table I also includes

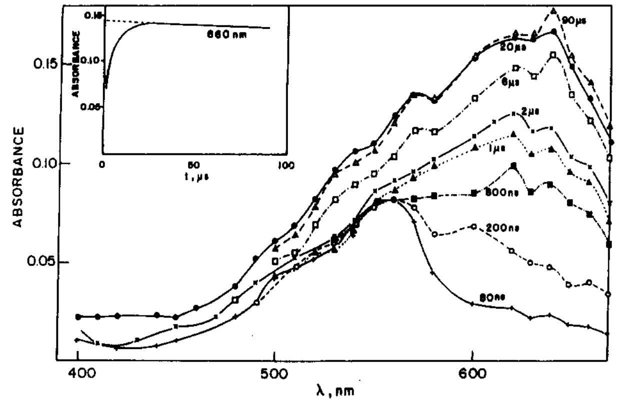

Figure 5. Laser photolysis of 2×10^{-3} M BS + 2 M HCO_2^-, pH 11.2, N_2 saturated. Transient spectra at various times after flash. Insert, kinetic trace. See text for dashed linear extrapolation.

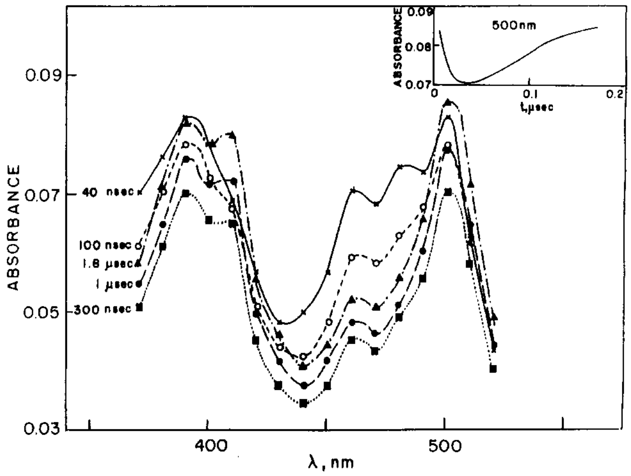

Figure 6. Laser photolysis of 2×10^{-4} M AQS + 0.8 M HCO_2^-, pH ~ 8, N_2 saturated. Transient spectra at various times after flash. Insert, kinetic trace.

rate constants for quenching of ^3AQS and ^3BC by DCO_2^- in D_2O.

Long-Lived Intermediates ($\tau \gtrsim 1\ \mu s$). Figures 4–7 show the time evolution of transient spectra for several air-free M/HCO_2^- systems, at relatively high formate concentrations at which more than 90% of this triplet is quenched (see Table II footnote). About 1 μs after the flash, the spectrum of each system corresponds to that of $M^{\bullet-}$, the semiquinone or ketyl anion radical (compare Figure 2). This species continues to grow in at longer times and at a reduced rate, reaches a limiting yield, and then slowly decays. In the case of AQS there appears an additional band around 410 nm (Figure 6). From the spectral evolution data and the shape of the kinetic traces (Figures 4–7, inserts), it is seen that $M^{\bullet-}$ is formed in two consecutive stages. The kinetics of the second stage are pseudo-first-order, with rate constant proportional to the concentration of M, the ground-state parent molecule. Second-order rate constants derived from this analysis are listed in Table I and compared with those obtained by PR for the reactions between M and CO_2^-, the anionic form of the carboxyl radical (pK_a of $COOH^\bullet = -0.2$[20]):

$$M + CO_2^{\bullet-} \rightarrow M^{\bullet-} + CO_2 \qquad (1)$$

No PR data are available for BS. The observed agreement provides strong evidence that the second stage of $M^{\bullet-}$ formation occurs via reaction 1. The first stage must therefore supply the carboxyl radical, by a reaction whose overall stoichemistry is

$$^3M + HCO_2^- + B \rightarrow M^{\bullet-} + CO_2^{\bullet-} + BH^+ \qquad (2)$$

where B is an appropriate base.

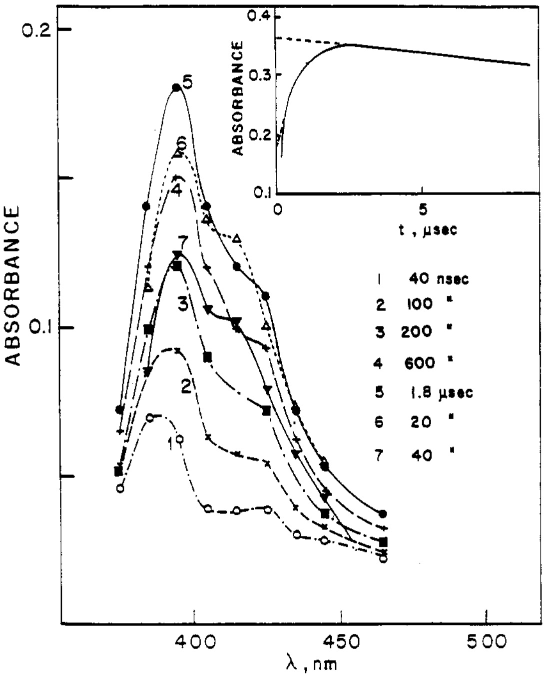

Figure 7. Laser photolysis of 3.5×10^{-4} M NQ + 2×10^{-2} M HCO_2^-, pH ~ 8, N_2 saturated. Insert: see legend for Figure 5.

