Table III. π CI Energies (eV) of Some Low-Lying States[a]

state	SDTQ[b]	MRSD[c]	state	SDTQ[b]	MRSD[c]
^1A_g	0	0	$^3B_{1u}$	0.22	0.29
$^1B_{3u}$	3.45	2.98	$^3B_{3u}$	2.77	2.46
$^1B_{2g}$	3.78	3.40	$^3B_{2g}$	3.28	3.08
2^1A_g	3.94	d	^3A_g	4.44	3.92
$^1B_{1u}$	5.08	4.94	2^3B_{1u}	4.76	d

[a] Calculations carried out at the optimized UHF geometry for $^3B_{1u}$, using K orbitals generated from $^3B_{1u}$ RHF MOs with the SV basis set. [b] π CI wave function with excitations through quadruples in the 10 orbital space of a conceptual minimal basis set and one reference configuration for all states except ^1A_g, for which two reference configurations were employed. Energies are relative to that (−384.3820 hartrees) of ^1A_g. [c] π CI wave function with excitations through doubles in the full 20 orbital space of the basis set from all configurations with coefficients >0.2 in the SDTQ–CI wave function, except for the lowest singlet and triplet states, for which the reference configuration cutoff was a coefficient >0.1. Energies are relative to that (−384.4096) of ^1A_g. [d] MRSD–CI energy not computed.

the low-lying singlet and triplet states of **1**, so that the singlet can be identified by UV spectroscopy. The calculations were performed with the SV basis set at the UHF geometry.

Two types of CI calculations were carried out. The first included SDTQ–CI in the 10 π orbitals of the conceptual minimal basis set. The second consisted of MRSD–CI calculations with the full set of 20 π orbitals, in which all configurations with coefficients larger than 0.2 in the SDTQ–CI were included in the

reference space for the excited states of each multiplicity. The results are shown in Table III.

Not surprisingly, the CI calculations that utilize the full set of 20 π orbitals give lower excitation energies, since they allow greater flexibility in the description of the excited states. However, even these MRSD–CI calculations give excitation energies that are probably too high, since the reference space for the lowest singlet and triplet included all configurations with coefficients larger than 0.1, instead of the 0.2 cutoff used for the excited states. Inclusion of σ–π correlation would probably also tend to lower at least some of the excitation energies by selectively stabilizing those excited states that are more ionic than the lowest singlet and triplet. Therefore, the vertical excitation energies given in Table III should be regarded as upper limits.

The data shown in Table III suggest that ^1A_g should have an absorption spectrum that is distinguishable from that of $^3B_{1u}$. Both states are predicted to have an allowed absorption around or slightly below 3.0 eV, polarized along the long molecular axis.[14] However, the triplet is expected also to have an absorption at lower energy, corresponding to the dipole–forbidden excitation to $^3B_{3u}$.

(13) A singlet ground state could be revealed indirectly by EPR if the singlet–triplet separation were small enough to permit detection of the signal from the triplet and if the Curie plot (signal intensity vs. $1/T$) were found to be convex.

(14) The oscillator strength calculated for the excitation in the singlet manifold is 7.6×10^{-2}, while that for the triplet is 5.9×10^{-2}. The lowest energy transitions that are polarized along the short molecular axis [$^1A_g \rightarrow {}^1B_{1u}$ and $^3B_{1u} \rightarrow {}^3A_g$] are calculated, respectively, to have $f = 3.0 \times 10^{-2}$ and 3.5×10^{-5}.

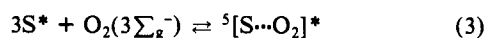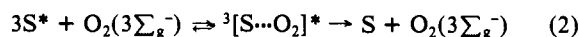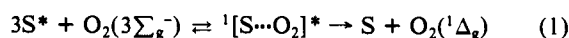# The Quenching of Aromatic Ketone Triplets by Oxygen: Competing Singlet Oxygen and Biradical Formation?

A. A. Gorman[*†] and **M. A. J. Rodgers**[*‡]

Contribution from the Chemistry Department, University of Manchester, Manchester M13 9PL, U.K., and the Center for Fast Kinetics Research, University of Texas at Austin, Austin, Texas 78712. Received September 3, 1985

Abstract: Singlet oxygen, $^1\Delta_g$, has been produced by pulsed laser excitation of benzophenone, acetophenone, 3'-methoxyacetophenone, and 2-acetonaphthone in benzene and acetonitrile. In some cases second-order decay of the $O_2(^1\Delta_g)$ luminescence, monitored at 1270 nm, has been observed and a similar effect was apparent when $O_2(^1\Delta_g)$ was produced in the initial presence of ketyl radicals. It is proposed that the general inefficiency of $O_2(^1\Delta_g)$ production on sensitization by aromatic ketone triplets is a consequence of competitive biradical formation. Subsequent reaction of these biradicals gives rise to one or more long-lived species which react with $O_2(^1\Delta_g)$.

