Equilibration in Photochemical Systems. The Photolysis of a Mixture of α-Diketones in Isopropyl Alcohol

By MORDECAI B. RUBIN* and ZVI HERSHTIK

(Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel)

Summary The photoreduction of mixtures of camphorquinone and tetramethyltetralindione in isopropyl alcohol is independent of initial excitation, on account of equilibration of intermediate semidione radicals.

WE report the results of irradiations of degassed isopropyl alcohol solutions containing camphorquinone (CQ) and

1,1,4,4-tetramethyltetralin-2,3-dione (TTD). The marked differences in absorption spectra of these diones (CQ: ϵ_{366} 0.4, ϵ_{388} 1, ϵ_{404} 5, ϵ_{436} 23, and ϵ_{470} (max) 40; TTD: ϵ_{366} 26.5, ϵ_{388} (max) 33, ϵ_{404} 30, ϵ_{436} 13, and ϵ_{470} 1.5) permit irradiation of both simultaneously, or selective irradiation of either CQ or TTD, and allow the resulting chemical changes to be followed spectroscopically. The results

obtained at 436 nm (2 \times 10⁻² M-CQ, 2·3 \times 10⁻² M-TTD; 40% of light absorbed by TTD) are shown in the Figure



FIGURE. Spectroscopic changes upon irradiation (436 nm) of a degassed isopropyl alcohol solution of CQ and TTD.

where it can be seen that TTD reacts rapidly while CQ only begins to react appreciably after TTD has been consumed. Identical results were obtained upon irradiating mixtures at 366 (99% of light absorbed by TTD) or 404 nm (85% abs. by TTD) or at $\lambda >470$ nm (<1% absorbed by TTD). Thus, the photochemical behaviour of this system is independent of the initial excitation.

The mechanism of photoreduction of diones in isopropyl alcohol,¹ as illustrated for CQ, involves excitation via singlet states to the n,π^* triplet followed

$$CQ \xrightarrow{h\nu} {}^{1}CQ \rightarrow {}^{3}CQ \qquad (1)$$

$$^{3}CQ \rightarrow CQ$$
 (2)

$$CQ + SH_2 \rightarrow CQH \cdot + SH \cdot$$
 (3)

$$CQ + SH \rightarrow CQH \rightarrow CQH \rightarrow S$$
 (4)

$$2CQH \cdot \rightarrow CQ + CQH_2 \tag{5}$$

by H-atom abstraction from alcohol (SH₂) to give semidione radical (CQH \cdot or TTDH \cdot) and 2-hydroxy-2-propyl radical (SH). A second semidione radical and acetone (S)are formed by H-atom transfer from SH. to dione. Finally, two semidione radicals disproportionate to give one molecule of hydroxy-ketone (CQH₂ or TTDH₂) and regenerate a molecule of dione. The rates of disproportionation of CQH· and TTDH· have both been found² to be about $4 \times 10^7 \,\text{m}^{-1}$. The additional reactions, involving equilibration of triplets or radicals, possible in a mixture of two diones are shown below. It should also be noted that SH. radical could transfer hydrogen to either dione irrespective of which triplet species was responsible for its formation.

$$^{3}CQ + TTD \rightleftharpoons CQ + ^{3}TTD$$
 (6)

$$CQH \cdot + TTD \rightleftharpoons CQ + TTDH \cdot$$
 (7)

$$CQH + TTDH$$
(8)

$$^{\checkmark}$$
 CQH₂ + TTD (9)

The possibility that ³TTD is formed via energy transfer from ³CQ (reaction 6) could be excluded on the basis of phosphorescence spectra of a mixture of CQ and TTD. Excitation of TTD (380 nm) resulted in appearance of both the phosphorescence maximum of TTD (530 nm) and of CQ (562 nm) indicating partial energy transfer to CQ; excitation of CQ (470 nm) resulted only in CQ emission. Thus, appreciable or exclusive ³CQ formation will occur at all wavelengths.



The preferential photoreaction of TTD must then be due to radical reactions (7 or 8). The e.s.r. spectrum[†] of an irradiated mixture of TTD and CQ in isopropyl alcohol showed a strong signal for TTDH and no signal for CQH. This is only possible if equilibrium (7) lies far to the right so that, whatever radical species may be formed initially, CQH· radicals will transfer hydrogen to TTD. Under these circumstances and since the rates of disproportionation of CQH· and TTDH· are comparable, TTD will react much faster than CQ at all wavelengths.

This method promises to be of value as a mechanistic probe in photoreactions as well as in determination of relative stabilities of semidione radicals.

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¹ M. B. Rubin, Forstschr. Chem. Forsch., 1969, 13, 251; B. M. Monroe and S. A. Weiner, J. Amer. Chem. Soc., 1969, 91, 450; G. E. Gream, J. C. Paice, and C. C. R. Ramsay, Austral. J. Chem., 1967, 20, 1671.
 ³ S. A. Weiner, E. J. Hamilton, jun., and B. M. Monroe, J. Amer. Chem. Soc., 1969, 91, 6350.

[†] This result was obtained through the co-operation of Drs. B. M. Monroe and E. J. Hamilton, jun., in the laboratory of Prof. G. S. Hammond.