Studies of Chemistry of Radical Cations of Perylene and Tetracene by a Flash-Photolytic Technique

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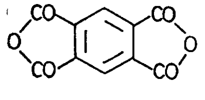
Summary Perylene radical cations ($Pe^{\dot{+}}$) and pyromellitic dianhydride radical anions ($PyAnh^{\dot{-}}$) are formed when acetonitrile solutions of the parent compounds are flash-irradiated with visible light and are annihilated by biomolecular combination ($k_r = 7{\cdot}6 \times 10^9$ l mol^{-1} s^{-1}) which does not form any new products; similar reactions are observed for tetracene (Tt) and an equilibrium $Pe^{\dot{+}} + Tt \rightleftharpoons Pe + T^{\dot{+}}$ ($K = 15$) is established when a mixture of both hydrocarbons is used, the lifetime of radical cations being greatly increased by the addition of $Fe^{3+}(ClO_4^-)_3$ but not by the addition of $AgClO_4$.

SOLUTIONS of electron donor and electron acceptor compounds in polar solvents often yield, on irradiation, the respective radical cation–radical anion pairs.[1] Several routes may lead to such ion pairs, including oxidation of an excited electron donor by an electron acceptor (a process



PyAnh

invoked by Weller[2] to account for quenching of fluorescence) and ionic dissociation of an excited charge-transfer complex.[3] In this note some of these reactions are described and it is shown how useful they are in studies of chemistry of radical-cations.

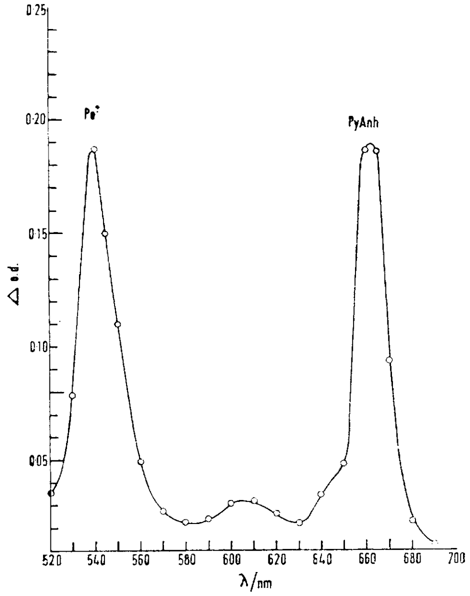


FIGURE 1. The difference spectrum of an acetonitrile solution of perylene, Pe (*ca.* 1 × 10^{-6} mol l^{-1}) and pyromellitic dianhydride, PyAnh (*ca.* 50 × 10^{-6} mol l^{-1}) at 100 μs after a flash.

Figure 1 shows the transient absorption spectrum of a mixture of 10^{-6} mol l^{-1} acetonitrile solution of perylene (Pe) with a 50-fold excess of pyromellitic dianhydride (PyAnh) after flash photolysis with visible light (*ca.* 25 μs). The two absorption peaks reveal the formation of $Pe^{+\cdot}$ (λ_{max} 540 nm, ϵ 4·9 × 10^4)[4] and $PyAnh^{-\cdot}$ (λ_{max} 663 nm, $\epsilon > 1 \times 10^4$)[5] by electron transfer according to equation (1).

$$Pe + PyAnh \xrightarrow{h\nu} Pe^{+\cdot} + PyAnh^{-\cdot} \qquad (1)$$

In acetonitrile perylene combines with pyromellitic dianhydride to form a charge-transfer complex absorbing around 520 nm (ϵ 500). Such complexes have been described in the literatrue;[6] the complex formed in $CHCl_3$ has λ_{max} at 592 nm while that formed in CH_2Cl_2 has λ_{max} shifted to 576 nm. The equilibrium constant of its formation in acetonitrile is 17 l mol^{-1} which is comparable with the reported value[6] of 19·4 l mol^{-1} in CH_2Cl_2 but lower than 57·8 l mol^{-1} in chloroform. However, photolysis of this complex seems to contribute only a little to the formation of Pe^{+} because its yield is reduced 10-fold when the flash light is filtered through a Pe solution. This prevents the formation of excited perylene molecules in the photolytic cell and hence it has to be concluded that most of the Pe^{+} is formed by oxidation of the excited perylene molecules by PyAnh.

The transient formed by flash decays by second order kinetics; the plots of 1/Δ o.d.(540 nm) and 1/Δ o.d.(665 nm) *vs.* time are linear as shown in Figure 2, and the ratio of optical densities at 540 and 665 nm is independent of time. Hence, the reaction in the dark results from the recombination shown in equation (2). This has been verified by

$$Pe^{+\cdot} + PyAnh^{-\cdot} \xrightarrow{k_r} Pe + PyAnh \qquad (2)$$

the analysis of the photolysed solution; no new products were formed. Accepting the value of ϵ reported in the literature,[4] the value of k_r was calculated from the slope of the 540 nm line as 7·6 × 10^9 l mol^{-1} s^{-1}. The value of ϵ (3·8 × 10^4) for $PyAnh^{-\cdot}$ at 665 nm was then calculated from the slope of the other line.