I. Introduction

The mechanism of the oxygen quenching of triplet states is a subject of some discussion and controversy. The collision complex can have singlet, triplet, or quintet multiplicity (eq 1–3), and it was originally concluded on both theoretical[1] and experimental[2] grounds that quenching proceeds exclusively via the singlet com-

plex and that each quenching act leads to a molecule of $O_2(^1\Delta_g)$. However, work by Garner and Wilkinson[3] and ourselves[4] presented evidence that the oxygen quenchings of several triplet states in benzene do not lead to $O_2(^1\Delta_g)$ with unit efficiency. Although the results were based on indirect techniques and have been

$$3S^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^1[S\cdots O_2]^* \rightarrow S + O_2(^1\Delta_g) \quad (1)$$

$$3S^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^3[S\cdots O_2]^* \rightarrow S + O_2(^3\Sigma_g^-) \quad (2)$$

$$3S^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^5[S\cdots O_2]^* \quad (3)$$

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(1) Kawaoka, K.; Khan, A. U.; Kearns, D. R. *J. Chem. Phys.* **1967**, *46*, 1842. Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. Gijzeman, O. L. J.; Kaufman, F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 721. Stevens, B. *J. Photochem.* **1973/4**, *3*, 157.
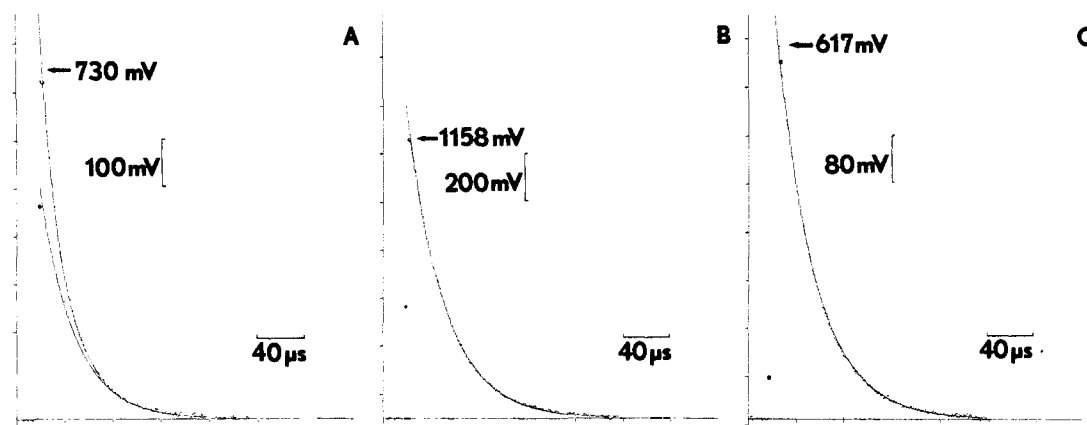
(2) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

(3) Garner, A.; Wilkinson, F. *Singlet Oxygen*; Ranby, B., Rabek, J. F., Eds.; Wiley: New York, 1978; p 48.

(4) Gorman, A. A.; Lovering, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4527.

Figure 1. Decay of $O_2(^1\Delta_g)$ infrared luminescence after absorption of a 10-ns laser phase (45 mJ cm^{-2}) by aerated benzene solutions of sensitizer: (A) at 355 nm by AP (OD$_{355}$ = 0.5), competing second- and first-order fit plus first-order component; (B) at 355 nm by 2-AN, first-order fit; (C) at 532 nm by *meso*-tetraphenylporphine (OD$_{532}$ = 0.5) in the presence of AP (OD$_{355}$ = 0.5), first-order fit.

questioned,[5] we have recently employed time-resolved $O_2(^1\Delta_g)$ luminescence measurements to confirm our original findings.[6] In this latter work it was shown that the fraction of triplet quenchings leading to $O_2(^1\Delta_g)$, the S_Δ value,[4] is 0.29 and 0.70 for benzophenone and 2-acetonaphthone, respectively, relative to the corresponding value for acridine which is likely to equal 1.0. Other types of sensitizer, the porphyrins in particular,[7] have also been shown to exhibit S_Δ values significantly less than unity.

There has been some speculation[3,4,8] concerning the nature of the processes whereby S_Δ values of less than unity result. All has been based on the assumption that the inefficiency has a photophysical as opposed to a photochemical basis, i.e., is a consequence of direct formation of sensitizer and oxygen ground states from the encounter complex. Since such a process is highly unfavorable on theoretical grounds,[1] we have addressed ourselves to an examination of the possibility that such oxygen quenchings involve chemical reaction between sensitizer triplet and oxygen and report here our findings for four high-energy aromatic ketone triplets.