TABLE II: Quantum Yields of Reduced Species in Laser Photolysis of M/HCO_2^- Systems[a]

triplet, M	ϕ_{M^-}-(second stage)/ ϕ_MN-(first stage)		first stage		ϕ_{M^-}[c] in M/N_3
	kinetic analysis	effect of O_2	ϕ_{M^-}	ϕ_{MH}	
NQ	1.1 ± 0.1	1.0	0.66 (0.77)[b]		
AQS	0.7 ± 0.2	0.8	0.32		0.13
BC	0.8 ± 0.2		(0.73)[e]	0.73[d]	0.015
BS	0.8 ± 0.2			0.66[d]	

[a] Except for NQ, the limiting yields given are constant over a considerable range of $[HCO_2^-]$. Because of the instability of NQ/HCO_2^- at high $[HCO_2^-]$, the formate concentration was not raised above 0.02 M (90% quenching). For definition of first and second stages, see text. [b] From the linear plot of ϕ^{-1} vs $[HCO_2^-]^{-1}$, extrapolated to infinite $[HCO_2^-]$. [c] Quenching by azide given for comparison; $E^\circ(N_3/N_3^-) = 1.32$. See ref 4. [d] Measured at both pH 11.2 and pH 6. [e] After deprotonation at pH 11.2.

According to this interpretation, the two stages should contribute equally to the yield of $M^{\bullet-}$ since under the conditions of the experiment, dimerization of $CO_2^{\bullet-}$ ($2CO_2^{\bullet-} \rightarrow C_2O_4^{2-}$[18a]) could not compete with reaction 1. The total yield of $M^{\bullet-}$ was determined by extrapolating back to zero time the slowly decaying final phase of the kinetic trace (see inserts, Figures 5 and 7). The contribution of the first stage, equal to the yield of $M^{\bullet-}$ at the start of the second stage, was determined by using the growing-in kinetics of the second stage and extrapolating back to the estimated midpoint of the first stage (inserts, Figures 5 and 7). A more careful analysis should make little difference in the results since the three reactions, the two processes of $M^{\bullet-}$ formation and its decay, are well separated in time. The ratios between the second and first stage yields, evaluated in this way, are given in Table II. This is close to unity for NQ but is about 20–25% smaller for the other cases.

The effect of oxygen on the quinone–formate systems further supports the view that the second stage involves reaction 1. In solutions saturated with O_2 this stage disappears and the total yield of $M^{\bullet-}$ now equals that of the primary stage, as determined in air-free solutions. The suppression of reaction 1 by O_2 is readily understood as a consequence of its scavenging effect on $CO_2^{\bullet-}$:

$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^- \qquad (3)$$

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(20) Jeevarajan, A. S.; Carmichael, I.; Fessenden, R. W. *J. Phys. Chem.* **1990**, *94*, 1372.

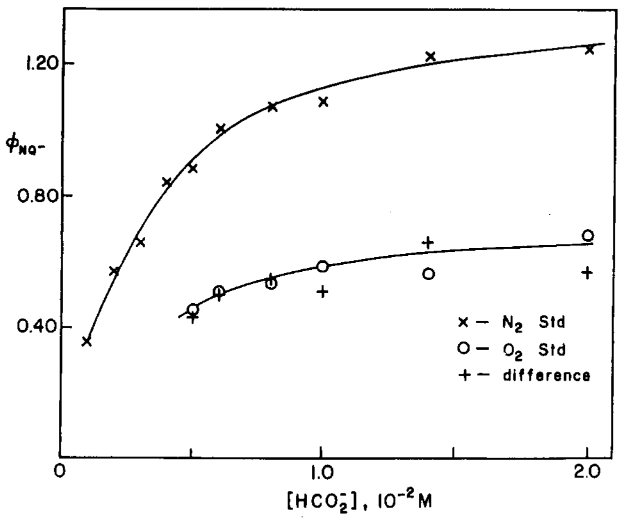

Figure 8. Quantum yield of $NQ^{\bullet -}$ as function of [HCO_2^-], in N_2 saturated (×) and O_2 saturated (O) solutions, and difference (+). [NQ] = 3.5 × 10^{-4} M.

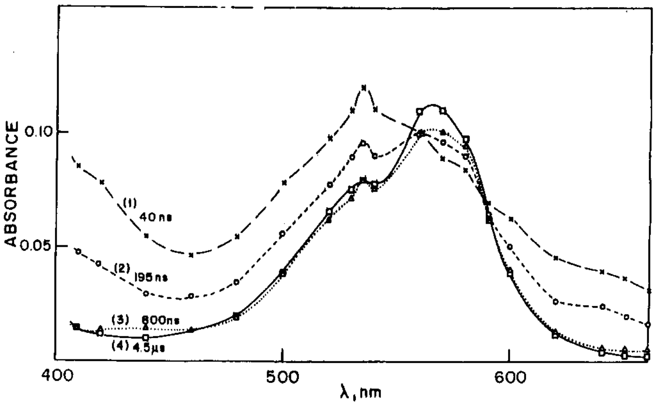

Figure 9. Laser photolysis of 4 × 10^{-3} M BC + 0.4 M HCO_2^-, pH 6, N_2 saturated. Transient spectra at various times after flash.

