

# Reaction Pathways Involved in the Quenching of the Photoactivated Aromatic Ketones Xanthone and 1-Azaxanthone by Polyalkylbenzenes

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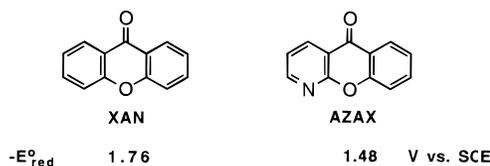
**Abstract:** The reactions of the photoexcited aromatic ketones, xanthone and 1-azaxanthone, with polyalkylbenzene donors yields the corresponding ketyl radicals as detected by nanosecond laser flash photolysis. On the basis of formation of these photoreduced products, the quenching of the photoexcited species is expected to occur either by a one-step hydrogen abstraction from the donor, electron transfer followed by proton transfer from the donor, or by formation of a charge-transfer type encounter complex prior to hydrogen atom transfer. The reactions of triplet xanthone and triplet 1-azaxanthone with polyalkylbenzene donors in acetonitrile were investigated to probe the effect of the nature of the triplet state and the redox properties on the relative importance of each quenching pathway. Determination of bimolecular rate constants, as well as analysis of kinetic isotope effects and ketyl radical yields, suggests that for both xanthone and 1-azaxanthone the quenching process is dominated by formation of charge-transfer encounter complexes between excited-state aromatic ketone acceptor and ground-state polyalkylbenzene donor. The reactivities of the xanthone  $\pi,\pi^*$  triplet and 1-azaxanthone  $n,\pi^*$  triplet toward these donors is shown to be governed by their reduction potentials, with their electronic configuration being unimportant to the kinetics of encounter complex formation. The only exception to this is found when sterically encumbered polyalkylbenzene donors are employed. Results with these compounds suggest that  $\pi,\pi^*$  and  $n,\pi^*$  states form encounter complexes of different structure which affects their ability to react with hindered donors. Additionally, product yields with all of the donors are controlled by both the extent of charge transfer within encounter complexes and the encounter complex structure.

## Introduction

Xanthone (XAN) and 1-azaxanthone (AZAX) are aromatic ketones whose transient photochemistry is well described, primarily due to the fact that XAN has proven to be useful as a probe for polarity<sup>1–3</sup> and AZAX as a potential probe for studying radical pair dynamics in heterogeneous systems.<sup>4–6</sup> In polar solvents, there is an appreciable difference in reactivity between the xanthone triplet ( $^3\text{XAN}^*$ ), which is predominantly  $\pi,\pi^*$  in character,<sup>7,8</sup> and the 1-azaxanthone triplet ( $^3\text{AZAX}^*$ ), which is predominantly  $n,\pi^*$  in character,<sup>4</sup> with various hydrogen- and electron-donating substrates. It is precisely these differences in the nature of the electronic states that motivated this study; XAN and AZAX have essentially the same geometry and very similar triplet energies. Thus, the pair provides an interesting system where the effects of the nature of the excited triplet state can be examined. The specific origin of the differences in reactivity cannot be immediately attributed to either the increased reactivity of  $n,\pi^*$  triplets toward hydrogen abstraction or electron acceptor properties of the triplets. The

uncertainty arises from the fact that the formation of ketyl radicals,  $\text{XAN}(\text{H})^*$  and  $\text{AZAX}(\text{H})^*$ , as products in these reactions can be visualized as occurring in one step via hydrogen abstraction from the donor, or in multiple steps via electron transfer followed by proton transfer or by formation of a charge-transfer (CT) type encounter complex<sup>9</sup> prior to hydrogen atom transfer. The involvement of each of these processes in the reduction of aromatic ketones is well established.<sup>10,11</sup> The potential competition between these pathways in the reactions of photoexcited aromatic ketones with polyalkylbenzene (ArH) donors appears in Scheme 1 with XAN used as an example.

In the case of singlet excited states the dynamics of bimolecular electron transfer reactions has been extensively studied by Gould and Farid.<sup>12</sup>



For systems involving ArH donors in which CT pathways are active they are believed to proceed predominantly via an encounter complex intermediate between excited acceptor and

- (1) Scaiano, J. C.; Selwyn, J. C. *Can. J. Chem.* **1981**, *59*, 2368.
- (2) Barra, M.; Bohne, C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8075.
- (3) Evans, C. H.; Prud'homme, N.; King, M.; Scaiano, J. C. *J. Photochem. Photobiol., A: Chem.* **1999**, *121*, 105.
- (4) Scaiano, J. C.; Weldon, D.; Pliva, C. N.; Martinez, L. J. *J. Phys. Chem.* **1998**, *102*, 6898.
- (5) Martinez, L. J.; Scaiano, J. C. *J. Phys. Chem. A* **1999**, *103*, 203.
- (6) Corrent, S.; Martinez, L. J.; Scaiano, J. C.; Garcia, H.; Fornes, V. J. *Phys. Chem. B* **1999**, *103*, 8097.
- (7) Garner, A.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1010.
- (8) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

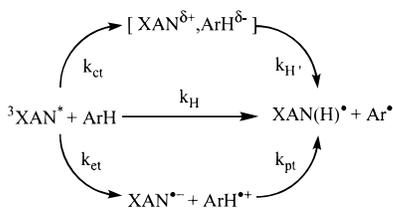
(9) We use the term "encounter complex" in place of "exciplex" to avoid confusion generated by the fact that "exciplex" often refers to an emissive species and is sometimes used to indicate which species may be better deemed "contact-ion pairs".

(10) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

(11) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.

(12) Gould, I. R.; Farid, F. *Acc. Chem. Res.* **1996**, *29*, 522.