II. Experimental Section

Laser excitation and kinetic absorption and emission spectroscopy were basically as previously described.[6] The laser beam (355 or 532 nm) was unfocused and was incident on the sample cuvette (10 mm × 10 mm) with a diameter of 8 mm. The maximum incident energy density used was 45 mJ cm^{-2} and was attenuated by combinations of wire screens and metal-coated filters. Computer-assisted data collection and analysis with interactive procedures for multiple parameter fits were as described.[9]

Benzene and acetonitrile (MCB Omnisolve) were used as received. 2-Acetonaphthone (Aldrich) and benzophenone (Bush) were recrystallized from ethanol. Acetophenone (Eastman) and 3'-methoxyacetophenone (Aldrich) were fractionated.

III. Results

The time-resolved decay of the weak infrared luminescence of $O_2(^1\Delta_g)$ has been described for a variety of solvents, subsequent to its formation via the oxygen quenching of a number of triplet sensitizers.[6,10] In every published case this decay has been strictly

(5) Stevens, B.; Marsh, K. L.; Barltrop, J. A. *J. Phys. Chem.* **1981**, *85*, 3079.

(6) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679.

(7) Reddi, E.; Jori, G.; Rodgers, M. A. J.; Spikes, J. D. *Photochem. Photobiol.* **1983**, *38*, 639.

(8) (a) Garner, A.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *45*, 432. (b) Smith, G. J. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1. (c) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1984**, *24*, 1. (d) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *Ibid.* **1985**, *30*, 81.

(9) Foyt, D. C. *Comput. Chem.* **1981**, *5*, 49.

(10) (a) Salokhiddinov, K. I.; Dzhagarov, B. M.; Byteva, I. M.; Gurinovich, G. P. *Chem. Phys. Lett.* **1980**, *34*, 892. (b) Salokhiddinov, K. I.; Byteva, I. M.; Gurinovich, G. P. *Zh. Prikl. Spektrosk.* **1981**, *34*, 892. (c) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065. (d) Parker, J. G.; Stanbro, W. D. *Ibid.* **1982**, *104*, 2067. (e) Ogilby, P. R.; Foote, C. S. *Ibid.* **1982**, *104*, 2069. (f) Rodgers, M. A. J.; Snowden, P. T. *Ibid.* **1982**, *104*, 5541. (g) Rodgers, M. A. J. *Ibid.* **1983**, *105*, 6201.

Table I. S_Δ Values and Oxgen Quenching Rate Constants, k_{ox} (L mol^{-1} s^{-1}), for Aromatic Ketone Triplets in Benzene[a]

ketone	S_Δ	k_{ox}
2-AN (π,π^*)	0.7[b]	1.54[d] (1.60)[e] × 10^9
BP (n, π^*)	0.29[b]	1.84[d] (2.53)[e] × 10^9
AP (n,π^*)	0.29[c]	3.95 × 10^9
3'-MAP (π,π^*)	0.27[c]	3.83 × 10^9

[a] This work unless otherwise stated. [b] Reference 6. [c] Determined by direct comparison with benzophenone. [d] Reference 4. [e] Reference 8a.

exponential in character and in benzene and acetonitrile has corresponded to lifetimes, τ_Δ, of 27–33 μs[6,10c,e,g] and 54–68 μs,[10c,e,g] respectively. In the work to be described we have produced $O_2(^1\Delta_g)$ by laser excitation of aerated solutions of benzophenone (BP), 2-acetonaphthone (2-AN), acetophenone (AP), and 3'-methoxyacetophenone (3'-MAP) in benzene and acetonitrile. These sensitizers were chosen because (a) they exhibit a range of S_Δ values (Table I)[11] and (b) they are representative of both photochemically important classes of aromatic ketone—those with lowest n,π^* and those with lowest π,π^* triplet states (Table I). Our aim was to examine the products of reaction of the triplet states with oxygen, using time-resolved emission and absorption spectroscopy, in the light of the considered possibility that species other than $O_2(^1\Delta_g)$ might be produced for those triplets where S_Δ values are significantly less than unity.

