AN INTENSITY FILTER FOR THE MERCURY LINE AT 253·7 mμ.

By H. W. Melville and H. J. Walls.

In photochemical chain reactions, the effect of the variation of the intensity of the incident radiation provides important information about the termination of the chains. If the rate of reaction is proportional to the first power of the intensity, it may be concluded that the chain carrier is destroyed in a bimolecular collision with another molecule or by a collision with the walls of the reaction tube. On the other hand, if the rate is proportional to the square root of the intensity, the chains are terminated by self-destruction, *e.g.*, by the combination of two atoms. Examples of these types of behaviour may be seen in the recent series of papers on the hydrogen-chlorine reaction by Ritchie and Norrish.[1] This differentiation in the mechanism of chain termination has now gained added importance, for it is believed that the position of the upper and the lower limits for explosion of thermal chain reactions is determined respectively by gas phase and by wall destruction of the carriers. Photo-chemical experiments on the intensity relationships outside these limits should be able, therefore, to give confirmation of the hypotheses which have been advanced to explain these phenomena.

No great difficulty occurs in measuring the variation in intensity when a thermopile or photoelectric cell is employed and the reaction vessel is at room temperature. If, however, the reaction bulb is in a furnace and the source of light is of considerable area, such as a mercury lamp, the difficulties are increased. Some means are, therefore, required to vary the intensity by a known and easily controllable amount. The rotating sector is not suitable for this type of work, as it really alters the duration of exposure and not the intensity.[2] In addition, matters are rendered more complicated by the possible existence of induction periods and photochemical after effects. Wire gauze screens, especially if constructed of round wire, are not, in general, reliable as it is difficult to calculate exactly how much light is cut off. There remains then some type of filter partly transparent to the radiation being used.

This paper is concerned with a liquid filter for use with the mercury resonance line at 253·7 mμ and hence is specially suitable for mercury sensitised reactions. In order to vary the transmission of a liquid filter, a solution is most convenient to use as only a single cell is required. The solution must, however, have the following properties if it is to be reliable (*a*) stability to light of 253·7 mμ, (*b*) components to be easily obtained in a pure state, (*c*) normal behaviour of the components so that Beer's law is obeyed exactly, (*d*) rapidity and ease of preparation.

These criteria are fulfilled by mixtures of carbon tetrachloride and *n*-hexane or cyclo-hexane. Ordinary sulphur free carbon tetrachloride is suitable, but the hexane or cyclo-hexane must be specially purified

[1] *Proc. Roy. Soc.*, **140A**, 99, 112, 713, 1933.
[2] Griffith and McKeown, *Photochemical Processes*, p. 664.

in order that its absorption at 253·7 mμ may be negligible. The n-hexane and cyclo-hexane purified for spectroscopic work, as supplied by British Drug Houses, were used in the present instance and found to be entirely satisfactory. The rapid rise in the extinction coefficient of carbon tetra-chloride to light of 253·7 mμ cuts out all light from the mercury arc which might be absorbed by the reactants directly. One advantage of using cyclo-hexane in preference to n-hexane is that its boiling-point is close to that of carbon tetrachloride and therefore any loss of the solution by evaporation, *e.g.*, when placed in the proximity of a furnace, does not lead to any disturbing change in concentration.

Experimental.

A 5 mm. absorption cell was employed for the photochemical experiments. A series of solutions was therefore made up to cut off from 20 per cent. to 80 per cent. of the light as measured approximately by the photochemical reaction. The extinction coefficients of the solutions were then
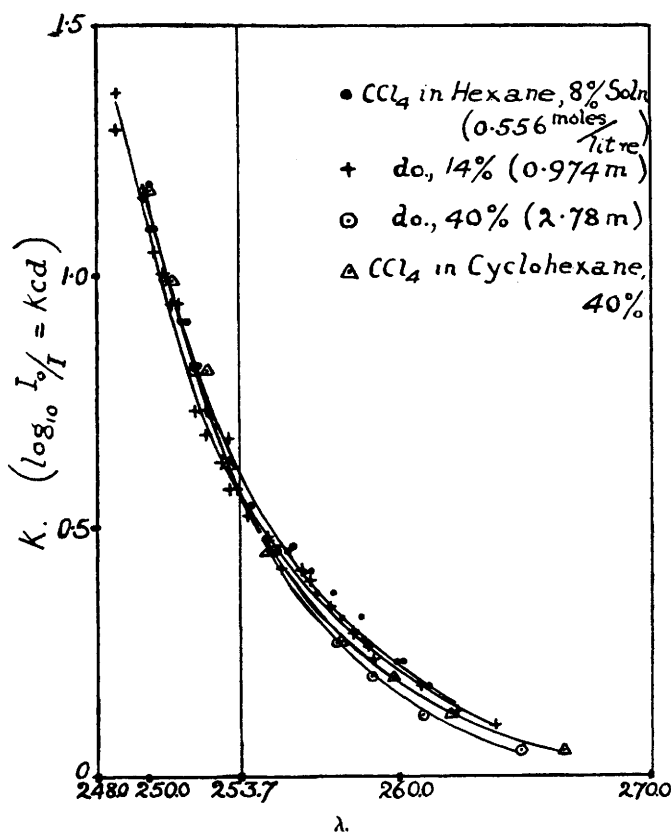