for which k_3 = 4.2 × 10^9 M^{-1} s^{-1}.[18b] Under the conditions employed here, reaction 3 predominates over 1. Figure 8 demonstrates the effect of O_2 in the case of NQ: at all formate concentrations studied, the total yield of $NQ^{\bullet -}$ in air-free solutions is twice that in O_2-saturated solutions. The AQS/HCO_2^- system behaved similarly, but the ratio between the two reduction contributions, thus evaluated, was only 0.8 ± 0.2, the same as obtained from the kinetic analysis (Table II). With BC/HCO_2^- in presence of O_2, a new, different pattern of transient absorption was observed whose nature is still unclear. As expected, the lifetime of M^- is also shortened in presence of O_2:

$$M^{\bullet -} + O_2 \rightarrow M + O_2^- \qquad (4)$$

The second-order rate constant for this reaction for the AQS/HCO_2^- system agreed quite well with that obtained for AQS/Cl^- (4.3 × 10^8 M^{-1} s^{-1} [3]), further supporting the identification of the long-lived intermediate as $AQS^{\bullet -}$. Under our conditions, this reaction is still sufficiently slow in all cases so that good values of initial ΔD_{M^-} could be obtained even in presence of O_2, by extrapolating the kinetic traces back to zero time.

The benzophenone systems were studied also at pHs close to neutrality. Figure 9 shows the evolution of transient spectra for BC + 0.4 M HCO_2^- at pH 6.0. Comparing these results with the spectra of ^{3}BC and $BCH^{\bullet}$, λ_{max} = 535 and 570 nm, respectively,[15] and noting the two isosbestic points at 565 and 585 nm (Figure 2) establish that we are following the reaction

$$^3BC + HCO_2^- \rightarrow BCH^{\bullet} + COO^{\bullet -} \qquad (5)$$

In support of this, we observe that the fast decay at 535 nm and growth at 570 nm proceed at the same rate, and the decay of the latter band is second order, with $2k/\epsilon_{max}$ = 2.8 × 10^5 cm s^{-1}, close to that previously observed for $BCH^{\bullet}$ (3.4 × 10^5 cm s^{-1}).[15] However, quite contrary to the behavior in alkaline solutions (Figure 4), there appears to be no distinct second stage of radical formation (either $BCH^{\bullet}$ or $BC^{\bullet -}$) via reaction 1. The reason for this is not clear.

In connection with these formate studies, it is of interest also to examine the behavior of formic acid. This was done for AQS, in 10^{-2} M $HClO_4$. Quenching of the triplet by HCO_2H is much slower than by HCO_2^- and could be followed only indirectly, by observing the effect of HCO_2H on transient B, which is the only long-lived intermediate formed under these conditions.[16] The rate constant for triplet quenching estimated in this way is $k_q^{HCO_2H}$ ~ 2 × 10^6 M^{-1} s^{-1}. To verify that the short-lived intermediate in formic acid solution is indeed the triplet and not E, the quenching rate by added Br^- in presence and absence of HCO_2H was measured and found to be the same in both cases.

Radical Quantum Yields. The *primary* quantum yields of the reduced species are given in Table II. These values represent the maximum yields measured at total quenching by formate, where any competing triplet-water reactions are completely suppressed. The limiting yields were found to be constant over a considerable range of formate concentration (0.4–1.0 M for AQS; 0.4–0.8 M for BC), with no clear indication of either a decline or rise. At lower formate concentrations and fractional quenching, the yields followed the expected linear Stern–Volmer correlations between ϕ_R^{-1} and [HCO_2^-]$^{-1}$. However, the quenching constants, k_q, derived from these plots differed by factors of 2–3 from those given in Table I. These discrepancies may be associated with the large corrections for the triplet-water reactions under conditions of partial quenching.

Short-Lived Intermediates (τ < *1* μs). With BC and BS in alkaline solution and with AQS, short-lived intermediates were observed following triplet decay.

(*1*) *BC and BS*: Figure 4 shows evolution of transient spectra in a BC solution containing 0.4 M HCO_2^- at pH 11.2. Three successive species may be identified. The *third*, λ_{max} ~ 650 nm, is the ketyl anion radical $BC^{\bullet -}$, which is formed, as previously discussed, in two stages, well separated in time (see insert). The first transient, λ_{max} = 535 nm, is clearly the triplet, with τ ~ 200 ns, in agreement with k_q = 1.3 × 10^7 M^{-1} s^{-1} (Table I).

Between them is a species, λ_{max} = 570 nm, which is the same as that produced at pH 6, namely, $BCH^{\bullet}$, but is now short-lived because of its fast conversion to $BC^{\bullet -}$ in alkaline solution. This transition is marked by the isosbestics at 570 and 500 nm, between the second transient and the first stage of $BC^{\bullet -}$ formation, which is essentially complete at about 2 μs. Further evidence supporting this assignment is the height of the 570-nm peak, relative to that at 650 nm (1.8 μs), corresponding to the relative intensities of $BCH^{\bullet}$ and $BC^{\bullet -}$ absorption respectively (Figure 1). The second stage of $BC^{\bullet -}$ formation via reaction 1 is well defined by both the final slow increase in 650-nm absorption and the breakdown of the isosbestic at 570 nm. Similar results were obtained at 2 M HCO_2^- for both BC and BS (Figure 5), with τ of the triplet (not shown) reduced to 40 ns, as expected.

