Triphenylene as a Singlet Sensitizer

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Summary Cyclohex-2-enone and 5,5-dimethylcyclopent-2-enone quench triphenylene fluorescence at near diffusion-controlled rates; these and earlier results indicate that triphenylene is often unsuitable as a triplet sensitizer.

TRIPHENYLENE possesses photochemical and spectroscopic properties which led some years ago to its being highly recommended[1] as a triplet sensitizer for photochemical investigations. These properties include strong u.v. absorption in experimentally convenient regions,[2] high efficiency of intersystem crossing to the lowest triplet ($\Phi_{ST} = 0{\cdot}90 \pm 0{\cdot}05$)[3], a useful triplet energy (E_T = 67 kcal/mole[1,4]), and unusual photochemical stability.[1] More recently, however, there have been several reports[5,6] that in certain cases triphenylene has acted as a *singlet* rather than a triplet sensitizer. These reports all have dealt primarily with other matters, and the authors generally have made only passing note of this singlet sensitization. For this reason, and also because recommendation of triphenylene as a triplet sensitizer recently has been repeated,[7] we report two additional properties of this hydrocarbon which should be kept in mind and which limit its usefulness as a source of triplet energy. These properties are the energy of the first excited singlet state of triphenylene ($E_S = 82 \pm 1$ kcal/mole[4,6]) and the decay time of this state ($\tau = 36{\cdot}6$ nsec. in cyclohexane at room temperature[8]). This lifetime is sufficiently long to allow transfer of singlet energy to acceptor molecules possessing a suitable energy level ($E_S <$ 82 kcal/mole), and indeed the singlet sensitizations previously observed all involve acceptors meeting this requirement.

We find that this energy transfer can proceed at high rates, as indicated by our measurement of the quenching of triphenylene fluorescence by two simple $\alpha\beta$-unsaturated

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ketones cyclohex-2-enone and 5,5-dimethylcyclopent-2-enone[9] (L_S *ca* 75 kcal/mole in each case[10]) These ketones gave quite similar results at 30° in methanol and in t-butyl alcohol Using the Stern–Volmer equation ($\Phi_0/\Phi = 1 + k_q\tau[Q]$) and with the assumption that the decay time of triphenylene singlet is uneffected by change of solvent from cyclohexane to the alcohols used, we calculate by least-squares analysis, with a confidence level of 90%, the rate constants for fluorescence quenching (k_q) given in the Table

Rate constants (k_q) *for quenching of triphenylene fluorescence*

Quencher	$k \times 10^9$, $M^{-1}sec^{-1}$ Methanol	 t Butyl alcohol
Cyclohex-2 enone	3 1	1 8
5,5-Dimethylcyclopent-2-enone	2 9	3 1
k_{dif}	19	3 0

For comparison we include the diffusion-controlled bimolecular rate constants (k_{dif}) for these solvents, estimated from the modified[11] Debye equation and appropriate viscosities [12] at 30° Since there are excellent grounds[13] for expecting the maximum k_q in methanol to be considerably less than k_{dif} (we estimate maximum k_q *ca* 0·4 k_{dif}) because of the low viscosity of this solvent, it is clear that these ketones quench triphenylene singlets at near maximum rates

Neither 2,3-dimethylbuta-1,3-diene at low concentrations nor acetone ($E_S > 83$ kcal/mole for each compound‡) has any effect on triphenylene fluorescence, cyclohexanone (E_S *ca* 81 kcal/mole‡) behaves as a quite inefficient quencher In view of these results and those reported earlier by others,[5,6] it seems wise to exercise considerable discretion in use of triphenylene as a triplet sensitizer

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‡ These singlet energies were estimated from the onset of absorption in the u v region

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