Fig. 1.

measured exactly by means of a Bellingham and Stanley rotating sector photometer used in conjunction with a Bellingham and Stanley quartz spectrograph, giving the spectrum from about 210 to 800 mμ on a 10 in. plate. An iron spark was employed as source of light. The wave-lengths

for the positions of equal blackening on the plate were determined by comparison with an enlarged calibrated photograph of the iron spark spectrum, the plates being examined with the aid of a lens. The positions were determined at least twice in each plate, with an interval in between, in order to eliminate possible errors due to fatigue. The wave-lengths could easily be determined to within 0.2 mμ in this way.

The extinction coefficient — wave-length curves for four solutions are shown in Fig. 1. The value of the extinction coefficient used is defined by the equation

$$\log_{10} I_0/I = kcd \qquad \qquad \qquad \qquad \text{(1)}$$

where k is the extinction coefficient, d the thickness of the layer in cm., and c the concentration in moles per litre. It will be seen that the curves for three different concentrations (0.56, 0.97, 2.78 moles per litre) fall practically together ; the difference in the ordinates may be put down to experimental error. This means that Beer's law is obeyed exactly within this region of concentration. The two solutions of equal concentration in hexane and in cyclohexane also show identical absorption in this region.

The values of k at 253.7 mμ as measured off a large scale graph are :—

$$0.56 \text{ moles per litre } 0.598$$
$$0.97 \quad ,, \quad ,, \quad 0.575$$
$$2.78 \quad ,, \quad ,, \quad 0.590$$
$$\text{Average } . \quad 0.588$$

Using this value of k, the percentage transmission for any concentration and layer thickness, or alternatively the concentration and/or layer thickness necessary to cut off a given amount of radiation at 253.7 mμ, can be rapidly calculated by means of equation 1.

To test the stability of the filter, a solution of concentration 2.78 moles per litre made up with hexane was exposed to a mercury lamp with a cool cathode running at 5 amps. and 40 volts for four hours. Some change occurred, for the liquid evolved some hydrochloric acid and it was found that the extinction coefficient at 253.7 mμ had increased by about 20 per cent. A similar result was obtained with cyclohexane. A filter was therefore not employed for much longer than fifteen minutes. As the quantity of solution required to fill the quartz cell only amounted to a few c.c., this procedure was not unduly extravagant in the use of the comparatively expensive hexane.

In the Tables below are given data of a few experiments on the mercury sensitised reaction between hydrogen and nitrous oxide. The investigation [3] of the thermal reaction had shown that it was of the chain type,

TABLE I.—LOW PRESS. 5 CM. REACTION BULB. TEMP. 580° C. 1 : 1 MIXTURE. TOTAL PRESS. 16·00 MM.

Composition of Filter.	Rate Rel. to Hexane (R).	Intensity Rel. to Hexane (I).	R/I.
n-hexane . . .	1·00	1·00	1·00
1·2 c.c. in 25 c.c. solution	0·86	0·80	1·07
2·0 ,, ,, ,,	0·70	0·68	1·03
2·0 ,, ,, ,,	0·73	0·68	1·07
3·5 ,, ,, ,,	0·53	0·51	1·04
10·0 ,, ,, ,,	0·183	0·15	1·20

The absolute rate of reaction with pure hexane was 0·82 mm. of water per min.

[3] Melville, *Proc. Roy. Soc.*, in the press.

TABLE II.—HIGH PRESS.   TEMP. 510° C.   1 : 1 MIXTURE.   PRESS., 100 mm.