## Scheme 1



ground state donor.<sup>13–18</sup> By invoking this as a reaction intermediate one introduces an interesting element into these types of reactions. That is, the necessity of consideration of both the kinetics for encounter complex formation as well as its subsequent reactivity. It has been established that the structures of the encounter complexes differ for  $n,\pi^*$  and  $\pi,\pi^*$  triplets and that stereoelectronic effects are important to the formation and reactivity of these encounter complexes.<sup>14</sup>

It has also been shown that the reaction between photoexcited quinones and ArH donors with bulky alkyl groups is slowed relative to their methylated counterparts.<sup>15,16</sup> This result was rationalized on the basis of a difficulty in forming CT type encounter complexes between photoexcited quinones and sterically encumbered aromatics.

To gain further insight into the competition between the various reaction pathways and the potential involvement of encounter complexes of different structures in the reaction between triplet XAN and AZAX with ArH donors we determine bimolecular rate constants,  $k_{\text{obs}}$ , isotope effects, and product yields for several combinations of donor and acceptor pairs. Additionally, experiments on sterically encumbered ArH donors are expected to aid in the investigation of the nature of the encounter complexes involved in these reactions.

## Experimental Section

Xanthone (Aldrich) and 1-azaxanthone (Lancaster) were recrystallized twice from ethanol. Acetonitrile, cyclohexane, benzene, and toluene (BDH) were Omnisolv grade and were used as received. 1,2,4,5-Tetramethylbenzene, 1,4-di-*tert*-butylbenzene, 1,3,5-trimethylbenzene, *p*-xylene, *o*-xylene, and *m*-xylene (Aldrich,  $\geq 98\%$ ) were used as received. 3,5-Di-*tert*-butyltoluene (Aldrich) was recrystallized twice from ethanol and heptane. Benzene- $d_6$ , cyclohexane- $d_{12}$ , toluene- $d_8$  (Cambridge Isotope Laboratories,  $>99.5$  atom %), and *o*-xylene- $d_{10}$  (Cambridge Isotope Laboratories, 98 atom %) were used as received.

Laser flash photolysis studies were performed using a Moletron UV-24 nitrogen laser (337 nm,  $\sim 10$  ns pulse width,  $\sim 3$  mJ) for the excitation. The relatively low energy of this laser source is a good spectral match to the xanthenes and tends to minimize problems related to triplet–triplet annihilation. The system is controlled by a Power Macintosh computer running LabVIEW 4.1 software (National Instruments). A Tektronix 2440 digital oscilloscope is used to capture and digitize the signal from the photomultiplier tube. Detailed descriptions of similar laser systems have been provided elsewhere.<sup>8,19</sup> Typically the concentrations of XAN and AZAX solutions were such that the absorbance at the laser wavelength in the laser flash photolysis cell was  $<0.5$ . Bimolecular rate constants for quenching were obtained using static cells while ketyl radical yields were determined using a flow system to avoid build-up of photoproducts.

(13) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669.

(14) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

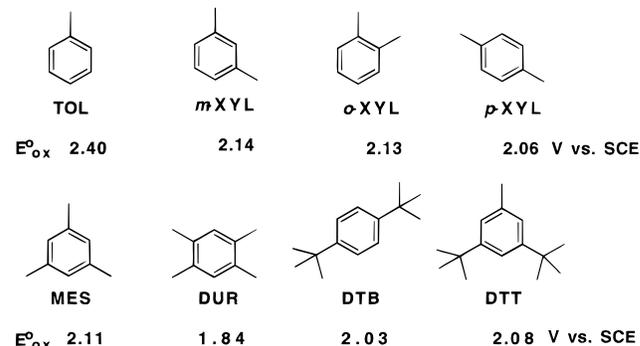
(15) Rathore, R.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 11468.

(16) Hubig, S. M.; Rathore, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 617.

(17) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 1688.

(18) Jacques, P.; Allonas, X.; Von Raumer, M.; Suppan, P.; Haselbach, E. *J. Photochem. Photobiol. A: Chem.* **1997**, *111*, 41.

## Chart 1



The ketyl radical yields,  $\Phi_{\text{ketyl}}$ , were determined by using cyclohexane as a standard for which we assume  $\Phi_{\text{ketyl}} = 1$ . The ratio of the transient change in absorbance ( $\Delta\text{O.D.}$ ) due to the ketyl radical and the initial  $\Delta\text{O.D.}$  due to the triplets was measured in the presence of cyclohexane to determine the ratio of their extinction coefficients,  $\epsilon$ . At 410 nm,  $\epsilon_{\text{XAN(H)}^{\bullet}}/\epsilon^{\text{3XAN}^*} = 0.5 \pm 0.1$  and at 500 nm  $\epsilon_{\text{AZAX(H)}^{\bullet}}/\epsilon^{\text{3AZAX}^*} = 1.0$ . Upon quenching with ArH donors with 95% efficiency the ratio of the initial  $\Delta\text{O.D.}$ , due to the triplet, and the final  $\Delta\text{O.D.}$ , due to the ketyl radical, was corrected based on ratio of the  $\epsilon$  values and used to determine  $\Phi_{\text{ketyl}}$ .<sup>20</sup>

Reduction potentials of XAN and AZAX were measured using a cyclic voltammeter (50 to 200 mV/s) with platinum, glassy carbon, and Ag/AgCl used as the counter, working, and reference electrodes, respectively. Tetrabutylammonium tetrafluoroborate was employed as the electrolyte for  $\sim 1 \times 10^{-4}$  M solutions of XAN and AZAX in acetonitrile. Ferrocene was employed as an internal standard ( $E_{1/2} = 0.51$  vs SCE).

