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ELECTRON TRANSFER REACTIONS FROM AROMATIC CARBONYL TRIPLETS TO PARAQUAT DICATION[1*]

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Abstract: The rate constants for electron transfer reactions from several aromatic carbonyl triplets to paraquat dication leading to the formation of paraquat radical ion have been measured by nanosecond laser flash photolysis and are found to be in the range, $1 - 9 \times 10^9\ M^{-1}s^{-1}$.

A majority of the photoreactions of carbonyl compounds involve either electron or hydrogen atom transfer to their triplets resulting in photoreduction.[2] Thus far, there has been no study concerning possible electron transfer from carbonyl triplets (rather than to them). Paraquat (1,1'-dimethyl-4,4'-bipyridylium, PQ^{2+}) and other viologen-type ions, well-known for their herbicidal and toxicological properties, are strong one-electron oxidants and have shown promise as potential mediators[3,4] in photoinduced redox reactions that are of use in harnessing solar energy. The electron transfer reactions of paraquat with many substrates including photogenerated ketyl radicals[5] and biradicals[6,7] (intermediates of Norrish type II reactions) have been found to be very efficient. In the present letter we wish to report briefly on the results of our laser flash photolysis study concerning the photoreduction of paraquat through electron transfer from a number of aromatic carbonyl triplets.

Using nitrogen laser pulses (337.1 nm, 8ns, 2-3 mJ) for excitation and nanosecond kinetic spectrophotometry[7] (350-700 nm) for monitoring transients, we have measured the first order rates (k_{exp}) of formation of paraquat radical ion ($PQ^{+\cdot}$) produced as a result of reaction of PQ^{+2} with carbonyl triplets in water:acetonitrile (1:9, v/v). The major steps in the reaction scheme are as follows:

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\begin{array}{lll}
{>}C{=}O \xrightarrow{h\nu} \xrightarrow{ISC} & {>}C{=}O^{*}\ (\text{triplet}) & (1) \\
{>}C{=}O^{*} \xrightarrow{k_2} & {>}C{=}O & (2) \\
{>}C{=}O^{*} + PQ^{2+} \xrightarrow{k_3} & [{>}C{=}O]^{+\cdot} + PQ^{+\cdot} & (3) \\
{>}C{=}O^{*} + PQ^{2+} \xrightarrow{k_4} & {>}C{=}O + PQ^{2+,*} & (4) \\
{>}C{=}O^{*} + PQ^{2+} \xrightarrow{k_5} & {>}C{=}O + PQ^{2+} & (5)
\end{array}
$$

In the above scheme, step (3) represents electron transfer, while steps (4) and (5) represent physical quenching with and without triplet excitation transfer, respectively. In some cases, e.g., benzophenone, 2-naphthaldehyde and 2-acetonaphthone, where the maximum of carbonyl triplet-triplet absorption is in the spectral region where $PQ^{+\cdot}$ does not absorb strongly, the rates of decay of carbonyl triplets were also measured, and were found to be practically the same as the corresponding rates of formation of $PQ^{+\cdot}$. The plots of k_{exp} vs. paraquat concentration were linear, with slopes equal to the quenching rate constant (k_q) according to the equation $k_{exp} = k_2 + k_q\ [PQ^{2+}]$ where $k_q = k_3 + k_4 + k_5$.

The kinetic data for several aromatic carbonyl triplets are given in Table I. The transient spectra at the end of triplet decay under the condition of nearly complete quenching have been determined in the case of some of the carbonyl compounds. These spectra were found to be practically identical with the spectrum[8] of paraquat radical ion with maxima at 400 nm (sharp) and 610 nm (broad), respectively. This indicates that the radical cations derived from the carbonyl triplets either have relatively short lifetimes or contribute very little to the transient spectra because of relatively low extinction coefficients[9] in the spectral region 350-700 nm. An estimate based on extinction coefficients of benzophenone triplet (ε = 6,500 $M^{-1}cm^{-1}$ at 520 nm in acetonitrile)[10] and paraquat radical ion (ε = 13,000 $M^{-1}cm^{-1}$ at 605 nm in water)[8] shows that ∿60% of the quenching events result in net electron transfer leading to photoreduction of PQ^{2+}. The deviation of primary quantum yield of photoreduction from unity could be either a result of back electron transfer following the formation of radical-radical ion pair in the solvent cage or due to contribution of physical quenching processes[11] represented by equations (4) and (5).

Based on the results presented in Table I, some observations can be made. First, except for benzil triplet, the quenching rate constants are relatively high. In particular, for benzophenone triplet, the quenching

Table I. Rate constants for the quenching of aromatic carbonyl triplets by paraquat in H_2O:acetonitrile (1:9, v/v)

Carbonyl triplet	k_q ($M^{-1}s^{-1}$)	Carbonyl triplet	k_q($M^{-1}s^{-1}$)
α,α,α-trifluoroacetophenone	2.6×10^9	benzophenone	2.6×10^9
p-methoxyacetophenone	8.3×10^9	2-naphthaldehdye	3.8×10^9
acetophenone	6.1×10^9	2-acetonaphthone	5.4×10^9
p-cyanoacetophenone	1.5×10^9	benzil	$<1\times10^6$
m-methoxyacetophenone	6.1×10^9		

rate constant observed in wet acetonitrile in the present study is more than two orders of magnitude higher than that obtained[3] for the quenching of benzophenone phosphorescence in acetonitrile. Second, there is a definite correlation between the rate constants and the nature (i.e. electron-withdrawing or electron-releasing) of the substituents in the carbonyl compounds. Thus, k_q's for the acetophenones in Table I are in the order: p-cyanoacetophenone < acetophenone < p-methoxyacetophenone, and α,α,α-trifluoroacetophenone < acetophenone. Third, with triplets of similar configuration (e.g. n,π^*), there is a decreasing trend in k_q's as the triplet energy (E_T) is lowered. Thus, acetophenone > benzophenone >> benzil. This is understandable in terms of the fact that E_T, in addition to oxidation potential, makes a dominant contribution to the free energy decrease associated with the electron transfer. In addition, there is the possibility that the quenching by triplet energy transfer i.e. equation (4) would be less and less important as the triplet energy of the carbonyl compound is lowered with respect to that of paraquat.[11]

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