1. Time-Resolved Emission Measurements. Aerated, optically matched solutions of the sensitizers (OD$_{355}$ = 0.5) in benzene were subjected to pulsed laser excitation with incident laser energies in the range 5–45 mJ cm^{-2} per pulse. In all cases emission at 1270 nm was observed, and in all cases hereafter discussed this emission was absent when nitrogen-purged solutions were employed. At laser energies of ~5 mJ cm^{-2} the $O_2(^1\Delta_g)$ infrared emission exhibited in all cases a strictly exponential decay with τ_Δ = 27–32 μs. Although this lifetime range is in agreement with published values[6,10c,e,g] there is no doubt, in our experience, that the values for AP, 3'-MAP, and BP (27–28 μs) are significantly shorter than for 2-AN (32 μs). On increasing the laser energy, even more significant changes became apparent. Whereas for 2-AN and BP the $O_2(^1\Delta_g)$ decay still followed first-order kinetics, this was no longer the case for AP and 3'-MAP. For these latter sensitizers computer-aided curve fitting, using iterative nonlinear regression routines,[9] showed that, for energies above 5 mJ cm^{-2} per pulse, the $O_2(^1\Delta_g)$ decay profile is governed by competing first- and second-order processes. In agreement with this finding, the second-order component increased with laser energy as a consequence of the second-power dependence of its rate on concentration. Typical kinetic traces and computer fits are shown in

(11) Preliminary evidence shows that, certainly for BP, AP, and 3'-MAP, S_Δ values in acetonitrile are also much less than unity.[12]

(12) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J.; Spence, H., to be published.

Figure 1, A and B, which compare the decays of $O_2(^1\Delta_g)$ luminescence sensitized by AP and 2-AN at a laser energy of 45 mJ cm^{-2}. It is to be emphasized that the maximum initial $O_2(^1\Delta_g)$ concentration, as measured in millivolts of signal, is much greater in the case of 2-AN which has the higher S_Δ value (Table I). This is a critical observation in that it clearly demonstrates that the second-order kinetic component is not a consequence of $O_2(^1\Delta_g)$ self annihilation. If this were the case the higher initial $O_2(^1\Delta_g)$ yield from 2-AN solutions, irradiated under identical optical conditions, would require a *higher* second-order contribution to the $O_2(^1\Delta_g)$ decay whereas experiment shows this to be strictly exponential.

In order to show that the effects described are a consequence of the ketone excitation process as opposed to fortuitous ground-state effects, impurities, etc., it was necessary to devise an experiment in which $O_2(^1\Delta_g)$ was produced in the same environment but not via ketone triplet sensitization. Thus a solution of AP in benzene identical with that leading to the trace of Figure 1A, apart from the presence of *meso*-tetraphenylporphine (OD_{532} = 0.5), was excited at 532 nm. The emission of the $O_2(^1\Delta_g)$ thus produced by porphyrin sensitization decayed exponentially (Figure 1C) at all laser energies with a "normal" lifetime identical with that observed for 2-AN (cf. Figure 1B).

Similar results have been obtained with acetonitrile as solvent with the distinction that in this case the second-order effect was observed with BP as well as AP and 3'-MAP. As in the case of benzene, 2-AN sensitized $O_2(^1\Delta_g)$ emission exhibited exponential decay, τ_Δ = 66 μs, in good agreement with literature values of 54–68 μs.[10c,e,g]

To convert the second-order parameters obtained by computer fitting (units of mV^{-1} μs^{-1}) into absolute rate constants it is necessary to have the instrumental calibration factor. To date this is not known, but an estimate may be obtained from a knowledge of the absorbed energy. At 355 nm, 8.5 mJ cm^{-2} per pulse is equivalent to 1.53×10^{16} photons cm^{-2} per pulse. This leads to a concentration of BP triplets (ϕ_T = 1.0) of 1.73×10^{-5} mol L^{-1} at an OD of 0.5 (68% absorption). At S_Δ = 0.29, this yields an $O_2(^1\Delta_g)$ concentration of 5.0×10^{-6} mol L^{-1}. A pulse of this intensity yielded 290 mV of luminescence at time zero, whence the instrument calibration factor is 5.8×10^7 mV L mol^{-1}. According to this analysis the rate constants for the second-order components of $O_2(^1\Delta_g)$ decay fall in the range 1–4×10^9 L mol^{-1} s^{-1}, i.e., approximately an order of magnitude down on diffusion control. These values were essentially independent of laser intensity.

2. Independent Generation of Conditions for Mixed-Order $O_2(^1\Delta_g)$ Decay. In order to independently demonstrate that, within our system, mixed first- and second-order contributions can occur during $O_2(^1\Delta_g)$ decay, we have created a situation wherein $O_2(^1\Delta_g)$ has been produced in approximately equal amounts to putative quenching species formed in a chemically independent reaction. Although the processes concerned are clearly of interest in their own right, their primary function in this work has been to confirm the validity of our data analysis procedures and the conclusions drawn therefrom.

