Photoreduction of Aromatic Hydrocarbons by Tri-n-butyltin Hydride

By D. R. G. BRIMAGE and R. S. DAVIDSON*
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary The triplet states of acenaphthylene, benz[*a*]anthracene, and phenanthrene abstract hydrogen from tri-n-butyltin hydride to give dihydro-compounds and the rate constants for the reactions with benz[*a*]anthracene and phenanthrene have been determined.

THERE have been previous reports of the photoreduction of benzenoid compounds,[1] polycyclic aromatic hydrocarbons,[2] and olefins[3] by amines and in the case of the polycyclic hydrocarbons it was concluded that the singlet state of the hydrocarbon was the reactive excited state. The recent findings that 1,1-diphenylethylene,[4] 9,9′-bifluorenylidene,[5] and 1,2-di-(4-pyridyl)ethylene[6] are photoreduced by isopropyl alcohol suggested that the triplet states of aromatic hydrocarbons may be susceptible to reduction.[7] Tri-n-butyltin hydride was chosen as a hydrogen donor in view of its known reactivity towards excited states.[8]

Irradiation of benzene solutions of naphthalene, perylene, and pyrene containing tri-n-butyltin hydride lead to no detectable reduction. Under similar irradiation conditions acenaphthylene gave acenaphthene, benz[*a*]anthracene gave 7,12-dihydrobenz[*a*]anthracene, and phenanthrene gave 9,10-dihydrophenanthrene.

The reductions of benz[*a*]anthracene and phenanthrene were found to be quenched by perylene. Since the concentration of the quencher was low enough to discount deactivation by singlet–singlet energy transfer, it was surmised that the quencher was deactivating the triplet state of the hydrocarbons. The quantum yields for reduction of the hydrocarbons by the hydride in the presence of perylene at different concentrations were determined. By means of the Stern–Volmer equation

$$\frac{1}{\phi} = \frac{1}{a}\left(1 + \frac{k_d}{k_r[\mathrm{RH}]} + \frac{k_q[\mathrm{Q}]}{k_r[\mathrm{RH}]}\right) \qquad (1)$$

a = quantum yield for triplet formation; k_d = rate constant for decay of the excited state of the hydrocarbon; k_r = rate constant for hydrogen abstraction; k_q = bimolecular rate constant for triplet quenching; [RH] = concentration of tri-n-butyltin hydride; [Q] = concentration of perylene.

(equation 1)[9] values for k_q/k_r were obtained.[10] Using a value of $5 \times 10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for k_q,[11] gave k_r values $1{\cdot}8 \times 10^5\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $4{\cdot}7 \times 10^5\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for the reductions of benz[*a*]anthracene and phenanthrene, respectively. The quantum yields for reduction of these hydrocarbons in the presence of the hydride at a variety of concentrations were also determined From these data values for k_d/k_r were obtained Substitution of the values for k_r determined in the quenching experiments gave the rate constants for the decay of the excited states of benz[*a*]anthracene and phenanthrene as $9 8 \times 10^{3}$ s^{-1} and $5 6 \times 10^{4}$ s^{-1} respectively Porter and Wilkinson[12] have determined the decay constants of triplet benz[*a*]anthracene (in benzene) and phenanthrene (in hexane) at room temperature to be $6 3 \times 10^{3}$ s^{-1} and $1 07 \times 10^{4}$ s^{-1} The closeness of these values to those for the excited state involved in the reduction reactions establishes that these reactions occur *via* the triplet state of the hydrocarbon

We acknowledge the award of a University of Leicester Scholarship to D R G B

(*Received, January 14th* 1971, *Com* 066)

---

[1] M Bellas D Bryce Smith and A Gilbert, *Chem Comm* 1967, 263

[2] R S Davidson, *Chem Comm* , 1969, 1450, J A Barltrop and R J Owers *ibid* , 1970 1462, J J McCullough, C W Huang and W S Wu, *ibid* , p. 1368

[3] R C Cookson, S M de B Costa, and J Hudec *Chem Comm* , 1969, 753

[4] H M Rosenberg and P Serve *J Amer Chem Soc* 1970 **92**, 4746

[5] J Nasielski M Jauquet E Vander Donckt and A Van Sinoy, *Tetrahedron Letters*, 1969, 4859

[6] D G Whitten and Y J Lee *J Amer Chem Soc* 1970, **92**, 415

[7] Whilst this work was in progress Prof Schaffner reported in a discussion at the 1970 I U P A C conference on Photochemistry that some substituted naphthalenes are photoreduced by tri n butyltin hydride

[8] G S Hammond and P A Leermakers *J Amer Chem Soc* 1962 **84** 207 G A Davis P A Carapellucci K Szoc and J D Gresser *ibid* , 1969 **91** 2264 P J Wagner *ibid* 1967 **89**, 2503, E Baggiolini H P Hamlow, and K Schaffner, *ibid* 1970 **92** 4906 W Trotter and A C Testa *ibid* 1968 **90** 7044

[9] W M Moore, G S Hammond and R P Foss *J Amer Chem Soc* 1961 **83** 2789

[10] Quantum yield for triplet benz[*a*]anthracene taken as 0 55 (H Labhart *Helv Chim Acta*, 1964, **47** 2279) and for triplet phenanthrene as 0 76 (A Lamola and G S Hammond, *J Chem Phys* , 1965 **43** 2129)

[11] A value of 5×10^{9} M^{-1} s^{-1} was used for k_q (P J Wagner and I Kochevar, *J Amer Chem Soc* , 1968 **90** 2232)

[12] G Porter and F Wilkinson, *Proc Roy Soc* , 1961, *A*, **264**, 1