Wave-length Effect in Flash Photolysis

When oxygen-free solutions of methylene blue or thionine in dilute sulphuric acid are subjected to flash photolysis using orange-red light filtered from a krypton- or xenon-filled flash-tube, reversible bleaching of the dyestuffs occurs. The bleaching is accompanied by increased absorption in the region 360–440 mμ where the dyestuffs themselves absorb very weakly. The transient species responsible for this absorption have the appearance of being triplet levels of the dyestuffs, disappearing with life-times of less than 30 μsec. The same species are also produced when the light of the flash is filtered through Chance *OX*7 glass (transmission approximately 250–390 mμ).

When the unfiltered light from the flash-tube is used for excitation, there are formed, in addition to the 'triplet' species, other species which disappear much more slowly (half-life of the order 0·5 msec. under the conditions of experiment). From the limited information at present available, the second type of species appears to be similar to the semiquinones which are formed by reduction of the dyestuffs when their solutions are flashed with orange-red light in the presence of $0\cdot1\,M$ ferrous sulphate (in the presence of the ferrous sulphate the 'triplet' species are no longer evident). If the long-lived species are indeed the semiquinones of the dyestuffs, it would appear that water itself can act as the reducing agent when short wave-length ultra-violet light is used for excitation.

Whatever the true nature of the long-lived and the short-lived species, they are formed by independent processes, the long-lived species by wave-lengths shorter than 250 mμ and the short-lived species by longer wave-lengths. These observations may be compared with the results obtained by Bridge and Porter[1] in the flash photolysis of solutions of duroquinone using the full light of the flash-tube. They observed the independent formation of both triplet and semiquinone radical, and it is interesting to speculate whether their results can be explained in terms of a similar wave-length effect, since many of the solvents they used are transparent to wave-lengths shorter than 250 mμ. Before the behaviour of duroquinone can be fully established, therefore, it would be necessary to carry out experiments with filtered exciting light. This same precaution naturally applies to all flash-photolysis work, and is of course particularly important in those investigations where photosensitization to daylight is in question.

The investigation of the effects observed with methylene blue and thionine is being continued and will be reported in detail elsewhere.

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[1] Bridge, N. K., and Porter, G., *Proc. Roy. Soc.*, A, **244**, 259, 276 (1958).

The fact that primary photochemical processes may depend on wave-length is, of course, well known, and investigations of wave-length effects in flash photolysis have previously been carried out[1]. Our work on duroquinone was concerned with the identification of the intermediates and of the kinetics of their reactions, which are, for any given intermediate, independent of wave-length.

A study of the effect of wave-length on the primary products of photolysis of duroquinone is now in progress. Mr. Michael Reed has found that when a glass filter (cut-off at 300 mμ) is used, triplet-state absorption in liquid paraffin and formation of semiquinone radicals in ethanol are still observed, though the concentration of radical is considerably reduced. Some reduction in concentration is to be expected on the basis of reduced light absorption, since the maxima of duroquinone lie at 270 mμ ($\log\varepsilon = 4\cdot3$), 340 mμ ($\log\varepsilon = 2\cdot3$) and 450 mμ ($\log\varepsilon = 1\cdot4$).

If Parker's assignments are confirmed, the methylene blue system provides another example where radical formation does not occur principally via the triplet state. So far as dependence on wave-length is concerned, it will be necessary to have observations on the quantity of light absorbed in each experiment and the effect of intensity, since both wave-lengths and intensity have been varied and the observed differences may be attributed to either.

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[1] Christie, M. I., Harrison, A. J., Norrish, R. G. W., and Porter, G., *Proc. Roy. Soc.*, A, **231**, 446 (1955).

A Methane-Conversion Detector for Gas Chromatography

Detectors most commonly found in gas chromatographic instruments involve the use of thermal conductivity cells. Such cells, particularly those of the thermistor type, decrease in sensitivity with increasing temperature. Since it is necessary sometimes to heat the cell to prevent condensation effects of high-boiling materials leaving the chromatographic column, new approaches to this problem were sought. Martin and Smart[1] were successful in improving the sensitivity by converting the resolved compounds as they emerged from the chromatographic column into carbon dioxide and water, and detecting the carbon dioxide by means of an infra-red gas analyser. This procedure was repeated by Green[2] using a thermal conductivity cell to measure the carbon dioxide ; however, loss of resolution and band spreading detracted from the increased sensitivity obtained. Green improved this technique by passing the water formed in the combustion process through a hot tube containing iron powder, thereby producing hydrogen, which was detected in the thermal conductivity cell. Nitrogen was the carrier gas.

The procedure presented here makes use of a small tube containing a 'hydrocracking' catalyst at the exit end of the chromatographic column. As each compound emerges from the column, it is converted to methane and water. The water is removed in a drying column, and the methane is measured by a thermal conductivity cell. Hydrogen is used as the carrier gas.

The methane converter consists of a tube of 'Pyrex' glass, 24 cm. long and 5 mm. in diameter, filled with a nickel catalyst of 30–60 mesh. The tube is kept at about 350–450° C. by means of a heated nichrome coil.

This procedure has the following advantages :

(1) Increased sensitivity is obtained by being able to operate the thermal conductivity cell at ambient temperatures, since only methane is being detected.