The kinetics of deprotonation

$$BCH^{\bullet} + OH^- \rightarrow BC^{\bullet -} + H_2O \qquad (6)$$

at pH 11.2 were first-order, with effective rate constant 3 × 10^6 s^{-1}, corresponding to k_6 = 2 × 10^9 M^{-1} s^{-1}.[21] The same value was found for $BSH^{\bullet}$. Since these radicals are actually anions, the rather low rates of proton transfer to OH^- are not unreasonable. The deprotonation rate varied qualitatively with pH as expected, but quantitative study was difficult because of the gradual overlap among reactions 6, 1, and 5. Moreover, below pH 11, the contribution of HCO_2^- to the rate of deprotonation may be quite significant at the concentrations of formate em-

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(21) The deprotonation of $BCH^{\bullet}$ at pH 11.2 was also studied by laser photolysis of BC with 5 M isopropyl alcohol as hydrogen donor to the triplet. The value of k_6 thus obtained is lower by a factor of 2 (1 × 10^9 M^{-1} s^{-1}), which may reflect a solvent effect on reaction of two negative ions in the formate system, BC and $HCO_2^{\bullet -}$.

ployed.[22] From one measurement of the ratio $[BS^{\bullet-}]/[BSH^\bullet]$ at pH 8.2, the pK_a of $BSH^\bullet$ is estimated to be ~8.1, close to that of $BCH^\bullet$.

The primary quantum yields of $BCH^\bullet$ at pH 11.2 and 6.0 were the same, $\phi_{BCH} = 0.73$, and for $BSH^\bullet$, somewhat lower, $\phi_{BSH} = 0.66$.

(*2*) *AQS*: We have designated as E the short-lived species resulting from initial triplet–formate interaction and observed directly after flashing at almost total quenching (Figure 6). This transient decays with first-order rate constant $k_d^E = (8 \times 10^6 + 3 \times 10^6[HCO_2^\bullet])\ s^{-1}$, very much faster than the decay of $AQS^{\bullet-}$ under these circumstances. Thus, over the range of $[HCO_2^-]$ studied, the lifetime of E is rather close to that of the triplet, but its removal by HCO_2^- is slower, thereby accounting for the apparent "halt" in the quenching effect of formate, described above. This halt is most clearly seen at wavelengths around λ_{max} of E (470 nm) and at formate concentrations corresponding to total quenching of the triplet, when the lifetime of the initial short-lived flash transient becomes only slightly dependent on $[HCO_2^-]$. Intermediate E can also be distinguished from the triplet by its failure to be quenched by Br^-, even up to 0.05 M Br^-, whereas bromide quenches the triplet strongly ($k_q^{Br^-} = 3.8 \times 10^9\ M^{-1}\ s^{-1}$.[3] The strong inhibiting effect of Br^- and Cl^- on the yield of E (Figure 3) at relatively low halide concentrations establishes that E is formed from the AQS triplet and not the singlet. The lifetimes of both the triplet and E are too short to be appreciably affected by 10^{-3} M O_2,[16] in contrast to the case with $AQS^{\bullet-}$.

Steady-State Photochemistry. The yield of H_2O_2 from irradiated AQS/HCO_2^- solutions, continuously bubbled with O_2, increased with $[HCO_2^-]$, reaching a limiting value of 0.16. The rise in $\phi_{H_2O_2}$ accompanied a decrease in the yield of hydroxylated AQS with associated depletion of AQS.[23] This reflects the progressive competition between triplet–formate and triplet–water reactions leading to hydroxylation (see ref 16 and references therein). The rise in $\phi_{H_2O_2}$ ran parallel to a rise in ϕ_{AQS^-}, as measured by laser photolysis.

Discussion

We note first that in the triplet interactions studied here, formate behaves as a typical group II anion. Quenching is accompanied by efficient radical formation; the quantum yield rises with $[HCO_2^-]$, levels off at concentrations corresponding to total triplet quenching, and does not increase at higher $[HCO_2^-]$ (see Introduction). This behavior is in accord with expectations based on the IRSOC model. The radicals $CO_2^{\bullet-}$ or $HCO_2^{\bullet-}$ have C_{2v} symmetry,[20,24] and therefore all their electronic states have zero orbital angular momentum. (In the radical $^\bullet COOH$ this asymmetry is somewhat distorted,[20] but its electronic states are still nondegenerate.) Quenching by energy transfer to a formate triplet level, as seems to occur with nitrite,[2] can be ruled out in all cases studied here, because of an energy mismatch between the donor and acceptor levels, $E_T(\text{formate}) > 80$ kcal/mol.[25,26]

Kinetics and Mechanisms. We discuss now the nature of the interaction between the triplets and HCO_2^-, whose overall stoichiometry is represented by eq 2. In the benzophenone case, ^3BC and ^3BS, the primary reaction product is unambiguously the $MH^\bullet$ radical, which is then deprotonated in alkaline solution to give $M^{\bullet-}$ (Figures 4 and 9). The triplet–formate interaction thus involves initial hydrogen abstraction, even at pH 11. On the other hand, for the more strongly oxidizing quinones, ^3AQS and ^3NQ, the flash transient spectra give no indication of a protonated radical prior to appearance of $M^{\bullet-}$. This is particularly evident in the case of AQS, where the absorptions of $AQSH^\bullet$ and $AQS^{\bullet-}$ are clearly differentiated; the $AQSH^\bullet$ spectrum peaks strongly around 390 nm, close to the triplet band,[16] but declines at $\lambda > 400$ nm and becomes quite negligible at 500 nm, where $AQS^{\bullet-}$ has an intense band[13] (Figure 2). While differences between absorption of $NQH^\bullet$ (370 nm) and $NQ^{\bullet-}$ (390 nm) are less clearly defined,[14] the flash transient spectra ($NQ^{\bullet-}$) show no corresponding time-dependent shift (Figure 7). We conclude that the interaction mechanism for the quinone triplets involves charge transfer only. This conclusion, based on the transient spectra alone must yet be taken as tentative. Thus, the strong absorption of the triplet as well as that of the new transient, E, may mask the conversion of $AQSH^\bullet$ to $AQS^{\bullet-}$. Another possible consideration is that the deprotonation of the radicals by formate itself may be too fast to be detected.[27] The pK_a values of $AQSH^\bullet$ (3.25[13]) and $NQH^\bullet$ (4.1[14]) are close to that of formic acid ($\Delta pK_a = 0.50$ and -0.45, respectively). Rate constants higher than $10^8\ M^{-1}\ s^{-1}$ were observed for the deprotonation of several free radicals by bases, with comparable ΔpK_a's.[28]