In the knowledge of the rate constant for oxygen quenching and the S_Δ value for triplet benzophenone in benzene (Table I) and the corresponding rate constant for H-abstraction from isopropyl alcohol in benzene (2.5×10^6 L mol^{-1} s^{-1}),[13] aerated benzene solutions of benzophenone (OD_{355} = 0.5) containing isopropyl alcohol (4×10^{-1} mol L^{-1}) were subjected to pulsed laser excitation. Under these conditions the initial concentrations of $O_2(^1\Delta_g)$ and ketyl radicals, produced by oxygen and isopropyl alcohol quenching of BP triplet, respectively, will be the same. The ketyl radicals will react rapidly with $O_2(^3\Sigma_g^-)$ to form α-hydroxyperoxy radicals (see Discussion). As demonstrated in Figure 2A, the emission from $O_2(^1\Delta_g)$ produced in these experiments exhibited clear competing first- and second-order decay. Both the rate constant for the second-order process and the in-
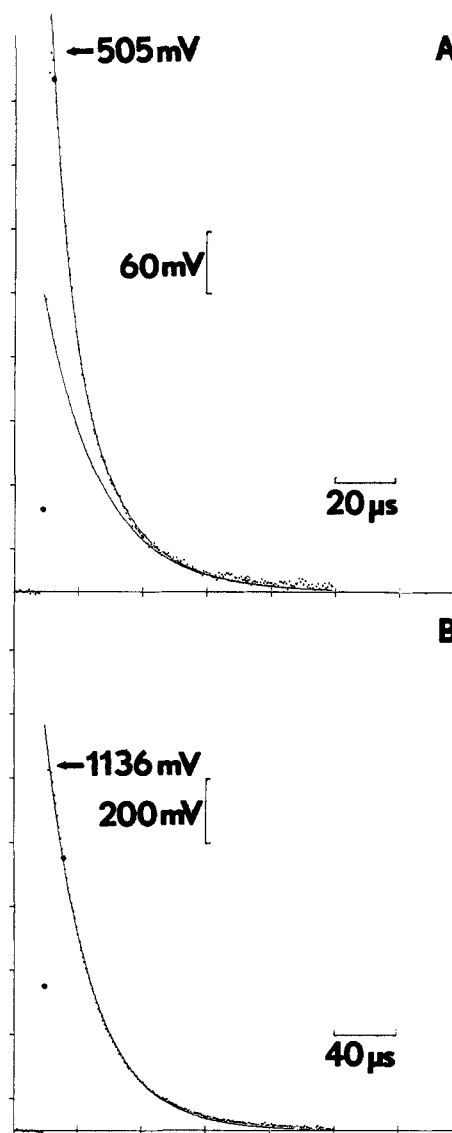
Figure 2. Decay of $O_2(^1\Delta_g)$ infrared luminescence after absorption of a 10-ns laser pulse (45 mJ cm^{-2}) at 355 nm by aerated benzene solutions of sensitizers (OD_{355} = 0.5) containing isopropyl alcohol (4×10^{-1} mol L^{-1}): (A) BP, competing second- and first-order fit plus first-order component; (B) 2-AN, first-order fit.

crease in the first-order rate constant relative to the natural decay of $O_2(^1\Delta_g)$ in benzene were (a) a factor of 4 to 5 higher than the corresponding values for the experiment shown in Figure 1A and (b) independent of laser energy. The contribution of the second-order component decreased with decreasing laser energy and became negligible at a laser energy of $\sim$3 mJ cm^{-2} per pulse. In contrast to the experiments with BP, the use of 2-AN as sensitizer gave strictly exponential decay with only a small decrease in lifetime, τ_Δ = 28 μs (Figure 2B). This is in agreement with the poor H-abstracting properties of π,π^* triplet states.
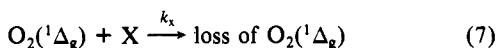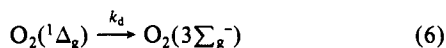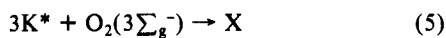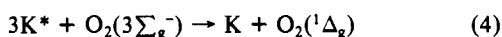
3. Time-Resolved Absorption Measurements. Pulsed laser excitation at 355 nm of each sensitizer (OD_{355} = 0.5) in aerated benzene or acetonitrile led to the formation of the corresponding triplet state which was rapidly quenched. No other transient absorbing species could be observed over the spectral range 370–800 nm. In addition, experiments carried out in the presence of benzoquinone, an $O_2^{\cdot-}$ trap, did not lead to detectable amounts of the quinone radical anion (cf. ref 14). The same results were obtained for the experiments in which oxygen and isopropyl alcohol competed for benzophenone triplet (section III.2)

(13) Determined by pulse radiolysis: Gorman, A. A.; Hamblett, I., unpublished data.

(14) Peters, G.; Rodgers, M. A. J. *Biochem. Biophys. Acta* **1981**, *637*, 43.