## Results

Photoexcitation of solutions of XAN and AZAX in acetonitrile with a 10-ns laser pulse at 337 nm generates their triplet states,  $^3\text{XAN}^*$  and  $^3\text{AZAX}^*$ , as judged by their characteristic absorption spectra<sup>4,7,8</sup> with lifetimes of  $\leq 3 \mu\text{s}$ .<sup>21</sup> In the presence of benzene and ArH donors (Chart 1) these lifetimes are shortened significantly. In the case of benzene and an ArH donor without benzylic hydrogens, such as DTB, the triplets decay to their spectral baseline (Figure 1). In contrast, in the presence of ArH donors with benzylic hydrogens the spectrum of the triplets is replaced by that of their ketyl radicals,  $\text{XAN(H)}^{\bullet}$  and  $\text{AZAX(H)}^{\bullet}$  (Figure 1).<sup>4</sup> The benzylic radicals of the ArH donors,  $\text{Ar}^{\bullet}$ , which are also generated, are not observed presumably because they are masked by overlap with the absorptions due to  $\text{XAN(H)}^{\bullet}$  or  $\text{AZAX(H)}^{\bullet}$ .<sup>22,23</sup> Interestingly, there is no evidence for the formation of the expected products from electron transfer, i.e., radical anions,  $\text{XAN}^{\bullet-}$  and  $\text{AZAX}^{\bullet-}$ ,<sup>4</sup> and radical cations  $\text{Ar}^{\bullet+}$ .<sup>24,25</sup> (vide infra). Whatever the specific nature of the reactions responsible for quenching, the  $k_{\text{obs}}$  values were determined for the quenching of  $^3\text{XAN}^*$  and  $^3\text{AZAX}^*$  by various ArH donors and appear in Table 1.

Kinetic isotope effects for these and some related reactions were determined and appear in Table 2. To determine the kinetic

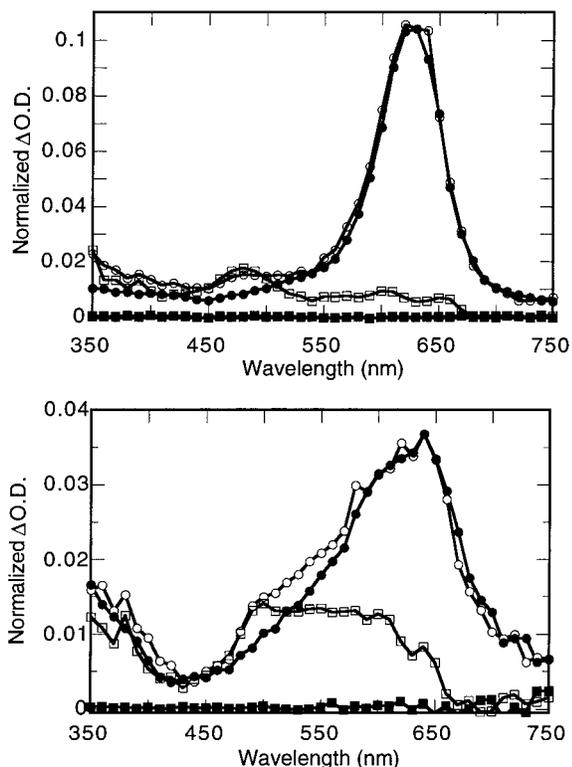
(19) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(20) The systematic errors in the extinction coefficients cannot influence the order within an homologous series.

(21) These are clearly not “intrinsic” lifetimes and may be partially determined by trace impurities in the solvent (including some residual oxygen), and to a lesser degree by some triplet–triplet annihilation. These effects do not interfere with the determination of accurate quenching rate constants based on the decay dependence with the quencher concentration.

(22) Christensen, H. C.; Sehested, K.; Hart, E. J. *J. Phys. Chem.* **1973**, *77*, 7, 983.

(23) Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 2826.



**Figure 1.** (Top) Transient absorption spectra of XAN in acetonitrile with 7.3 mM DUR recorded 0.056 (○) and 1.1 μs (□) following laser excitation, and 150 mM DTB recorded 0.2 (●) and 5.5 μs (■) following laser excitation. (Bottom) Transient absorption spectra of AZAX in acetonitrile with 1.0 mM DUR recorded 0.024 (○) and 1.1 μs (□) following laser excitation, and 605 mM benzene recorded 0.024 (●) and 1.1 μs (■) following laser excitation.

isotope effect for a simple hydrogen abstraction reaction, cyclohexane was used as a model compound in which only hydrogen abstraction is expected to occur due to its poor electron donation properties and its labile C–H bonds. As such, the observed kinetic isotope effects of 3.5 and 4.0 for XAN and AZAX, respectively, are attributed to a primary kinetic isotope effect for a hydrogen abstraction reaction. Similarly, the kinetic isotope effects observed with benzene of 1.25 and 1.0 for XAN and AZAX, respectively, are associated with an isotope effect for a CT interaction and are consistent with those appearing in the literature for electron-transfer reactions.<sup>23,26</sup>

The ketyl radical yields,  $\Phi_{\text{ketyl}}$ , from  $^3\text{XAN}^*$  and  $^3\text{AZAX}^*$  in the presence of ArH donors were determined by using cyclohexane as a standard for which we assume  $\Phi_{\text{ketyl}} = 1$ . These values also appear in Table 1.

$E_{\text{red}}^0$  values for XAN and AZAX were determined by cyclic voltammetry to be  $-1.76$  and  $-1.48$  V vs SCE, respectively; both were reversible. Consideration of these values along with the triplet energies of XAN, 74.1 kcal,<sup>27</sup> and AZAX, 72.7 kcal,<sup>4</sup> as well as the oxidation potential of the ArH donors,<sup>28</sup> permits calculation of the energetics associated with an electron-transfer

pathway as determined by the Rehm–Weller<sup>29</sup> equation:

$$\Delta G_{\text{et}} = E_{\text{ox}}^0(\text{D}) - E_{\text{red}}^0(\text{A}) - E^* + C$$

where here  $E_{\text{ox}}$  is the oxidation potential of the ArH donor,  $E_{\text{red}}$  the reduction potential of the aromatic ketone acceptor A,  $E^*$  the triplet energy of the aromatic ketone, and  $C$  the Coulomb energy of the ion pair formed after electron transfer. The  $C$  term was neglected in view of the solvent used being acetonitrile. The energetics of electron transfer as determined by this equation appear in Table 1.

