Olefins as Triplet-state Scavengers in Irradiated Systems

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RECENTLY there have been a number of reports which discuss the detection and estimation of triplet states by ionizing radiations in benzene solutions.[1-6] There are a number of difficulties in interpreting the results of such experiments. In many systems singlet–singlet electronic energy transfer followed by intersystem crossing of the excited acceptor to the triplet state is possible. The efficiency of the latter process is usually unknown. Also in such cases it has not been possible hitherto to separate contributions from triplet states which have been produced directly from those derived by intersystem crossing from the singlet manifold. If the lifetime of the triplet state is comparable with that of the singlet, as appears to be the case in liquid benzene,[5] the concentration dependency does not provide a method for distinguishing the states involved.

Olefins undergo triplet–triplet energy transfer from donors for which $E_T > 3ev$ but do not undergo singlet–singlet transfer below at least $5ev$.[7] Energy-transfer processes involving olefin triplets as donors have not been observed. Olefin triplet states are probably very short lived ($< 10^{-9}$ sec.) because of rapid intersystem crossing due to overlap of ground-state singlet and triplet potential-energy surfaces in the twisted configuration. Thus it should be possible to scavenge triplet states with olefins but without appreciable effect on excited singlets or acceptor triplets with energies below that of the olefin.

These predictions have been confirmed in an investigation of the irradiation of benzene solutions of biacetyl or anthracene with 2μsec. pulses of 4 Mev electrons. The observations were made with the pulse radiolysis apparatus developed by Dr. J.P. Keene.[8] The addition of cyclohexene caused a reduction in the triplet yields of both solutes. In the case of a $3{\cdot}7 \times 10^{-2}$M-solution of biacetyl there was a decrease of 44% in the intensity of biacetyl phosphorescence at 520mμ in a $5{\cdot}0 \times 10^{-1}$M-cyclohexene solution. Anthracene triplet absorption spectra at 424mμ observed in a 2×10^{-2}M-anthracene solution showed a decrease of 40% in a $5{\cdot}0 \times 10^{-1}$M-cyclohexene solution. The effect is attributed to the removal of triplet ($^3B_{1u}$) states of benzene produced in the primary processes.

The cyclohexene fulfills two roles. An efficient deactivation of the solvent triplet occurs which studies of the concentration dependencies indicate to be diffusion-controlled. There is also a slower deactivation of the added-solute triplet which was measured by the effect of cyclohexene concentration on the lifetime of the acceptor triplet. If the efficiency of singlet–triplet intersystem crossing of biacetyl is unity as found by Backström and Sandros,[9] then 45% of the excited states of benzene produced by irradiation are initially formed in the triplet states. The extensive production of excited-singlet solutes by the effect of ionizing radiations on benzene is consistent with the behaviour reported by Kemp, Salmon, and Wilkinson.[10] The maximum in the G(triplet) curve for benzene probably results from concentration quenching of acceptor singlets.

The ability of olefin to remove triplet states as shown in these experiments may be used in both photochemical and high-energy-irradiated systems. It becomes possible to separate the roles of singlet and triplet states and study their behaviour separately by either spectroscopic and/or energy-transfer effects. By using conjugated diolefins excited states of lower energy than those quenchable by mono-olefins may be examined.

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[1] J. M. Nosworthy and J. P. Keene, *Proc. Chem. Soc.*, **1964**, 114.
[2] J. M. Nosworthy, *Trans. Faraday Soc.*, 1965, **61**, 1138.
[3] E. A. Cherniak, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, 1964, **60**, 1408.
[4] H. P. Lehmann, G. Stein, and E. Fischer, *Chem. Comm.*, 1965, 583.
[5] R. B. Cundall and P. A. Griffiths, *Discuss. Faraday Soc.*, 1963, **36**, 111; *Trans. Faraday Soc.*, 1965, **61**, 1968.
[6] J. P. Keene, T. J. Kemp, and G. A. Salmon, *Proc. Roy. Soc.*, 1965, *A*, **287**, 494.
[7] R. B. Cundall and A. S. Davies, *Proc. Roy. Soc.*, in the press (and references cited therein).
[8] J. P. Keene, *J. Sci. Instr.*, 1964, **41**, 492.
[9] H. L. J. Backström and K. Sandros, *Acta Chem. Scand.*, 1960, **14**, 48.
[10] T. J. Kemp, G. A. Salmon, and F. Wilkinson, *Chem. Comm.*, 1966, 73.