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IV. Discussion

The immediate inference from the experimental data described is that the oxygen quenching of AP, 3'-MAP, and BP triplets can lead to $O_2(^1\Delta_g)$ *plus* at least one other species. This species manifests itself, under appropriate conditions, as a second-order contribution to the early part of the $O_2(^1\Delta_g)$ luminescence decay. Thus, denoting the unknown entity as X, the kinetic scheme of eq 4–7 (K = ketone) leads to the rate law for decay of $O_2(^1\Delta g)$ summarized in eq 8. When $k_x[X] \ll k_d$ this reduces to a simple

$$3K^* + O_2(3\textstyle\sum_g^-) \rightarrow K + O_2(^1\Delta_g) \quad (4)$$

$$3K^* + O_2(3\textstyle\sum_g^-) \rightarrow X \quad (5)$$

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(3\textstyle\sum_g^-) \quad (6)$$

$$O_2(^1\Delta_g) + X \xrightarrow{k_x} \text{loss of } O_2(^1\Delta_g) \quad (7)$$

$$-\frac{d[O_2(^1\Delta_g)]}{dt} = (k_d + k_x[X])[O_2(^1\Delta_g)] \quad (8)$$

first-order situation, when $k_x[X] \gg k_d$ to that of a bimolecular elementary process. In intermediate situations, mixed kinetics can result if the initial concentrations of $O_2(^1\Delta_g)$ and X are sufficiently close. The decay of $O_2(^1\Delta_g)$ will then be mixed first and second order until such time as $[X] \gg [O_2(^1\Delta_g)]$. Then the decay becomes kinetically first order with a time constant given by eq 9, i.e. τ_{Δ}' ($=1/k'$) is smaller than τ_{Δ} ($=1/k_d$) as a consequence of the formation of X in reaction 5.

$$k' = k_d + k_x[X] \quad (9)$$

With AP and 3'-MAP as sensitizers we observed early second-order contributions in both benzene and acetonitrile, indicating that in these solvents reactions 4 and 5 are approximately of equal efficiency. A similar situation exists for BP in acetonitrile but not in benzene. Thus, in benzene AP, 3'-MAP, and BP show significantly faster first-order components (27–28 μs) relative to 2-AN (32 μs). That only AP and 3'-MAP exhibit second-order effects reflects a lower initial concentration of the corresponding unidentified species in the case of BP.

The above interpretation receives support from the experiments in which ketyl radicals and $O_2(^1\Delta_g)$ have been produced in comparable amounts under identical conditions of laser excitation (section III.2; Figure 2A). Ketyl radicals react with oxygen at close to the diffusion-controlled rate to give α-hydroxyperoxy radicals.[15] It therefore seems likely that the latter or species derived therefrom (cf. ref 16) are responsible for both the second-order component and the enhanced first-order component of the $O_2(^1\Delta_g)$ decay. The fact that *both* the second- and first-order contributions to this decay are 4–5 times larger than the corresponding values for oxygen quenching of AP triplet is in line with the kinetic analysis and lends strong support to our interpretation of the complex decay profiles.

That singlet–singlet annihilation is not the reason for the observed second-order contribution is, as already mentioned, unequivocally ruled out by the data shown in Figure 1, A and B.

1. Mechanism of the Oxygen Quenching of Aromatic Ketone Triplets. The aromatic ketones examined in this work are essentially inert to light and oxygen. Any mechanism for oxygen quenching of the respective triplets must therefore conclude with the formation of both ketone and oxygen in their ground states. In addition, since the nonexponential region observed in our experiments occurs over tens of microseconds (Figure 1A), the quenching intermediate X must be produced with a *minimum* lifetime in this range. Its formation is independent of the electronic

Scheme I
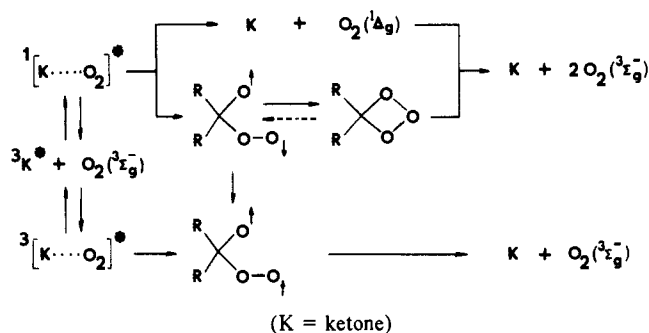
(K = ketone)

configuration of the ketone triplet, given that both AP and 3'-MAP exhibit the second-order effect.

In the light of these facts and our failure to detect ions (section III.3), we conclude that the unidentified species are *derived* from biradicals of type 1.[17] Although the mechanism outlined in

1
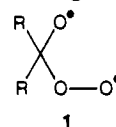
Scheme I is speculative, it fulfills the overall requirements derived from our experimental data and therefore serves as a working hypothesis. Individual points concerning Scheme I are made below.