## Discussion

**I. Competition between Direct Hydrogen Abstraction and CT Pathways.** As can be seen from Figure 2 (top) for XAN and Figure 2 (bottom) for AZAX there is a fairly good correlation between  $\log(k_{\text{obs}})$  and the oxidation potential of the methylated ArH donors. Additionally, the reactions of benzene and pyridine, both of which are expected to be very poor hydrogen donors, with XAN and AZAX also correlate well with the ease of oxidation of the donor aromatic molecules.<sup>30</sup> These observations suggest that the dominant reaction pathway is one that involves some degree of electron transfer. We felt that such an assumption may be an oversimplification in light of the fact that Figure 2 also shows a fairly good correlation between  $\log(k_{\text{obs}})$  and the number of sites at which one can generate a benzylic radical. This correlation suggests some importance of hydrogen abstraction pathways in these reactions.

These seemingly conflicting interpretations demonstrate an important point of interest when considering these reactions. An increase in the alkyl substitution of ArH donors, which should facilitate hydrogen abstraction, is accompanied by an increase in the ease of oxidation of these donors, which should facilitate CT pathways. As such, it is difficult to delineate between these two mechanisms based solely on a simple comparison of  $k_{\text{obs}}$  values and properties of the donors. Hence, a more careful consideration of acceptor properties is also required.

From Table 1 it can be seen that the  $k_{\text{obs}}$  for  $^3\text{AZAX}^*$  with any given ArH donor is ca. 10 times larger than that determined for  $^3\text{XAN}^*$ . This difference in reactivity can be rationalized in terms of both potential deactivation pathways.

First, the relative reactivities of  $^3\text{XAN}^*$  and  $^3\text{AZAX}^*$  toward electron-transfer reactions can be inferred by comparing their  $k_{\text{obs}}$  values obtained in the reaction with benzene.<sup>30</sup> On the basis of these values, we assume that, in general, the rate of quenching of  $^3\text{AZAX}^*$  strictly by CT processes is ca. 10 times faster than the same reaction with  $^3\text{XAN}^*$ .<sup>31</sup> The increased reactivity toward CT processes by  $^3\text{AZAX}^*$  relative to  $^3\text{XAN}^*$  is expected given its lower  $E_{\text{red}}^0$  of AZAX, which makes the reaction more energetically favorable.

In a similar manner, the relative reactivities of  $^3\text{XAN}^*$  and  $^3\text{AZAX}^*$  toward hydrogen abstraction can be inferred by comparing their  $k_{\text{obs}}$  values for quenching by cyclohexane, which are  $8.8 \times 10^5$  and  $7.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. On the basis of these values, we assume that, in general, the rate of quenching of  $^3\text{AZAX}^*$  strictly by hydrogen abstraction is ca. 10 times faster

(24) Bockman, T. M.; Karpinski, Z. J.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1970.

(25) Sehested, K.; Holcman, J.; Hart, E. J. *J. Phys. Chem.* **1977**, *81*, 1363.

(26) Pal, H.; Nagasawa, Y.; Tominaga, K.; Yoshihara, K. *J. Phys. Chem.* **1996**, *100*, 11964.

(27) Herkstroeter, W. K.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.

(28) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, R. M.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(29) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(30) The  $k_{\text{obs}}$  values for XAN with benzene and pyridine are  $6.3 \times 10^5$  and  $7.23 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These values for AZAX are  $9.3 \times 10^6$  and  $7.75 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. For the oxidation potentials for benzene and pyridine see: Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1971**, *37*, 916–918.

(31) Although some moderation of the selectivity could be expected for the higher reactivities, a rather common observation.

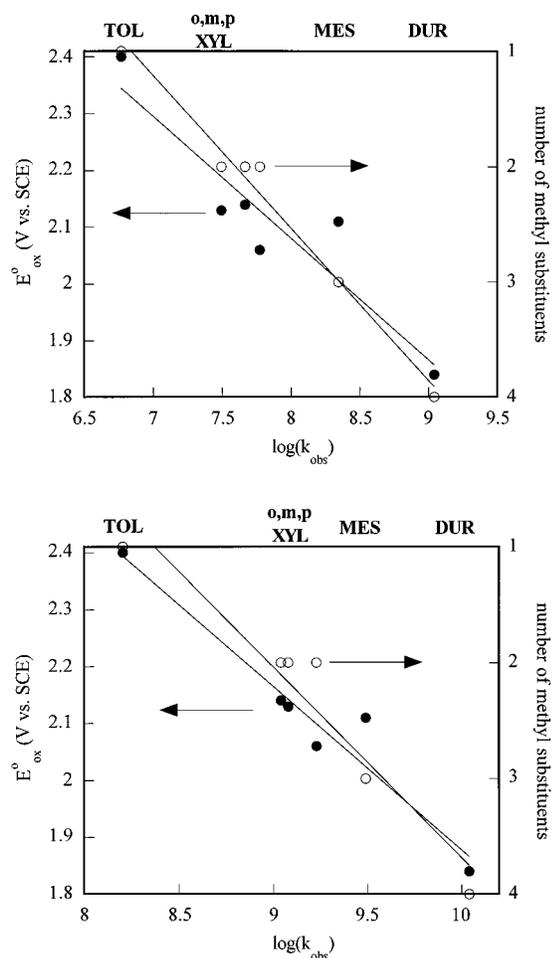
**Table 1.** Kinetic and Quantum Yield Data for the Quenching of Aromatic Ketones by Substituted Benzenes in Acetonitrile