These uncertainties notwithstanding, an electron-transfer mechanism in the quinone case is strongly supported by other characteristics of the quenching process, including the very high and comparable rates of quenching by *both* formate and chloride and the absence of a detectable isotope effect (Table I).[29] The ketones, on the other hand, show much lower quenching rates by formate ($k_q \sim 10^7\ M^{-1}\ s^{-1}$), large differences between the rates for formate and chloride ($k_q \sim 10^5\ M^{-1}\ s^{-1}$) and appreciable isotope effects.

Some thermodynamic values are needed in considering the factors governing H abstraction vs electron transfer in the quenching process. The formyloxyl radical, $HCO_2^\bullet$, is the species immediately produced when formate functions as an electron donor. To evaluate its reduction potential, we first consider the carboxyl radical, $^\bullet COOH$, which is the relaxed form of $HCO_2^\bullet$.[20] From the measured standard potential of $CO_2 + e \rightarrow CO_2^{\bullet-}$ in water, $E^\circ(CO_2/CO_2^{\bullet-}) = -1.90$ V[30] and $E^\circ(CO_2,H^+/HCO_2^-) = -0.18$ V,[31] one obtains $E^\circ(CO_2^-,H^+/HCO_2^-) = 1.54$ V. Values close to this were derived in related experimental[32] and theoretical[33] studies. Using the recently measured dissociation constant of $^\bullet COOH$, $pK_a = -0.2$,[20] gives $E^\circ(^\bullet COOH/HCO_2^\bullet) = 1.55$ V. To obtain $E^\circ(HCO_2^\bullet/HCO_2^-)$, we require ΔG° for the reaction $^\bullet COOH \rightarrow HCO_2^\bullet$. A theoretical analysis yields $\Delta E \sim 0.6$ eV.[20] Taking $\Delta S \sim 0$, we finally obtain $E^\circ(HCO_2^\bullet/HCO_2^-) \sim 2.1$ V. However, we believe that the correct value is higher and indeed close to that of the $Cl^\bullet/Cl^-$ couple, i.e., 2.5 V,[34] for the following

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(22) From the pK_a's of $BCH^\bullet$ (8.2) and HCOOH (3.75), one obtains $K_{eq} = 3.5 \times 10^{-5}$ for the reaction

$$BCH^\bullet + HCO_2^- \rightarrow BC^{\bullet-} + HCOOH$$

Assuming the back reaction to be diffusion controlled ($k \sim 10^{10}\ M^{-1}\ s^{-1}$), we estimate $k(BCH^\bullet + HCO_2^-) \sim 4 \times 10^5\ M^{-1}\ s^{-1}$. Thus, at 1 M, formate may contribute ~10% to the deprotonation rate of $BCH^\bullet$ at pH 11.2, and this may rise to ~30% at pH 10.5.

(23) Formate also affects the nature of the hydroxylated product. (See: Clark, K. P.; Stonehill, H. I. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 577, 1676. Broadbent, A. D.; Matheson, H. B.; Newton, R. P. *Can. J. Chem.* **1975**, *53*, 826.) In water alone, the main products are α- and β-monohydroxy derivatives ($\alpha/\beta \sim 1.5$ at pH below 9), whereas with formate, the β derivative appears to be the main product, independent of [AQS] in the range 10^{-4}–2×10^{-3} M. This compound was identified by its spectrum ($\lambda_{max} = 475$ nm), unchanged over pH range 8–12.

(24) Atkins, D. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Amsterdam, 1967.

(25) Johnson, L. W.; Maria, H. J.; McGlynn, S. P. *J. Chem. Phys.* **1971**, *54*, 3823.

(26) McGlynn, S. P.; Azumi, T.; Kumar, D. *Chem. Rev.* **1981**, *81*, 475.

(27) The limiting lifetime for deprotonation by water is estimated to be $\tau \gtrsim 20$ ns from the pK of $AQSH^\bullet$ (3.25) and $k(AQS^{\bullet-} + H^+) \lesssim 10^{11}\ M^{-1}\ s^{-1}$.

(28) Bell, J. A.; Grunwald, E.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 2995. The repulsion between two negative ions, such as $AQSH^\bullet$ and HCO_2^-, may well reduce the rate below $10^8\ M^{-1}\ s^{-1}$, see this reference, Table III.

(29) Roy and Aditya (Roy, A.; Aditya, S. *J. Photochem.* **1983**, *22*, 361) have studied the reaction of ^3AQS and formate using flash apparatus of low time resolution and conclude that electron and not H-atom transfer occurs over a wide pH range. Their evidence for this is the observation of long-lived (millisecond) transients at 500 nm, even down to pH 2. However, at pH 2, the absorbing species is not $AQS^{\bullet-}$ but transient B, as noted above. Other intermediates may also be formed at the high AQS concentrations used in their work. Their value for the pK_a of $AQSH^\bullet$ (8.2) is in error because of confusion with the spectrum of $AQSH_2$, as shown by: Wakisaka, A.; et al. *J. Phys. Chem.* **1987**, *91*, 6547.