Although there is some variation in the rate constants for oxygen quenching of the ketone triplets, as exemplified for benzene in Table I, none significantly exceeds one-ninth of the diffusion-controlled value of $\sim 3 \times 10^{10}$ L mol^{-1} s^{-1}.[21] It is therefore not possible to say whether or not quenching proceeds in part via the triplet encounter complex.

The singlet and triplet encounter complexes would give singlet and triplet biradicals, respectively. On the basis of current experimental[22] and theoretical[23] knowledge of the factors influencing the lifetimes of 1,4-biradicals, it appears certain that both the singlet and triplet biradicals of Scheme I will have lifetimes in the tens of nanoseconds range at most and cannot be responsible themselves for the observed second-order decay of $O_2(^1\Delta_g)$. 1,4-Biradicals either ring close to four-membered rings or fragment.[22] In the present case the spin-allowed processes are closure of the singlet and fragmentation of the triplet. We therefore feel that the putative trioxetane of Scheme I is the most likely candidate responsible for the rapid second-order contribution to $O_2(^1\Delta_g)$ decay. Intersystem crossing from singlet to triplet biradical can clearly compete with ring closure to an extent dependent on the individual sensitizer. Thus, although observation of a second-order effect would demand an S_Δ value significantly less than unity, the reverse is not necessarily the case.

V. Conclusions

We have detected for the first time mixed first- and second-order decay of the emission of $O_2(^1\Delta_g)$, formed as a consequence of the oxygen quenching of certain aromatic ketone triplets. A series of control experiments have shown that the second-order contribution is a result of bimolecular reaction between $O_2(^1\Delta_g)$ and a long-lived species which is also formed as a consequence of the oxygen-quenching act. We propose that a short-lived biradical is initially formed by addition of oxygen to the carbonyl

(15) Adams, G. E.; Willson, R. L. *Trans. Faraday Soc.* **1969**, *65*, 2981.
(16) Schenck, G. O.; Becker, H.-D.; Schulte-Elte, K.-H.; Krauch, H. C. *Berichte* **1963**; *96*, 509. Stockhausen, Von K.; Fojtik, A.; Henglein, M. *Ber. Bunsenges. Phys. Chem.* **1970**, *74*, 34. Downes, M. J.; Sutton, H. C. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 263. Schutze, H.; Schulte-Frohlinde, D. *Ibid.* **1975**, *71*, 1099.

(17) Such a biradical, of unspecified multiplicity, was originally proposed by Quinkert as an intermediate in the light-induced oxidation of menthone.[18] A similar species has been proposed as the key intermediate in the photooxidation of benzil[19] and the α-diketone-sensitized photooxidation of alkenes.[20]
(18) Quinkert, G. *Pure Appl. Chem.* **1964**, *9*, 607.
(19) Saltiel, J.; Curtis, H. C. *Mol. Photochem.* **1969**, *1*, 239.
(20) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934 and references therein.
(21) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455.
(22) Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139. Caldwell, R. A.; Tetsuro, M.; Chyongjin, P. *J. Am. Chem. Soc.* **1982**, *104*, 629. Caldwell, R. A. *Pure Appl. Chem.* **1984**, *9*, 1167.
(23) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

carbon of the ketone triplet. It is the competition between the formation of this species and $O_2(^1\Delta_g)$ which leads to S_Δ values of less than unity. Observation of the second-order effect will be dependent on the subsequent fate of the initially produced biradical. Further work on these and related systems is in progress.

Anionic Homoaromaticity: A Gas-Phase Experimental Study

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Abstract: The gas-phase acidities of several bicyclic and monocyclic alkenes and dienes have been measured in a model study of anionic homoaromaticity. Bicyclo[3.2.1]octa-2,6-diene (1), the precursor for what is considered to be a prototype bishomoaromatic carbanion, is found to have an acidity close to that of ethanol ($\Delta H_{acid}(1) = 379.6 \pm 1.0$ kcal/mol). The model compounds bicyclo[3.2.1]oct-2-ene (3) and 5-methylene-2-norbornene (12) yield allylic carbanions that are incapable of homoaromatic stabilization and are found to be nearly 10 kcal/mol less acidic than 1, with measured gas-phase acidities of 389.1 ± 1.0 and 389 ± 2 kcal/mol, respectively. A maximal 3–4 kcal/mol contribution to the enhanced acidity of 1 can be ascribed to an inductive effect of the remote C6–C7 double bond since the vinyl C–H acidities measured for norbornene and norbornadiene differ by only 3.1 kcal/mol. Kinetic measurements and experimentally derived acidity estimates for the related hydrocarbons cyclohexene, cyclooctene, 1,3-cyclohexadiene, and the cyclooctadienes are also presented which show that homoconjugation can be an important stabilizing influence in carbanions.