quencher	xanthone			1-axaxanthone		
	$\Delta G_{et}$ (eV)	$k_q$ ( $M^{-1} s^{-1}$ )	$\phi_{ketyl}$ radical	$\Delta G_{et}$ (eV)	$k_q$ ( $M^{-1} s^{-1}$ )	$\phi_{ketyl}$ radical
TOL	1.00	$5.8 \times 10^6$	0.53	0.66	$1.6 \times 10^8$	0.38
<i>o</i> -XYL	0.73	$3.1 \times 10^7$	0.43	0.39	$1.2 \times 10^9$	0.31
<i>m</i> -XYL	0.74	$4.6 \times 10^7$	0.49	0.40	$1.1 \times 10^9$	0.36
<i>p</i> -XYL	0.66	$5.9 \times 10^7$	0.74	0.32	$1.7 \times 10^9$	0.58
MES	0.71	$2.2 \times 10^8$	0.45	0.37	$3.1 \times 10^9$	0.46
DUR	0.44	$1.1 \times 10^9$	1.0	0.10	$1.1 \times 10^{10}$	0.70
DTB	0.63	$7.9 \times 10^6$	0	0.29	$2.0 \times 10^8$	0
DTT	0.68	$2.7 \times 10^7$	0.55	0.34	$5.2 \times 10^8$	0.52

**Table 2.** Kinetic Isotope Effects Observed in Selected Systems<sup>a</sup>

quencher	xanthone			1-axaxanthone		
	$k_{obs}$ ( $M^{-1} s^{-1}$ )	$k(H)/k(D)^b$	$\phi_{ketyl}$	$k_{obs}$ ( $M^{-1} s^{-1}$ )	$k(H)/k(D)^b$	$\phi_{ketyl}$
cyclohexane- <i>d</i> <sub>12</sub>	$2.2 \times 10^5$	3.9	1.0	$2.6 \times 10^6$	2.9	1.0
benzene- <i>d</i> <sub>6</sub>	$5.0 \times 10^5$	1.3	0.0	$9.3 \times 10^6$	1.0	0.0
TOL- <i>d</i> <sub>8</sub>	$3.8 \times 10^6$	1.5	0.20	$1.0 \times 10^8$	1.4	0.16
<i>o</i> -XYL- <i>d</i> <sub>10</sub>	$2.7 \times 10^7$	1.1	0.16	$7.6 \times 10^8$	1.6	0.14

<sup>a</sup> Same conditions as in Table 1. <sup>b</sup> Errors estimated as  $\pm 10\%$ .



**Figure 2.** (Top) Coinciding effect of the number of methyl substituents (○) and oxidation potential,  $E^{\circ}_{ox}$ , (●) of ArH donors on the logarithm of the rate constant,  $\log(k_{obs})$ , for reaction with <sup>3</sup>XAN\*. (Bottom) Coinciding effect of the number of methyl substituents (○) and oxidation potential,  $E^{\circ}_{ox}$ , (●) of ArH donors on the logarithm of the rate constant,  $\log(k_{obs})$ , for reaction with <sup>3</sup>AZAX\*.

than the same reaction with <sup>3</sup>XAN\*. Although the lowest triplet of XAN in acetonitrile is  $\pi, \pi^*$  in nature, a low-lying  $n, \pi^*$  triplet which is thermally accessible is probably responsible for much of the hydrogen abstraction behavior.<sup>32–34</sup> The increased

**Table 3.** Calculated Contribution of  $k_H$  to  $k_{obs}$ , See Text

quencher	xanthone		1-axaxanthone	
	$k_H^a$ ( $M^{-1} s^{-1}$ )	$k_H/k_{obs}$ ( $\times 100$ )	$k_H^a$	$k_H/k_{obs}$ ( $\times 100$ )
TOL	$1.3 \times 10^5$	2.3	$1.7 \times 10^6$	1.07
<i>m</i> -XYL	$3.1 \times 10^5$	0.67	$4.0 \times 10^6$	0.36
<i>p</i> -XYL	$4.0 \times 10^5$	0.68	$5.2 \times 10^6$	0.31
MES	$5.0 \times 10^5$	0.23	$6.5 \times 10^6$	0.21

<sup>a</sup> See text for the method of determination of the rate constants.

reactivity toward hydrogen abstraction by <sup>3</sup>AZAX\* relative to <sup>3</sup>XAN\* is expected owing to its low-lying  $n, \pi^*$  character.

To gain some insight into the reactivities of the ArH donors under consideration to a strictly hydrogen abstraction pathway, one can consider their reactivities toward *tert*-butoxy radicals. Given that it is well established that  $n, \pi^*$  ketone triplets show parallel and comparable reactivity toward hydrogen abstraction reactions as alkoxy radicals,<sup>35</sup> we anticipate that any triplet ketone that reacts with ArH donors only by hydrogen abstraction should display the same ratio of rate constants as their reaction with *tert*-butoxy radicals.<sup>35–39</sup> The ratio of the rate constants for hydrogen abstraction,  $k_H$ , from TOL, *m*-XYL, *p*-XYL, MES, and cyclohexane by *tert*-butoxy radicals is 1.0:2.3:3.0:4.0:6.0.<sup>40</sup> On the basis of the  $k_H$  values between the *tert*-butoxy radicals with TOL and MES,  $2.3 \times 10^5$  and  $8.3 \times 10^5 M^{-1} s^{-1}$ ,<sup>39</sup> respectively, and cyclohexane with XAN and AZAX,  $7.94 \times 10^5$  (ref 41) and  $1.03 \times 10^7 M^{-1} s^{-1}$  (ref 4), respectively, we can estimate the contribution of  $k_H$  to the  $k_{obs}$  for the reactions of ArH donors with XAN and AZAX. The results from this analysis appear in Table 3. The important idea to extract from these data is that while the expected  $k_H$  values are all within a factor of 5 of one another, the  $k_{obs}$  values obtained span 2 orders of magnitude. Typically, <sup>3</sup>XAN\* and <sup>3</sup>AZAX\* react ca. 100

(32) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(33) Berger, M.; McAlpine, E.; Steel, C. *J. Am. Chem. Soc.* **1978**, *100*, 5147.