TABLE

o.d. of $Tt^{+\cdot}$ (345 nm, ϵ 4·8 × 10^4)	o.d. of $Pe^{+\cdot}$ (540 nm, ϵ 4·9 × 10^4)	Tt/mol l^{-1}	Pe/mol l^{-1}	*K*
0·0864[a]	0·0158[a]	6·75 × 10^{-6}	19·63 × 10^{-6}	16·3
0·0510[a]	0·0053[a]	3·65 × 10^{-6}	4·77 × 10^{-6}	12·8

[a] o.d. (optical density) of $Tt^{+\cdot}$ and $Pe^{+\cdot}$ are measured at λ 345 and 540 nm, respectively. The corresponding concentrations of the radical cations were calculated using extinction coefficients given in ref. 4.

It was expected that flash photolysis could be utilized for studies of equilibrium of electron-transfers involving radical cations [equation (3)]. Indeed, when mixtures of tetracene

$$Tt^{+\cdot} + Pe \rightleftharpoons Tt + Pe^{+\cdot} \qquad (3)$$

(Tt), Pe, and PyAnh were flash-photolysed, all the three species, $Tt^{+\cdot}$, $Pe^{+\cdot}$, and $PyAnh^{-\cdot}$, were formed. The ratio of their concentrations did not vary with time in any run, and at any time the ratio $[Pe^{+\cdot}]:[Tr^{+\cdot}]$ was proportional to the ratio [Pe] : [Tt].† The results are summarized in the Table and imply that equilibrium [equation (3)] is rapidly

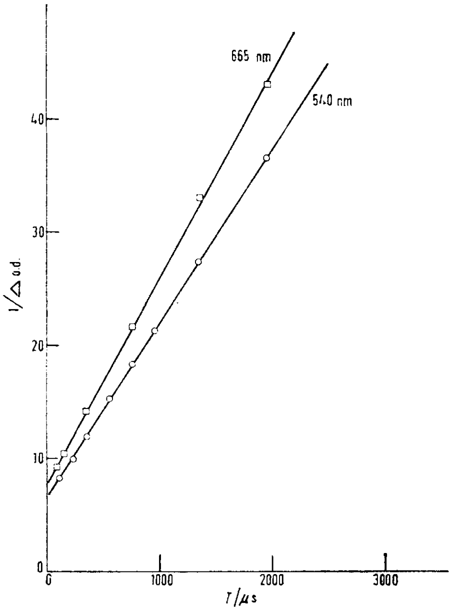


FIGURE 2. Plots of inverse of optical density (1/Δ o.d.) at 540 and 665 nm *vs.* time. The composition of the solution is given in the caption to Figure 1.

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† Only 10% of hydrocarbons were oxidized to the respective radical cations.

established and is maintained during the decay process. The pertinent equilibrium constant was found to be 15 as compared with 21 determined by the electrochemical technique.[7]

Photolysis of mixtures of PyAnh with a variety of aromatic hydrocarbons has been investigated in the past,[5,8]. Although the transient absorption spectrum of $PyAnh^{\cdot-}$ was observed, the absorption of the pertinent radical cations was not observed, in contrast with the results reported here. However, we have observed that $Pe^{\cdot+}$ disappears more rapidly than $PyAnh^{-}$ whenever the solvent or the reagents are not meticulously purified.

The lifetime of radical cations, *e.g.* $Pe^{\cdot+}$, should be prolonged if $PyAnh^{\cdot-}$ could be substituted by some inert anion. In an attempt to achieve this, anhydrous $AgClO_4$ was added to the solution to be photolysed. Surprisingly, such an addition did not affect the course of the photolysis or of the reaction in the dark, although a copious silver precipitate was formed when $AgClO_4$ was added to tetrahydrofuran (THF) solution of Na^{+} $PyAnh^{\cdot-}$. Cyclic voltammetry performed in acetonitrile demonstrated also that the reduction potential of Ag^{+} ions is substantially less negative than that of PyAnh, verifying the behaviour observed in THF. The apparent contradiction with the photolytic results may be explained if the short duration of the reaction in the dark is considered. The electron-transfer, $PyAnh^{\cdot-} + Ag^{+} \rightleftharpoons PyAnh + Ag^{0}$, apparently produces a very low equilibrium concentration of Ag atoms, but their aggregation to silver metal drives the reaction further to the right, $Ag^{0} \rightleftharpoons Ag_{solid}$. The short lifetime of $PyAnh^{\cdot-}$ in the flash-photolysis experiments prevents the aggregation and therefore minimizes the reduction of Ag^{+} ions.

Radical cations were stabilized when $Fe^{3+}(ClO_4^{-})_3$ was added to the solution of Pe and PyAnh. Such an addition did not increase the yield of $Pe^{\cdot+}$, but the absorbance due to $PyAnh^{\cdot-}$ disappeared in about 30 μs. The ferric salt undoubtedly oxidized $PyAnh^{\cdot-}$, but it is also likely that it competed with PyAnh in oxidation of the excited Pe molecules.

The decay of $Pe^{\cdot+}$ became very slow in the presence of $Fe^{3+}(ClO_4^{-})_3$ (*ca.* 10% μs^{-1}). Thus, a system was designed that allows studies of reactions of radical cations.

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