

## Short Communication

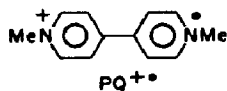
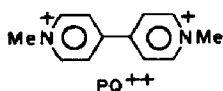
### One electron reduction of paraquat dication by photogenerated biradicals

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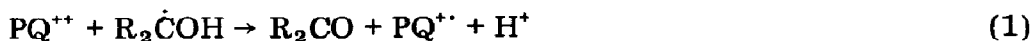
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The one-electron reduction of paraquat dichloride (1,1'-dimethyl-4,4'-bipyridylium dichloride) is believed to be a process of importance in determining the herbicidal and toxicological properties of these ions [1 - 5]. In addition to its biological importance, it has been proposed that electron phototransfers of the type mentioned above may be applicable systems for the photochemical storage of solar energy [6].



A number of reactions leading to the reduction of  $PQ^{++}$  to  $PQ^{+•}$  have been reported [7, 8]; among them is the reaction of photogenerated ketyl radicals, leading to the formation of the corresponding carbonyl compound and the radical-ion:



The high efficiency of this reaction suggested by Hyde and Ledwith [8], led us to believe that a similar process could take place when the ketyl radical site is part of a biradical. In order to test this possibility we have examined the photochemistry of a series of phenyl-alkyl ketones in the presence of paraquat dichloride. In those cases where the carbonyl compound has  $\gamma$ -hydrogens it generates biradicals in a process which occurs exclusively from the triplet manifold. In the absence of  $PQ^{++}$  reaction (2) illustrates the mechanism [9].

Table 1 gives a summary of the results obtained for the reaction of paraquat dichloride and the carbonyl compounds. The quantum yields of reaction, as measured by the quantum yield of radical-ion formation, increase with decreasing triplet lifetime. This is conclusive evidence that the reaction

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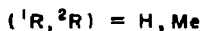
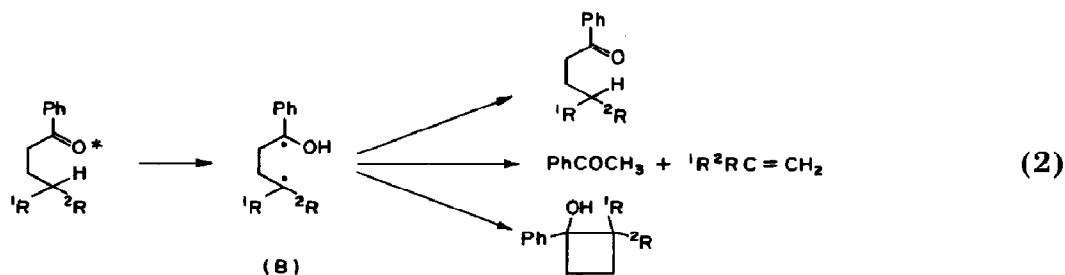


TABLE 1

Photochemistry of phenyl alkyl ketones in the presence of paraquat dichloride<sup>a</sup>.

Ketone	$\Phi_{PQ^+}$	$(\Phi/\Phi^\circ)_{ACP}^b$	$\tau_T^c$
None	$\ll 0.002$	—	—
Acetophenone	0.06 <sup>d</sup>	—	$3.3 \times 10^{-6}$ [11]
Butyrophenone	0.10	0.41	$1.2 \times 10^{-7}$ [12]
Valerophenone	0.15	0.38	$7.6 \times 10^{-9}$ [12]
$\gamma$ -Methyl valerophenone	0.24	0.43	$1.9 \times 10^{-9}$ [12]

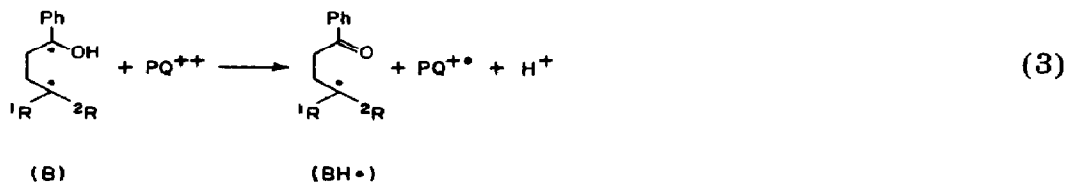
<sup>a</sup>Conditions: 0.0034 M paraquat dichloride in 1:4 water-acetonitrile at room temperature;  $\lambda = 337.1$  nm. Reaction followed spectrophotometrically at 603 nm.

<sup>b</sup>Ratio of the quantum yields of photofragmentation in the absence ( $\Phi^\circ$ ) and presence ( $\Phi$ ) of paraquat.