(30) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(31) Literature data for this E° are confusing. In refs 32 and 33, the values given are for $2E^\circ$, while in the *Handbook of Chemistry and Physics*, -0.199 V is given for $E^\circ(CO_2,H^+/HCOOH)$.

(32) Surdhar, P. S.; Mezyk, S. P.; Armstrong, D. A. *J. Phys. Chem.* **1989**, *93*, 3360.

(33) Koppenol, W. H.; Rush, J. D. *J. Phys. Chem.* **1987**, *91*, 4429.

reasons: (a) The spectrum of HCO_2^- in aqueous solution shows an intense band, peaking at $\lambda < 170$ nm, with $\epsilon_{max} > 9 \times 10^3$ M^{-1} cm^{-1}. Weak shoulders also appear around $\lambda \sim 204$ and ~ 190 nm, which have been assigned respectively to $n \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ transitions.[25] The main intense band is markedly blue-shifted on replacing H_2O by D_2O, which strongly suggests that it corresponds to a charge-transfer-to-solvent (ctts) transition, possibly overlapped by $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations.[35] The ctts assignment is also supported by the appearance of solvated electron absorption upon irradiation. This places the ctts band of HCO_2^- close to that of Cl^-.[36] (b) The standard potentials calculated from thermodynamic data by using various approximations were $E°(CH_3CO^•/CH_3CO_2^-) = 2.41$ V and $E°(C_2H_5CO_2^•/C_2H_5CO_2^-) = 2.23$ V, suggesting $E° > 2.4$ V for the $HCO_2^•/HCO_2^-$ couple. The resemblance between formate and chloride is further manifest by the very similar quenching behavior toward the quinone triplets, as noted above. It is particularly noteworthy that this similarity extends also to their quenching of triplet anthraquinone-1-sulfonate, for which we find the remarkably low but again comparable rate constants: $k_q^{Cl^-} = 4.8 \times 10^6$ and $k_q^{HCO_2^-} = 2.5 \times 10^6$ M^{-1} s^{-1}.[37]

The fact that formate is a much better quencher than chloride for the ketone triplets is presumably related to the different interaction mechanisms, H atom vs electron transfer, which are involved. If we may assume that the one-electron potentials of the formate and chloride couples are similar and that these potentials parallel charge-transfer rates,[38] then the H-atom-transfer mechanism provides a 100-fold faster reaction pathway than simple charge transfer for formate. In this connection, it is of interest to examine the CH bond strength in formate. The dissociation energy of this bond to give H and $CO_2^{•-}$ has not been measured, but it is expected to be relatively low because of the "lone-pair trans effect".[39] It can be estimated to be about 90 kcal/mol by two independent methods: (a) In an ab initio analysis, the dissociation of HCO_2^- to H^- and CO_2 was computed as ~ 59 kcal/mol.[40] Taking the electron affinities of H and CO_2 to be respectively 17.4 and ~ -14 kcal/mol,[33] a value of ~ 90 kcal/mol is obtained. (b) Vibrational analysis of HCO_2^- and HCOOH indicates that the CH bond order in the latter is higher by about 4%.[41] The H–CO_2H bond dissociation energy is 92.7 kcal/mol,[32] leading to D(CH) $\sim$ 90 kcal/mol in HCO_2^-. While this bond energy is substantially higher than those of many weakly bound H donors (toluene, isopropylbenzene, etc.), the formate–^{3}BC quenching rate is nevertheless much faster.[42] Moreover the isotope effect, $(k_H/k_D) = 1.6$, is also much smaller than that found in "radical-like" H transfers.[42,43] These kinetic characteristics are typical of ketone triplet H-transfer reactions involving partial charge transfer in the reaction complex, in which rates correlate with donor IPs and triplet redox potentials.[38,43,44] Tunnelling effects, which depend strongly on the width of the potential barrier, may be important in these reactions.[43] H abstraction from HCO_2^- may begin with some degree of charge-transfer interaction and proceed to a transition state for hydrogen (proton) transfer, with its associated bond stretching. An additional factor involved in competing hydrogen vs electron transfer processes from a given donor may be measured by the basic strength of the incipient acceptor (anion) radical. Thus, we find here H transfer for the more strongly basic BC^- (pK_a(BCH$^•$) = 8.2)[15] compared with electron-transfer for AQS^- (pK_a(AQSH$^•$) = 3.25).[13] Conversely, some degree of "hydrogen transfer" may also be involved in overall electron-transfer mechanisms, to the extent that bond stretching or hydrogen bonding occur in the reaction complex.[43,44]