(34) Wagner, P. J.; Siebert, E. *J. Am. Chem. Soc.* **1981**, *103*, 7329.

(35) Scaiano, J. C. *J. Photochem.* **1973/74**, *2*, 81.

(36) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(37) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

(38) Walling, C.; Gibian, M. A. *J. Am. Chem. Soc.* **1965**, *87*, 3361.

(39) Paul, H.; Small, R. D. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *100*, 4520.

(40) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108.

times faster with the various ArH donors than one would expect for a simple hydrogen abstraction reaction. Therefore, on the basis of these simple arguments >99% of the reaction with ArH donors can be attributed to some form of CT interaction.

While results based on this type of indirect analysis should be interpreted cautiously, they do suggest rather clearly that the greater reactivity of  $^3\text{AZAX}^*$  toward hydrogen abstraction is balanced by its increased reactivity toward electron transfer. The somewhat serendipitous implication of this is that the competition between hydrogen abstraction and charge-transfer pathways is similar for  $^3\text{XAN}^*$  and  $^3\text{AZAX}^*$ .

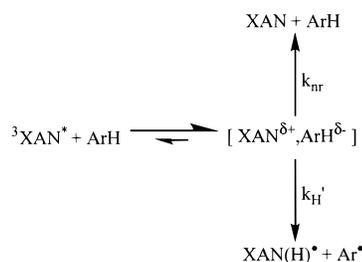
A confirmation of the lack of direct hydrogen abstraction is the absence of any significant isotope effects in the reactions with ArH donors as shown in Table 2. Experiments were performed using benzene and cyclohexane as model compounds for which quenching should occur entirely via charge transfer and direct hydrogen abstraction; the values obtained are 1.0 to 1.3 and 2.9 to 3.9, respectively. The kinetic isotope effects observed for TOL and *o*-XYL, compounds for which both electron transfer and hydrogen abstraction can potentially occur, are intermediate to those observed for the isolated processes and range from 1.1 to 1.6. Given the absence of any discernible trend in these isotope effects either in acceptor or donor properties, we conclude that they are small enough to be consistent with a mechanism based entirely on CT interactions.

Given the apparent lack of involvement of direct hydrogen abstraction in these reactions we proceed and address the specific nature of the CT pathway, that is, direct electron transfer or partial electron transfer within an encounter complex.

**II. Involvement of an Encounter Complex as a Reaction Intermediate.** In light of the assessment that direct hydrogen abstraction is an unimportant pathway, the fact that efficient quenching is observed even though electron transfer is an endergonic process for all of the XAN and AZAX/ArH pairs (as shown in Table 1) suggests that quenching does not involve full electron transfer. It is more likely due to CT within an encounter complex between excited ketone and ArH donor and is followed by facile hydrogen atom transfer to yield ketyl and benzylic radicals. Such CT complexes have been detected in the interaction of quinones with alkylbenzenes.<sup>15</sup> Further to this point, we do not favor a pathway involving direct electron transfer, which would yield a solvent separated radical ion pair, to be a reasonable one since products from electron transfer ( $\text{XAN}^{\bullet-}$ ,  $\text{AZAX}^{\bullet-}$ , and  $\text{Ar}^{\bullet+}$ ) are not observed under our experimental conditions. In a polar solvent such as acetonitrile we would not expect proton transfer or back electron transfer between a triplet derived solvent separated radical ion pair to completely overwhelm ion separation.

Full electron transfer after the formation of the encounter complex is also deemed to be an unimportant pathway since it should yield a contact radical ion pair which typically dissociates or recombines in polar solvents with rate constants much larger than those expected for proton transfer.<sup>42-45</sup> Our inability to detect ionic products coupled with the large yields of radical products does not support a pathway involving full electron transfer. While we cannot rule out a contact-pair that undergoes no escape, this seems somewhat unlikely for a triplet-derived pair in a low-viscosity solvent. This result is consistent with

## Scheme 2



the low ion yields and large radical yields reported for the reactions of benzophenone with ArH donors in acetonitrile; a system in which encounter complex intermediates are proposed to be important.<sup>18</sup>

The involvement of an encounter complex is more directly indicated by the difference in  $k_{\text{obs}}$  obtained for ArH donors with similar  $E_{\text{ox}}^{\circ}$  but very different steric characteristics. As previously mentioned, sterically encumbered ArH donors have been shown to have reduced reactivity toward formation of CT encounter complexes relative to their unencumbered analogues in systems where encounter complexes are important. Here we employ DTB and DTT as sterically encumbered donors which have similar  $E_{\text{ox}}^{\circ}$  to *p*-XYL and MES, respectively. In the reactions with both XAN and AZAX the  $k_{\text{obs}}$  obtained are reduced by ca. 6–8 times relative to their unencumbered analogues. We reasonably attribute the reduction in reactivity in these systems to a difficulty in forming encounter complexes and assume that the involvement of this reaction intermediate can be extended to all of the donor/acceptor pairs currently under consideration.

**III. Kinetics of Encounter Complex Formation.** The reversibility of the formation of a CT encounter complex in these types of reactions is specifically a matter of the competition between decay of the encounter complex to regenerate excited state species with other decay processes to yield ground state species. Since complete electron transfer has been ruled out as a likely pathway, these deactivation processes include only hydrogen atom transfer and nonradiative decay. To determine the extent of reversibility of the complexes formed in our systems we consider the kinetic isotope effects obtained.