<sup>c</sup>Lifetime in seconds in benzene solvent. The values in wet acetonitrile might be slightly shorter [10]. The value given in parenthesis is the reference to the lifetime.

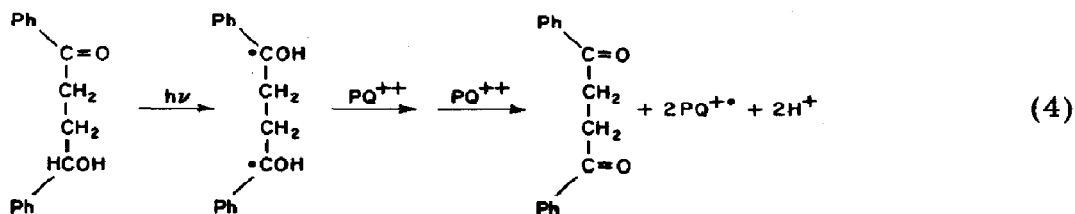
<sup>d</sup>Expected  $\Phi \cong 0$ . Some  $PQ^+$  probably arises from energy transfer from acetophenone to paraquat and the subsequent reaction of  ${}^3PQ^{++}$  [6].

does not proceed *via* the triplet state\*, as has been shown in related papers [13, 14]. We propose that the formation of  $PQ^+$  proceeds *via* a biradical mechanism:



\* Further, the limiting quantum yield for *any* type of triplet reaction would be, for example, less than 0.06 for  $\gamma$ -methyl-valerophenone assuming diffusion controlled reaction with 0.0034 M paraquat.

We have also prepared 1,4-diphenyl-1-hydroxy-4-butanone, which produced a diketyl biradical *via* a short lived triplet ( $\tau_T \sim 1$  ns). Preliminary results indicate that a very efficient trapping of both radical ends takes place. For example, under the conditions of Table 1,  $\Phi(\text{PQ}^{+\cdot}) \sim 0.7$ . The reaction takes place with production of 1,4-diphenyl-1,4-butanedione:



It is worth noting that reaction (4) is probably the cleanest source available for the generation of  $\text{PQ}^{+\cdot}$  radical-ions.

The relatively high quantum yields observed suggest that triplet quenching is not extensive, although this should not be taken to mean that quenching is slow\*. The differences in quantum yields for the different ketones (Table 1) and the fact that  $(\Phi/\Phi^\circ)_{\text{ACP}}$  is nearly constant indicate that either the biradical lifetime or the quantum yield of biradical formation increases with increasing substitution at the  $\gamma$ -position.

In conclusion, the experiments reported herein indicate that paraquat cations are efficient traps of biradicals containing ketyl radical sites. If the solvated biradicals have lifetimes of the order of  $1 \mu\text{s}$  [15] then  $k_3$  is of the order of  $1 - 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This is the first example of trapping of Type II biradicals by ions and the first system where the trapping reaction occurs at the ketyl site; this probably implies that the rate constant for biradical trapping is the same for all the ketones in Table 1, since the only differences are alkyl substitutions four atoms away from the reactive center. This is particularly important, because it will hopefully allow us to measure accurate ratios of biradical lifetimes. Detailed kinetic studies are currently in progress.

### Experimental

Paraquat dichloride was a K & K product. All the ketones were commercial products with the exception of 1,4-diphenyl-1-hydroxy-4-butanone which was prepared by reduction of 1,4-diphenyl-3-butene-1,3-dione [16]. The photofragmentation of valerophenone in benzene was used as an actinometer taking  $\Phi = 0.30$  [17].

\*For example, in the case of valerophenone, a rate constant for quenching of  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  would quench only 20% of the triplets under our experimental conditions.

The samples were contained in (a) square  $1 \times 1$  cm Suprasil quartz cells, or (b) in 9 mm o.d. matched Pyrex tubes. In all cases argon was bubbled through the solution, which was then degassed by five freeze-pump-thaw cycles. Irradiations were carried out using 337.1 nm light from a Molelectron UV-400 nitrogen-laser. The laser was pulsed at a frequency of 2.5 pps. The samples were vigorously stirred using micro magnets introduced during the preparation of the sample.

All quantum yields of radical-ion formation are based on  $\epsilon = 1.2 \times 10^4$   $\text{l mol}^{-1} \text{ cm}^{-1}$  at 603 nm. The reaction was monitored using a Cary 14 spectrophotometer.

Preliminary experiments using a B & L SP-200 mercury lamp and monochromator system indicated that the reaction had an induction period. On further examination using laser irradiation it was clear that the radical-ion  $\text{PQ}^{\bullet}$  is produced from the first pulse, but is consumed initially, presumably by trace impurities present in the system. In terms of radiation dose the induction period corresponds to  $\sim 1 \times 10^{-8}$  einstein/ml.

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