New AQS Transients. We have noted that the ^{3}AQS–formate system shows a short-lived transient band around 470 nm (E), accompanying triplet quenching, and another band appearing later at 410 nm (Figure 6). The status of these species in the overall pattern of the AQS–formate reaction is not clear. It is tempting to assign E to a ^{3}AQS–formate exciplex whose spectrum is expected to be close to that of $AQS^{•-}$ itself. The decay constant of E, 8×10^6 s^{-1}, is similar in magnitude to those of other triplet exciplexes involving quinones (including anthraquinone) and aromatic amines in benzene and more polar solvents[45] as well as amines and benzophenones.[44,46] If E is indeed the exciplex and $AQS^{•-}$ is formed only through its dissociation, then the transient absorption observed immediately after the flash should represent the overall spectrum of the exciplex, two bands near 400 and 500 nm, as in $AQS^{•-}$, and an additional band around 470 nm, perhaps related to the shoulder observed in the $AQS^{•-}$ spectrum (Figure 2). Against this view, however, is the observation that the lifetime of E is appreciably shortened by high formate concentration while the quantum yield of AQS^- does not fall. This is seen even up to 1 M HCO_2^-, where one would expect a readily detected drop of $\sim$30% in ϕ_R. Indeed, such a decrease in radical yield at very high quencher concentrations has previously been observed in the reaction of azide with ^{3}AQS.[3] It is possible that E may be a product of nucleophilic addition of formate to AQS, perhaps analogous to the water adducts B and C observed in earlier work.[16,17] If this interpretation is correct, then E and $AQS^{•-}$ are formed from ^{3}AQS in parallel and not sequential processes. The spectrum of E may therefore be obtained by subtracting the absorption of $AQS^{•-}$ at about 300 ns (i.e., before appreciable decay of $AQS^{•-}$ has occurred) from the total transient absorption at about 40 ns, corresponding to completion of triplet quenching at 1 M formate. The spectrum thus derived from the data of Figure 6 shows only a single broad band at 470 nm. For comparison, the absorption of the water adduct, B, peaks at 480 nm.[16,17] The question of sequential vs parallel processes in the ^{3}AQS–formate reaction is being studied further by using flash equipment of higher time resolution.

The quantum yield of the final product, H_2O_2, in steady irradiation of oxygenated AQS–formate solutions, is expected to be equal to that of $AQS^{•-}$, since each $AQS^{•-}$ molecule and its associated $CO_2^{•-}$ should yield two molecules of O_2^- (eqs 3 and 4) or one molecule of peroxide. Instead we obtain $\phi_{H_2O_2} = 0.16$, which within experimental error is half that of $\phi AQS^{•-}$. This discrepancy may be associated with the appearance of the unassigned transient at 410 nm (Figure 6). While side reactions with scavenging impurities may also be responsible (since the disproportionation reaction of O_2^- at pH 8 is rather slow[47]) the stoichiometric relationships, if real, point to more specific dissipative pathways.

Radical Quantum Yields. While both chloride and formate quench the quinone triplets by electron transfer, and with at least roughly comparable ΔG^* and k_q values, there is a very marked difference between the net radical yields ($\phi_R = 0$ for Cl^{-3}). This is, of course, representative of the different behavior of group I and group II anions and indicates that there is no simple correlation between the energetics of electron transfer and radical yield for triplet quenching where spin rephasing must accompany back reactions to the ground state.

We may write the simplified expressions

$$\phi_R = \frac{k_{fr}}{k_{fr} + k^*_{ISC}} \qquad k^*_{ISC} = \frac{k_{ISC} k_G}{k_{ISC} + k_G}$$

where k_{fr} is the rate constant for separation of radicals from the exciplex and k^*_{ISC} is the effective rate constant for transition of

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(34) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(35) Arvis, M.; Lustig, H.; Hickel, B. *J. Photochem.* **1980**, *13*, 223.

(36) Blandamer, M. J.; Fox, M. *Chem. Rev.* **1970**, *70*, 59.

(37) Unpublished results.

(38) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 41.

(39) Gregory, A. R.; Kidd, K. G.; Burton, G. W. *J. Mol. Struct.* (*THEOCHEM*) **1983**, *104*, 9.

(40) Nguyen, M. T. *J. Mol. Struct.* (*THEOCHEM*) **1985**, *133*, 269.

(41) Hahn, E. *Z. Chem.* **1987**, *27*, 454.

(42) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1667, 1672.

(43) Formosinho, S. J. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1313, 1332.

(44) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048 and references therein.

(45) Levin, P. P.; Pluzhnikov, P. F.; Kuzmin, V. A. *Chem. Phys.* **1989**, *137*, 331.

(46) Devadoss, C.; Fessenden, R. W. *J. Phys. Chem.* **1990**, *94*, 4540.

(47) Czapski, G. *Annu. Rev. Phys. Chem.* **1971**, *22*, 171.

the triplet exciplex to the ground state. This is denoted by k^*_{ISC} since this process comprises two clearly distinguishable mechanisms. We first have an isoenergetic spin rephasing between triplet and singlet exciplex states,[45] which is then followed by back electron transfer and vibrational dissipation leading to the ground state. The first step (k_{ISC}) will evidently depend on spin–orbit coupling within the exciplex, and the second (k_G) will involve Franck–Condon energy-gap considerations.[48] For $k_{fr} \ll k^*_{ISC}$, $\phi_R \sim 0$, as in group I anions, while for $k_{fr} \gtrsim k^*_{ISC}$, high radical yields are expected (group II). The nature of k^*_{ISC} depends on whether spin rephasing or Franck–Condon effects are rate-controlling. Yet another factor will be the detailed electronic structure of the exciplex, more specifically, the degree of resonance stabilization arising from interaction between charge transfer and locally excited configurations, which will influence k_{fr}. For situations in which an essentially constant SO coupling can be imposed, as in quenching of triplet methylene blue by a series of substituted ferrocenes, a treatment based on such resonance derives a linear correlation between ln ($\phi_R^{-1} - 1$) and $\Delta G^*_{ET}{}^{-1}$.[49] An increase in ϕ_R with increasingly negative ΔG^*_{ET}, i.e., as the exciplex approaches more closely to the pure CT state, is suggested also in these group II anion quenching studies. Thus, in electron-transfer quenching by formate, we find a decrease in ϕ_R in passing from NQ to AQS (Table II), although the change in ΔG^*_{ET} is small.[50] For azide quenching, ϕ_R is less with BC (0.01)[4] than with AQS (0.13). However, much more extensive data are needed on series of triplets quenched by various anions to generalize these interpretations.