Composition of Filter.			Rate Rel. to Hexane (R).	Intensity Rel. to Hexane (I).	R/I.	R^2/I.
n-hexane	.	.	1·00	1·00	1·00	1·00
2 c.c. CCl_4 in 25 c.c solution			0·80	0·68	1·17	0·94
3·5	,,	,, ,,	0·67	0·51	1·31	0·87
5·0	,,	,, ,,	0·49	0·38	1·29	0·64

The absolute rate of reaction with pure hexane was 0·80 mm. water per min.

initiated by the dissociation of a nitrous molecule into N_2 and O, followed by the reaction $O + H_2 \rightarrow OH + H$.   The chain is probably propagated by the reactions

$$OH + H_2 \rightarrow H_2O + H$$
$$H + N_2O \rightarrow OH + N_2.$$
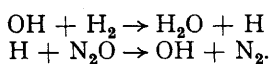
Further, there was indirect evidence that the chains were terminated principally in the gas phase by self-neutralisation at pressures of the order of 100 mm., whereas at 10 mm., wall deactivation was most important. It would be expected then that in the photochemical experiments, (a) at
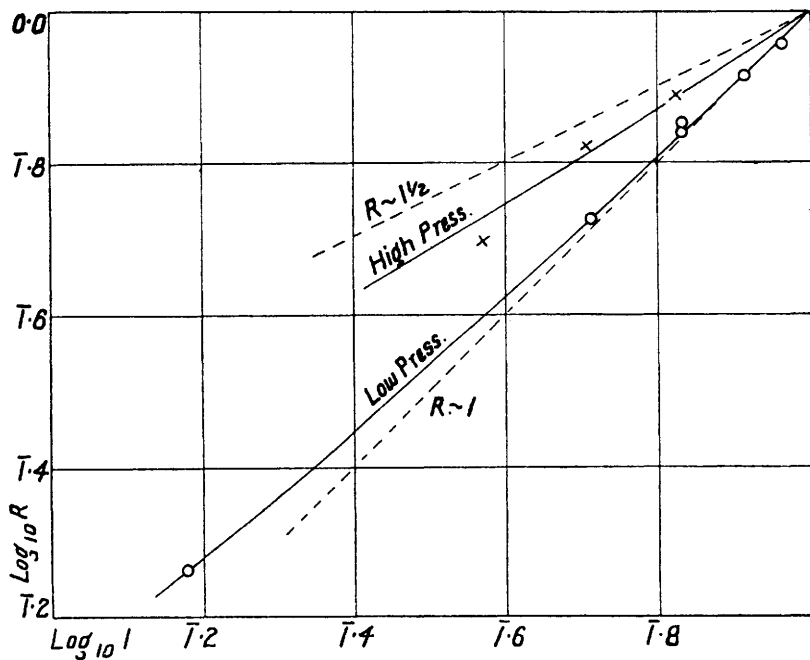

FIG. 2.

high pressures the rate should be proportional to the square root of the intensity, and (b) at low pressures, a linear relation should hold between rate and intensity.

Full details are not given of the experiments (they will be published later) as the results quoted are solely for the purpose of indicating the

usefulness of the filter in providing independent confirmation of the mechanism of the termination of the chains.

In Table I., it will be observed that the rate (R) is very nearly proportional to the intensity (I) as is indicated by the constancy of the quantity R/I.   At high pressures R/I is no longer constant and neither is R^2/I so that the rate must be proportional to a power of the intensity between 0·5 and 1·0.   Even at 100 mm., however, wall termination was quite noticeable and the latter result is to be expected.   The dark reactions were negligible in both cases ;   the chain length was of the order 10^2.

In Fig. 2, $\log_{10} R$ has been plotted against $\log_{10} I$ using the results in Tables I. and II., and it will be observed that the high pressure experiments lie fairly close to a line having a slope of 0·5, whereas the low pressure experiments conform nearly to a line of unit slope.

Summary.

A liquid filter is described for altering the intensity of the 253·7 mμ line from a mercury arc lamp.   The absorbing liquid is sulphur free carbon tetrachloride which is mixed with n-hexane or cyclohexane.   The extinction coefficients of a number of solutions were determined and found to obey Beer's law.   The applicability of the filter is shown by experiments on the photochemical chain reaction between hydrogen and nitrous oxide at high and at low pressures where the rate is respectively proportional to the square root and to the first power of the intensity.

Chemistry Department,
    University of Edinburgh.