

Photochemical Reaction of Anthracene in Cyclohexane Polycrystals Dispersed in Liquid Nitrogen

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Summary U.v. photolysis of a polycrystalline solution of anthracene in cyclohexane at 77 K followed by separation of the stable photoproducts at room temperature, yielded 9,10-dihydroanthracene, 9-cyclohexyl-9,10-dihydroanthracene, 9-cyclohexylanthracene, and oxidized derivatives of anthracene.

We found recently that polynuclear aromatic hydrocarbons (p.a.h.) in dilute rigid solutions in alkanes or alcohols at 77 K undergo photolysis upon intense u.v. irradiation, whereas this reaction does not occur in degassed liquid solution.¹ Photoproducts were tentatively identified on the basis of the developing electronic spectra and their modification upon melting. The new bands were assigned to monohydrogenated radicals and products of addition of solvent molecules to the aromatic skeleton. The first assignment could be made with good confidence, but confirmation was needed for the assignment of stable photoproducts involving the reaction with the solvent molecules of the cage.

We report here results obtained upon irradiation of anthracene incorporated in cyclohexane crystals. An aerated cyclohexane solution of anthracene (10^{-3} M) was quickly frozen to 77 K. The crystalline mass was coarsely ground and the polycrystals were immediately immersed in liquid nitrogen contained in a clear silica Dewar flask surrounded by a Vycor envelope. The light source was a low pressure resonance Hg lamp and irradiation lasted for ca. 3 h.

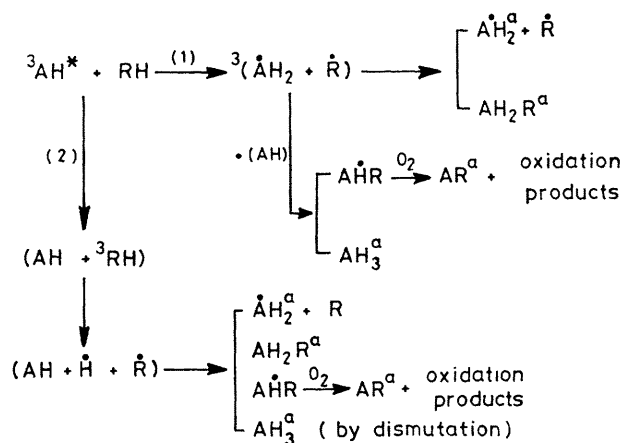
To isolate the photoproducts the liquid nitrogen suspension was evaporated *in vacuo* and the residue taken up in methanol. The photoproducts were separated by high performance liquid chromatography (h.p.l.c.) using Spherisorb 5 μ DOS with detection by the u.v. absorption at λ 265 nm and g.l.c. on 3% OV-1 on Chromosorb W. The main products were identified on the basis of their mass spectra (VG Micromass 16 F), g.l.c. retention times, and u.v. spectra compared to authentic samples.[†]

The fractions eluted before unchanged anthracene were identified, by h.p.l.c., as the oxidized derivatives of anthracene: bianthryl, 9-anthrone, and 9,10-anthraquinone. Since oxygen is present, oxidation reactions can occur during the irradiation *via* singlet oxygen, but are much more likely to occur during the warming process when the dissolved oxygen can react with the radical intermediates.

Of greater interest is the identification of 9-cyclohexylanthracene (AR), 9,10-dihydroanthracene (AH₃), and 9-cyclohexyl-9,10-dihydroanthracene (AH₂R). On the h.p.l.c. trace only the AR fraction is well separated; AH₂R appears as a shoulder on the unchanged anthracene peak and AH₃ is masked by anthraquinone. Gas chromatography readily separated AH₃, AH₂R, and AR, the latter two anthracene derivatives being in equal amount.

These experiments establish definitely that anthracene reacts photochemically with cyclohexane provided the solution is frozen. This behaviour seems typical of p.a.h.s in alkane solvents whether they be crystalline or glassy.

We have some evidence that the reactive state is an upper triplet state reached through a double photon absorption *via* the lowest triplet state.² On the basis of the data obtained earlier¹ and those reported here, two mechanisms can be put forward (Scheme), where ³AH* represents the excited anthracene molecule in its upper triplet state and RH is a cyclohexane molecule.



SCHEME. ^aCompounds which have been identified.

In the first mechanism (1) we propose a direct hydrogen abstraction by an upper triplet state. Hydrogen abstraction by anthracene has been reported in fluorene crystals at room temperature.³ This reaction requires thermal activation which, in our case, could be provided by the internal conversion of the T_n state to a highly vibrational state of T_1 . To account for the presence of cyclohexylanthracene it must be assumed that the radicals are formed in aggregates of anthracene. This is quite plausible since fairly concentrated solutions are used.

In the second mechanism (2) an energy transfer to a 'triplet' dissociative state of the alkane is envisaged. Such a mechanism has already been proposed by Orlandi *et al.*⁴ to interpret the sensitized hydrogen abstraction from alkane by mercury atoms (³P₁, ³P₀). The energy attained by anthracene molecules absorbing a second photon at ca. 350 nm from T_1 is around 43 000 cm⁻¹ and could meet the energy requirement for a C-H dissociation whose energy has been estimated to be about 38 000 cm⁻¹.⁵

[†] Samples that were not commercially available were synthesized and had satisfactory analytical and spectroscopic data.

Both mechanisms account for the formation of the identified photoproducts, but further data are needed to establish the most likely pathway

a photochemical reaction proceeding *via* a hot or an excited triplet state already discussed by Michl *et al*⁶

This reaction may be considered as a further example of

(Received, 10th April 1980; Com 378.)

¹ M Lamotte, S Risemberg, J Pereyre, and J Jousset-Dubien in 'Polynuclear Aromatic Hydrocarbons,' eds P W Jones and P. Lever, Ann Arbor Science Publishers, 1979, p 159, M Lamotte, R Lapouyade, J Pereyre, and J Jousset-Dubien, *C R Acad Sci, Ser C*, 1980, **290**, 211

² J Jousset-Dubien, M Lamotte, R Lapouyade, and J Pereyre in 'Quantum Theory of Chemical Reactivity,' eds R Daudel, A Pullman, L Salem, and A Veillard, D Reidel, Dordrecht, Holland, 1980, in the press

³ H M Vieth, V Macho, and D Stehlik, *J Phys Chem*, 1979, **83**, 3435

⁴ G C Marconi, G Orlandi, and C Poggi, *Chem Phys Lett*, 1976, **40**, 88, G C Marconi, G Orlandi, G Poggi, and F Bari Gelletti, *J Chem Soc, Faraday Trans 2*, 1977, **73**, 1034

⁵ W Rothman, F Hirayama, and S Lipsky, *J Chem Phys*, 1973, **58**, 1300

⁶ J Michl, A Castellan, M A Souto, and J Kolc in 'Excited States in Organic Chemistry and Biochemistry,' eds A Pullman and N Goldblum, D Reidel, Dordrecht, Holland, 1977, p 361