The high ϕ_R's obtained in BC– or BS–formate interactions may be ascribed to slow reversal of the "heavy particle" H-atom transfer, compared to rapid thermal dissipation of reaction energy within the exciplex and trapping of reaction products.

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(48) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

(49) Tamura, S.; Kokuchi, K.; Kokubun, H.; Weller, A. *Z. Phys. Chem. (Munich)* **1980**, *121*, 165.

(50) The triplet energy of NQ in water is not known. The value of $E^{\circ*}$ for ^{3}NQ in Table I uses $E_T = 2.48$ eV, measured in rigid hydrocarbon matrix: Vo-Dinh, H.; Wild, U. P. *Spectrochim. Acta* **1984**, *40A*, 411. Taking E°(Cl/Cl$^-$) $\sim$ 2.5 V makes $\Delta G^*_{ET} \sim$ 0.1–0.2 V, for which the observed value of $k_q^{Cl^-}$ is surprisingly high. See: Shizuka, H.; Obuchi, H. *J. Phys. Chem.* **1982**, *86*, 1297 and references therein.

Diffuse Reflectance Laser Flash Photolysis Studies of Reactions of Triplet Benzophenone with Hydrogen Donors on Silica[1]

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The reactions of triplet benzophenone adsorbed on silica with several hydrogen donors have been examined by using diffuse reflectance laser flash photolysis techniques. The triplet is efficiently quenched by substrates such as cyclohexane, benzhydrol, and diphenylmethane with the concomitant formation of a transient that shows an absorption maximum at 545 nm and that is assigned to the diphenylketyl radical. The triplet decays with exponential kinetics in the presence of these substrates, with rate constants that increase linearly with the hydrogen donor concentration. Rate constants for hydrogen abstraction of 3.9×10^{14} and 4.4×10^{14} dm^2/(mol s) are measured for diphenylmethane and benzhydrol, respectively. These reactions are over an order of magnitude slower than energy transfer from triplet benzophenone to naphthalene, for which a rate constant of 6.4×10^{15} dm^2/(mol s) has been measured. The rate constants for decay of triplet benzophenone are also decreased at higher ketone loadings or in the presence of moderate amounts of inert substrates such as benzoic acid or phenyl benzoate.

The photochemistry of molecules adsorbed on solid supports such as silica and alumina is currently an area of considerable interest.[2,3] Most of the work in this area has focused on product studies or luminescence spectroscopy. These studies have yielded a substantial amount of information on the nature of the interaction between the adsorbate and the surface and the mobility of species on surfaces.[2–4] Time-resolved luminescence techniques, usually fluorescence lifetime measurements of aromatic hydrocarbons, have been used in a few cases to estimate rate constants for reactions on surfaces.[5–7] However, this method suffers some limitations in terms of the relatively short time scales that are available for interaction of the excited probe with other species. Further, with the exception of energy-transfer processes that generate excited-state species, luminescence methods do not give any information on the products of reaction of the probe with adsorbed quenchers.

The recent development of diffuse reflectance flash photolysis now permits direct absorption measurements of transients in opaque samples.[8–11] This means that it is straightforward to obtain kinetic data for a variety of transient species that are not amenable to luminescence methods. To date, the technique has been applied to the study of triplets, radicals, and radical cations on a variety of metal oxide and zeolite supports.[12–21] The transient absorption

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(1) Issued as NRCC 32825.

(2) Thomas, J. K. *J. Phys. Chem.* **1987**, *91*, 267–276.

(3) Turro, N. J. *Tetrahedron* **1987**, *43*, 1589–1616.

(4) Oelkrug, D.; Flemming, W.; Fullemann, R.; Gunther, R.; Honnen, W.; Krabichler, G.; Schafer, M.; Uhl, S. *Pure Appl. Chem.* **1986**, *58*, 1207–1218.

(5) Bauer, R. K.; Borenstein, R.; de Mayo, P.; Okada, K.; Rafalska, M.; Ware, W. R.; Wu, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4635–4644.

(6) de Mayo, P.; Natarajan, L. V.; Ware, W. R. *ACS Symp. Ser.* **1985**, *No. 278*, 1–19.

(7) de Mayo, P.; Natarajan, L. V.; Ware, W. R. *J. Phys. Chem.* **1985**, *89*, 3526–3530.

(8) Kessler, R. W.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 309–320.

(9) Kessler, R. W.; Krabichler, G.; Uhl, S.; Oelkrug, D.; Hagan, W. P.; Hyslop, J.; Wilkinson, F. *Opt. Acta* **1983**, *30*, 1099–1111.

(10) Oelkrug, D.; Honnen, W.; Wilkinson, F.; Willsher, C. J. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 2081–2095.

(11) Wilkinson, F.; Willsher, C. J. *Tetrahedron* **1987**, *43*, 1197–1209.

(12) Wilkinson, F.; Willsher, C. J. *Chem. Phys. Lett.* **1984**, *104*, 272–276.

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