The presence of a sizable isotope effect is expected if the reaction involves either direct hydrogen atom abstraction or hydrogen atom transfer following reversible complexation. Hydrogen atom transfer following irreversible complexation will not affect the observed kinetics because there is no means by which a decrease in the rate of the hydrogen transfer can feed back on the initial complexation dynamics. The magnitude of the isotope effects expected for a hydrogen abstraction reaction has already been discussed and an isotope effect for proton transfer following electron transfer of 2.4–5.6 has been reported in similar systems.<sup>23</sup> The negligibly small values obtained in our work are much more consistent with those expected to occur in the situation in which complex formation is rate determining and irreversible. Additional evidence for this kinetic scheme is that while there is no appreciable isotope effect on the kinetics there is an isotope effect of >2.5 on the  $\Phi_{\text{ketyl}}$ . This clearly indicates that the hydrogen atom transfer occurs after the rate-determining step, i.e., complexation. The relevant processes involved in these reactions are shown in Scheme 2.

Given that the rate-determining step appears to be charge transfer following the formation of the encounter complexes it is not surprising that the kinetics correlate well with the energetics of electron transfer as shown in Figure 3. Interest-

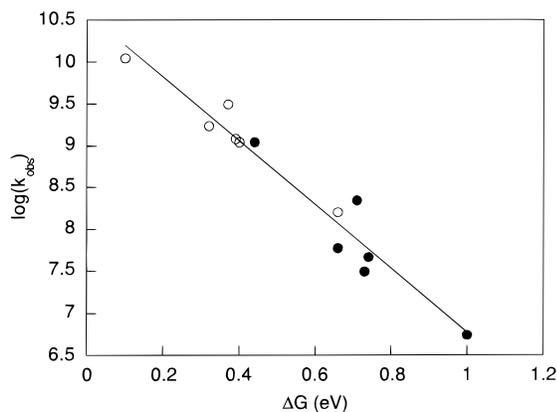
(41) This work.

(42) Hubig, S. M. *J. Phys. Chem.* **1992**, *96*, 2903.

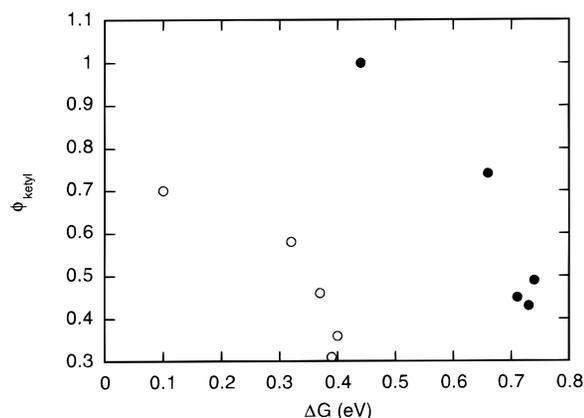
(43) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1387.

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

(45) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263.



**Figure 3.** Correlation between the logarithm of the rate constant,  $\log(k_{\text{obs}})$ , for reaction of  ${}^3\text{XAN}^*$  (●) and  ${}^3\text{AZAX}^*$  (○) and the driving force for an electron-transfer reaction,  $\Delta G$ .

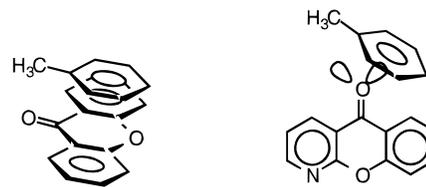


**Figure 4.** Effect of changes in the driving force for electron transfer,  $\Delta G$ , on the quantum yield for ketyl radical formation,  $\Phi_{\text{ketyl}}$ , for XAN (●) and AZAX (○) in the reaction with ArH donors (excluding TOL).

ingly, XAN and AZAX not only respond to changes in the energetics in the same manner but reactions with similar  $\Delta G$  values give almost the same  $k_{\text{obs}}$ . We note that a larger group of donors and acceptors which span a greater  $\Delta G$  may reveal a trend indicating different reactivities. For our purposes it is satisfactory to state that for the systems studied here the quenching is entirely controlled by redox properties of the pairs forming the encounter complex and the electronic configuration of the triplet nature is important only inasmuch as it affects the reduction potential of the ketone.

**IV. Reactivity of the Encounter Complex.** To determine which factors control the reactivity of the encounter complex once formed we consider the competition between the possible deactivation pathways: hydrogen transfer within the encounter complex and nonradiative decay of the encounter complex as gauged by  $\Phi_{\text{ketyl}}$  values. Though these values are governed by the relative rates of both deactivation pathways we rationalize the results based entirely on the expected effects on the rate of hydrogen transfer because it is easier to conceptualize factors which affect this well-defined process as compared to the more general process of nonradiative decay.

With the exception of TOL, the  $\Phi_{\text{ketyl}}$  values for XAN and AZAX correlate well with the energetics for an electron transfer reaction and decrease with increasing endergonicity as shown in Figure 4. We rationalize the observed trend based on the presumed degree of CT within the encounter complexes. On the basis of the observation of a kinetic acidity affect on the product ratios in the quenching of *p*-cymene by aromatic ketones Wagner et al. suggest that the more energetically favorable



**Figure 5.** Suggested excited-state interactions, see text.

electron transfer is for a given donor/acceptor pair, the greater the amount of charge separation within an encounter complex between the two.<sup>14</sup> This conclusion is further supported by an observed red-shift in the near-IR bands assigned to the encounter complex between photoexcited quinones and ArH donors as the driving force for electron transfer increases.<sup>15</sup> The greater the charge separation in an encounter complex the lower the activation energy for hydrogen atom transfer,<sup>14</sup> which should allow hydrogen atom transfer to compete more favorably with other deactivation pathways and result in a higher  $\Phi_{\text{ketyl}}$ .

