

LETTERS TO THE EDITORS

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Chemical Reactions Produced by Very High Light Intensities

It has been a matter of general experience that photochemical reactions are not much altered in their courses by change of light intensity. The range of light intensity hitherto available, however, has been limited by that obtainable from the sun and from such sources as high-pressure mercury vapour lamps, the total usable output of which in the region between 2,000 and 5,000 Å. does not exceed 10^{20} quanta/second. There are many cases, particularly those photochemical reactions where free radicals are involved, where it would be desirable to extend investigations to much higher intensities into the region where the concentration of intermediates is comparable with that of the reactants.

The gas-discharge flash-lamp which has been developed recently for photographic purposes seemed to offer great possibilities for experiments of this kind, and we have found that this type of lamp is a very efficient source of light in the photochemically useful region. The flash is produced by the discharge of a large condenser through a tube filled with rare gas, and up to energies of about 100 Joules almost any of the usual types of discharge lamp may be used. By using quartz tubes and large tungsten electrodes, we have worked with energies up to 10,000 Joules/flash in a tube 1 metre long. The duration of this flash was 4 m.sec., and the useful light output in the region of absorption of uranyl oxalate, was 10^{24} quanta/second. The output is continuous down to at least 2,000 Å. and appears to be fairly evenly distributed, and the output at wave-lengths less than 3,500 Å. may be further increased by the addition of a little liquid mercury to the gas filling.

The following figures give the percentage decomposition obtained in a few typical substances with a single flash of 4,000 Joules lasting less than 2 m.sec., the substance being contained in a quartz tube, one metre long, lying parallel to the lamp:

Gas	Pressure (cm.)	% Decomposition
NO ₂	4	Nearly 100
CH ₃ COCH ₃	3	15
CH ₃ COBr	3	15
CH ₃ COCOCH ₃	2.5	50
CH ₂ CO	10	40

The gas volume was 500 c.c. in each case, and mercury had been added to the lamp in the cases of acetone and ketene. In addition, with chlorine at a pressure of 1 cm., the enormous Budde effect of 2 cm. was observed.

Three examples of the different behaviour of well-known photochemical systems under these high light intensities will be given.

Acetone and ketene. Instead of the hydrocarbons and carbon monoxide which are normally produced with these compounds, a complex mixture of substances including hydrogen and a high proportion of carbon was obtained. The carbon appeared in an unusual fine cobweb-like formation which hung across the tube from wall to wall.

Chlorine and carbon tetrachloride. Carbon tetrachloride is usually considered to be the final product of the photochemical reaction of chlorine with methane. At these high light intensities, however, when

the partial pressure of atoms and radicals present is relatively high, a mixture of chlorine at 1 cm. pressure and carbon tetrachloride at 2 cm. pressure showed an increase of pressure of about 0.3 cm., and a considerable amount of solid product was formed.

Chlorine and carbon monoxide. This well-known photochemical system exhibits one of the most striking examples of the effect of intensity on the course of a reaction. Illumination in the ordinary way of a mixture of chlorine and carbon monoxide produces phosgene quite rapidly, and the reaction can be taken almost to completion. We find that irradiation by a 4,000-Joule flash, however, produces no detectable pressure change in this mixture, and that if phosgene is added it is rapidly decomposed to chlorine and carbon monoxide. The reaction is quite reversible and can be made to proceed either way at will by changing the intensity of the illumination. That the important primary act is the photochemical decomposition of chlorine in both cases was shown by the very small pressure changes produced when pure phosgene was used.

Two effects seem to play a part in changing the mechanism of photochemical reactions at high intensities. First, since the concentration of the intermediates is comparable with that of the reactants, inter-atomic and inter-radical collisions are as frequent as collisions of these intermediates with more stable molecules. Thus, for example, the reversibility of the phosgene reaction may be explained by the reversibility of the reaction $\text{COCl} + \text{Cl}_2 = \text{COCl}_2 + \text{Cl}$ followed by $\text{COCl} + \text{Cl} = \text{Cl}_2 + \text{CO}$, in full agreement with the schemes of Bodenstein, and Lehner and Rollefson. Secondly, the process is nearly adiabatic, and very high instantaneous temperatures may be reached, due in part to the exothermic reactions of the labile intermediates with each other and in part to the thermal degradation of the absorbed light energy.

The mechanism of some reactions at high light intensity will be discussed in more detail elsewhere; the above examples serve to show that this type of source, which extends the available upper limit of intensity some 10^4 times, produces photochemical effects of unusual magnitude, and in some cases may alter profoundly the normal course of the reaction.

R. G. W. NORRISH
G. PORTER

Department of Physical Chemistry,
Cambridge. Aug. 6.

An Examination of Praseodymium, Neodymium and Samarium for α -Activity

A PHOTOGRAPHIC method for the detection of extremely weak α -activities has recently been described¹. The method has now been applied to the examination of elements 59, 60 and 62. The results have some bearing on the question whether an unidentified pleochroic halo of a certain type, found in very old mica, is due to an α -active isotope of element 61².

Ilford C2 plates of 50 microns thickness were impregnated for 30 min. with solutions of praseodymium acetate (2.3 per cent), neodymium nitrate (0.1 per cent), or samarium nitrate (0.1 and 1 per cent anhydrous salt) at pH 7. The plates were kept for $t = 22, 19, 10$ and 9 days, respectively, developed, and a certain area of plate searched for α -tracks in the usual way. Every track observed was measured.

In the neodymium experiment, no tracks running entirely inside the emulsion were found in $n = 1,000$