A long-standing problem in physical organic chemistry, one which continues to incite controversy even today, involves the viability of homoconjugative stabilization in carbanions. Alternatively termed "extensive" and "elusive", this unusual electronic delocalization mechanism which is, in principle, available to certain cyclic and polycyclic carbanions has traditionally proven difficult to establish unambiguously by both experiment and theory. The colorful history of anionic homoconjugation clearly illustrates its fluctuant status. The initial discovery by Brown and Occolowitz[1] of the 30 000-fold rate enhancement for base-catalyzed H/D exchange of diene 1 relative to olefin 3 was followed by a general

1   2a   2b   3   4
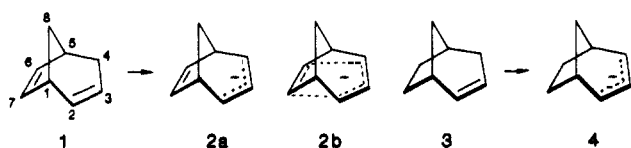
topological analysis of bishomoconjugation and bicycloaromaticity by Goldstein and Hoffmann.[2] Carbanion 2 was cited as but one example of a larger class of neutral, cationic, and anionic compounds in which transannular interactions between proximally held polyene "ribbons" may lead to extra stability or unstability, depending upon the symmetries and occupancies of the fragment molecular orbitals involved. Thus, facile H/D exchange in 1 was attributed to the bishomoaromatic character of the intermediate carbanion 2b.[3] Direct observation of the ^{1}H NMR spectrum of ion 2[3,4] provided additional support for homoconjugative charge delocalization, as extraordinarily high-field shifts for the C6, C7,

and C8 protons were found which could be attributed to weak diamagnetic ring currents. The qualitative appeal of homoconjugation,[5] its successful applications in carbonium ion chemistry,[6] and mounting reports of its existence in other anionic systems[4,7] led to a relatively comfortable status for the idea by the early 1970's. However, questions were raised concerning the interpretation of the earlier NMR experiments when Trimitsis and Tuncay demonstrated in 1976[8] that the 2,4-diphenyl derivative of 1 exhibited only a weak kinetic acidity enhancement over the corresponding derivative of 3, yet showed upfield shifts in the C6, C7, and C8 protons which were comparable to those found for 2. Subsequently, a detailed analysis of the ^{1}H and ^{13}C NMR spectra, computed geometries, and electronic structures of cyclohexadienyl anions appeared[9] in which it was concluded that homoaromaticity was absent in these ions. The general failure of homoaromaticity in neutral, closed-shell π-systems was convincingly demonstrated by Houk and Paquette;[10] in fact, compelling arguments were put forth for a *destabilizing* effect of homoconjungation in such systems. The status of anionic homoaromaticity reached its nadir in 1981 when Grutzner and Jorgensen[11] and Kaufmann, Mayr, Chandrasekhar, and Schleyer[12] presented combined semiempirical and ab initio MO results for

(1) (a) Brown, J. M.; Occolowitz, J. L. *J. Chem. Soc., Chem. Commun.* **1965**, 376. (b) Brown, J. M.; Occolowitz, J. L. *J. Chem. Soc. B* **1968**, 411.
(2) (a) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357. (b) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193.
(3) (a) Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1967**, 638. (b) Winstein, S.; Ogliaruso, M.; Sakai, M.; Nicholson, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 3656. (c) See also: Staley, S. W.; Reichard, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 3998.
(4) Grutzner, J. B.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 6562. Grutzner, J. B.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2200.

(5) (a) Winstein, S. *Chem. Soc., Spec. Publ.* **1967**, *21*, 5. (b) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.
(6) For a comprehensive review, see: Warner, P. M. *Top. Nonbenzenoid Arom. Chem.* **1976**, 2.
(7) (a) Rosenthal, J. W.; Winstein, S. *Tetrahedron Lett.* **1970**, *31*, 2683. (b) Brown, J. M.; Cain, E. N.; McIver, M. C. *J. Chem. Soc. B* **1971**, 730. (c) Moncur, M. V.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 6451. (d) Birch, A. J. *J. Chem. Soc.* **1947**, 1642. (e) Ley, S. V.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 6670.
(8) (a) Trimitsis, G. B.; Tuncay, A. *J. Am. Chem. Soc.* **1976**, *98*, 1997. (b) Trimitsis, G. B.; Zimmerman, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1506.
(9) Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.
(10) Houk, K. N.; Gandour, R. W.; Stozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.
(11) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372.
(12) Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1375.