Though the  $\Phi_{\text{ketyl}}$  for XAN and AZAX follow the same trend, those for AZAX are lower than XAN despite the much increased exergonicity. On the basis of the previous argument these systems should have greater CT within the encounter complex than the XAN systems, thereby facilitating hydrogen atom transfer. To rationalize this result we must consider the structure of the encounter complexes. It is generally accepted that encounter complexes of this kind involve overlap between donor HOMO and a half-filled orbital in the excited-state acceptor.<sup>14,46,47</sup> Therefore, for XAN we expect an encounter complex to form between overlap of an ArH  $\pi$  orbital and the benzoyl  $\pi$  orbital while for AZAX we expect the involvement of the carbonyl  $n$  orbital as demonstrated in Figure 5. The different geometries of the encounter complexes formed have been used to rationalize stereoelectronic effects observed due to tighter  $\pi, \pi^*$  encounter complexes and more loose  $n, \pi^*$  encounter complexes.<sup>14</sup>

As can be seen in Figure 5, in the case of  $\pi, \pi^*$  encounter complexes there is the potential for formation of structures in which the carbonyl oxygen is located in close proximity to a benzylic hydrogen. As charge separation occurs the donor begins to develop a positive charge and the methyl group bears some of this charge. The carbonyl oxygen of the  $\pi, \pi^*$  triplet is initially nucleophilic and becomes even more so as charge separation increases and it develops a negative charge. A structure in which these groups are close to one another obviously facilitates hydrogen atom transfer and should be favored over other structures due to electrostatic interactions.

In contrast, in the case of  $n, \pi^*$  encounter complexes the  $n$  orbital is buried in the  $\pi$  system, much less closely associated with the benzylic hydrogens than in the case of the  $\pi, \pi^*$  encounter complexes. Given the  $n, \pi^*$  nature of the triplet the carbonyl oxygen is actually electrophilic, the electrostatic preference displayed in the case of  $\pi, \pi^*$  triplets is less important. As such, one would expect slower rates of hydrogen atom transfer and this leads to lower  $\Phi_{\text{ketyl}}$ .

Toluene breaks the trend described above by giving larger  $\Phi_{\text{ketyl}}$  than expected based on the energetics of the reaction as compared to other ArH donors. TOL is unique among the donors in that it contains only one methyl group to stabilize the positive charge which develops in the aromatic ring of the donor as the encounter complex forms. As such, that methyl should bear a

(46) Turro, N. J.; Dalton, J. C.; Farrington, G.; Niemczyk, M.; Pond, D. *M. J. Am. Chem. Soc.* **1970**, *92*, 6978.

(47) Wolf, W. M.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526.

greater charge than in a donor with multiple substituents in which the positive charge is shared more evenly throughout the molecule. Consequently, the encounter complex geometry in which this group and the carbonyl oxygen are closely associated should be even more favored than for other ArH donors. Additionally, given that CT within the encounter complex activates the benzylic C–H bond, when there is only one such group this so-called activation is entirely focused on one group and a larger  $\Phi_{\text{ketyl}}$  results.

The involvement of encounter complexes of different structure is further established if one reexamines the  $k_{\text{obs}}$  obtained using DTB and DTT. DTB and DTT have been classified by others as fully hindered and partially hindered donors, respectively.<sup>16</sup> This classification arises from their different abilities to form encounter complexes of a certain van der Waals separation attainable between donor and acceptor molecules. For XAN the reduction in  $k_{\text{obs}}$  relative to their unencumbered counterparts is essentially the same, 7.5 and 8. It would seem that while forming the  $\pi, \pi^*$  type encounter complex is sensitive to steric factors in general it is insensitive to the small changes in steric encumbrance present between a fully and a partially hindered donor. For AZAX the  $k_{\text{obs}}$  for DTB is still reduced by 8.4 times while, contrarily, that for DTT is reduced by only 5.9 times. While complete encumbrance of donors inhibits  $\pi, \pi^*$  and  $n, \pi^*$  encounter complexes to the same extent,  $n, \pi^*$  encounter complexes have less difficulty forming with partially hindered donors. Apparently, encumbrance hinders intimate contact less for  $n, \pi^*$  systems, which it has been suggested form encounter complexes of less rigidity and more rotational freedom, and we suggest that this can tolerate a looser approach or contact.

## Conclusions

The reactions of the photoexcited aromatic ketones, XAN and AZAX, with ArH donors has been studied by laser flash photolysis. The main reaction pathway is the irreversible formation of CT encounter complexes followed by hydrogen atom transfer in competition with nonradiative decay via reverse charge transfer. There was no need to invoke direct hydrogen abstraction or complete electron transfer as competitive processes in these reactions.

The reactivity of the XAN  $\pi, \pi^*$  triplet and AZAX  $n, \pi^*$  triplet toward these donors is governed by their reduction potentials, with their electronic configuration being unimportant to the kinetics of encounter complex formation with sterically unencumbered donors. With sterically encumbered donors which do not allow formation of tight encounter complexes the  $\pi, \pi^*$  and  $n, \pi^*$  states may react with different kinetics. Sensitivity to this steric effect in the reaction kinetics arises from the differing structures of the encounter complexes. Encounter complexes with  $\pi, \pi^*$  photoactivated acceptors require more intimate contact between donor and acceptor than do those involving  $n, \pi^*$  acceptors.

The extent of CT within the encounter complexes increases as the energetics for electron transfer become more favorable as judged by an increase in ketyl radical yields with decreasing endergonicity. This effect arises from the fact that CT facilitates hydrogen atom transfer. The aforementioned different structures of the encounter complexes create a difference in response to this stereoelectronic effect as the  $n, \pi^*$  encounter complexes have structures in which hydrogen transfer is less facile due to the lack of proximity between the benzylic groups.

Though Wagner et al. found no involvement of steric effects in the reactions between aromatic ketones and polyalkylbenzene donors, they did demonstrate the importance of stereoelectronic effects in the formation and reactivity of these encounter complexes. Their strategy involved extensive variation in acceptor properties. Here we have demonstrated that many of the same effects can be observed by adjusting the oxidation properties of the donor.

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