Triplet Formation in the Vapour Phase

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Summary The pressure-dependence of triplet yield in the gas phase has been confirmed for several aromatic molecules and a mechanism is suggested in which vibrational relaxation becomes the rate-determining process at low pressures.

SOME years ago Porter and Wright[1] observed that the extent of triplet formation in aromatic vapours was pressure-dependent, but since that time no further studies of the effect have appeared. In view of the significance of photoprocesses in the vapour state and their relevance to the theories of radiationless conversion, a re-investigation of the subject has been undertaken.

The experiments were performed using a flash photolysis apparatus equipped with a multiple traversal system such that long absorption paths could be used. Generally, these were between 1 and 8 m. The temperature of the furnace, housing the absorption cell and photolysis lamps, could be varied between room temperature and 500°.

Our results confirm the earlier findings of Porter and Wright that the extent of triplet formation, as monitored by the initial triplet-state absorption, is dependent upon the pressure of the added inert gas, and extrapolates to zero at zero pressure. The half-formation pressures (argon and krypton) for triplet naphthalene, anthracene, and pyrene were 7·5, 8, and 8·5 mm. Hg, respectively.

In vapour-phase flash-photolysis experiments the possibility of thermal effects must always be considered. The sensitive detection system employed allowed very low concentrations (10^{-7} moles/l.) of aromatic species to be studied so that, although the total pressure was reduced to low values, the ratio of added inert gas to the aromatic compound was high (at least 1000 : 1). Calculations show that under these conditions the temperature rise after the absorption of light is negligible. This was supported by the absence of any spectral changes, the independence of anthracene triplet yield on temperature over the range 100—250°, and the independence of the half-formation pressure on the ratio of aromatic to inert gas.

The nearly identical pressure effects for the different molecules suggests that the pressure-dependent process is vibrational relaxation. The simplest scheme involving vibrational relaxation is as follows:

$$S_1 \rightarrow S_0$$
$$S_1 \rightleftharpoons T_n$$
$$T_n + M \rightarrow T_1$$

where S_0 is the ground singlet state

S_1 is some excited singlet level

T_n is some triplet level degenerate with S_1

T_1 is the vibrationally-relaxed lowest triplet

M is the inert gas

which leads to a reciprocal–reciprocal relationship between the inert-gas pressure and the quantum yield of triplet formation. Such plots for anthracene, naphthalene, and pyrene are shown in the Figure. This relationship holds at low pressures, but a limiting value of the triplet yield is reached at high pressures.

Our interpretation of this limit is as follows. At high pressures vibrational relaxation of the S_1 state may precede intersystem crossing. When intersystem crossing occurs from a vibrationally relaxed S_1 state to T_1 the reverse crossing will be slow because of the low density of states in the relaxed S_1 state, and vibrational relaxation of the T_1 state will no longer be a rate-determining process. Calculations based on this scheme and using an expression similar to that of Siebrand[2] to relate the radiationless crossing rate to the density of states show that it leads to a limiting yield at high pressures in accordance with our experimental findings.

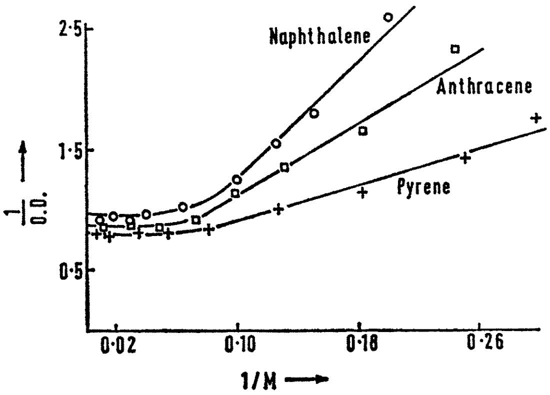

FIGURE. *Plot of the reciprocal of the optical density* (O.D.) *of triplet state formed against reciprocal pressure* (M) *of inert gas* (*argon*).

Further work is in progress with other triplet states and other inert gases and particularly with monochromatic radiation.

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[1] G. Porter and F. J. Wright, *Trans. Faraday Soc.*, 1955, **51**, 1205.

[2] W. Siebrand, *J. Chem. Phys.*, 1967, **47**, 2411.