XCIX.—*On the Alleged Retardation of Certain Reactions by Light.*

By Arthur John Allmand and Robert Edwin Witton Maddison.

About twenty years ago, Trautz published some papers (*Physikal. Z.*, 1906, **7**, 899; *Z. wiss. Phot.*, 1906, **4**, 351; *Z. Elektrochem.*, 1907, **13**, 550) in which he discussed the possibility of the retardation of chemical reactions by light, supporting his deductions by a series of experimental observations. The dissertation published later by Thomas (Freiburg i. B., 1908) contains further details with regard to the latter. In all cases but one (the decomposition of hydrogen peroxide), the reactions studied were those between oxygen and an aqueous solution of some oxidisable substance. A manometric method was usually employed, solution and oxygen standing in contact with one another inside a vessel similar to a gas pipette, which was closed by a U-shaped manometer open on one side to the air. Several such pipettes were used simultaneously, each being enclosed in a glass sheath containing a certain filter solution, except that the pipette serving for the dark control experiment was contained in a galvanised-iron sheath filled with water. The whole set of pipettes with their sheaths was placed in a large vessel filled with water which stood near a window. The water was stirred from time to time and it was assumed that comparable temperature conditions were obtained, although, as the experiments in some cases extended over several days and nights, this appears doubtful. In any case, the results are said to have been reproducible. In some experiments (notably those with sodium sulphide solutions and red light), a shaking apparatus in a thermostat was employed.

The following remarkable results were claimed. Violet light retards the reaction of oxygen with aqueous solutions of sodium sulphide, of sodium sulphite, and of pyrogallol, and with cuprous chloride dissolved in ammonia or in hydrochloric acid. Red light retards the decomposition of aqueous hydrogen peroxide, and the oxidation of cuprous chloride in hydrochloric acid, of aqueous pyrogallol, and of benzaldehyde. Below 23°, it also retards the oxidation of sodium sulphide, but above 25° it accelerates it. Green light retards the oxidation of solutions of cuprous chloride in ammonia, whilst both green and yellow light retard the oxidation of aqueous sodium sulphite. Almost equally striking results are reported with regard to the accelerating effects of light of different colours on the same reactions.

To explain these results, Trautz suggests that the observed velocity in the dark must be regarded as compounded of two opposed velocities, forward and back, and that these opposed reactions are affected in different degrees by light. If the reverse reaction is accelerated to a greater extent than the forward reaction, a net retardation will result on illumination. This view involves the consequence that the thermal (dark) equilibrium ultimately reached in the reaction concerned must be displaced by light. No evidence that this is so is brought forward, nor do the known facts of photochemistry suggest that such a displacement occurs frequently. Trautz leaves it open as to whether the reaction obeys the same laws of kinetics in the light as in the dark, with mere alteration of coefficients, or whether the total reaction in light is to be regarded as made up of separate light and dark reactions, superposed additively on one another.

Several reasons led us to carry out experiments on this subject. They were (1) the remarkable nature of the effects claimed, even when " colourless " solutions, with negligible absorption in the visible region, were employed; (2) the lack of confirmatory data on equilibrium displacement in light (not merely in these experiments, where the detection of the displacement might well be difficult, but in photochemical reactions generally); (3) the probability that, in some reactions at all events, *diffusion* rates were in reality being measured; (4) the facts that the detailed figures given by Thomas, are, in general, irregular when plotted, and that, in the experiments on the oxidation of sodium sulphide solutions, " retardation " by violet light was observed to have taken place *during the night hours* almost as frequently as during the day, whilst on several occasions " acceleration," not " retardation," was noted during the day hours (points which only become apparent when the data for an experiment lasting over several days are considered in detail); (5) the absence of any indication that the use of a particular pipette did not in some way lead to specific results; (6) the fact that the degree of temperature control obtained did not seem adequate when the manometric method of following the rate of reaction is considered.

EXPERIMENTAL.

The majority of our experiments were carried out on the oxidation of sodium sulphite solutions, where the high transparency in the visible region, maintained during the whole reaction, ensures a uniform light field throughout the solution from start to finish. Instead of allowing the oxygen to diffuse into the solution, as did Thomas, we passed a brisk current of air through continuously, and any likelihood of a diffusion reaction being measured was thus eliminated. The type of reaction vessel used (a cell composed of quartz plates cemented on to the ends of a 7·5 cm.-diameter circular cavity drilled through a glass block) has been described elsewhere (J., 1925, **127**, 829). In the present case, the glass block was 5 cm. in thickness. Two holes bored through its upper surface into the central cavity served for the introduction of a thermometer and of the pipette for abstracting samples of liquid for analysis, whilst a similar hole passing through the side of the block into the interior of the cell at its lowest level had cemented into it a glass tube for leading in the air-stream. In front of this vessel was placed a combined water-cooling and filter cell of similar construction (four quartz plates alternating with three glass frames of thickness 1·0, 0·5 and 0·5 cm., respectively, the whole cemented together). Through the compartment of this cell nearest the light source (1 cm. in depth), a current of tap-water was kept continuously flowing, whilst the other compartments (0·5 cm. in depth) contained the filter solutions (or distilled water in other cases). The whole was placed in a wooden box, blackened inside, covered with tin foil outside, and furnished with sliding shutters on each of two opposite sides, for entry of the light beam and, when required, for inspection. Holes in the lid were provided for the air-supply tube, the thermometer, and the pipette, and also for an additional thermometer used to register the temperature in the box itself (outside the reaction cell). The air stream was produced by a motor-driven positive blower, and passed through a tube packed with activated charcoal, a simple calibrated differential flow-meter, and a wash-bottle filled with some of the sodium sulphite solution, before entering the reaction vessel. A steady rate of supply was maintained by regulating a resistance in the motor circuit, and by adjusting a screw-clip on a rubber connexion between the blower and the flow-meter. 150 C.c. of solution were generally employed.

The analysis was carried out by removing 5 or 10 c.c. in a pipette, running them into 20 c.c. of 0·1N-iodine, acidified with dilute hydrochloric acid, and titrating back with 0·1N-sodium thiosulphate.

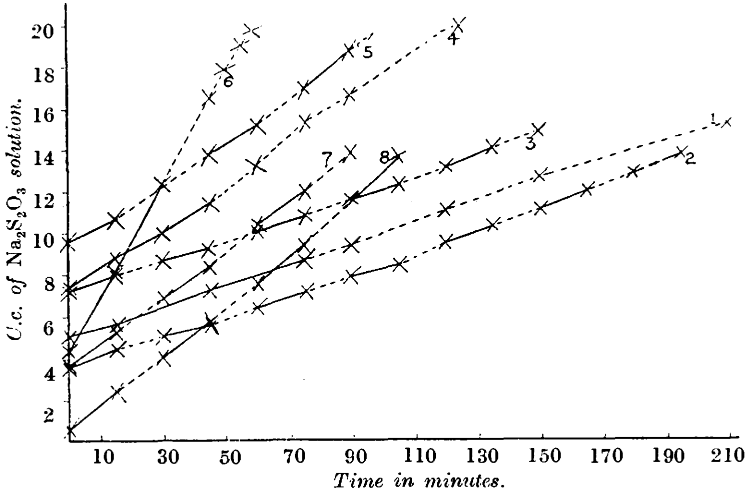
For most of the experiments, the light source was a quartz mercury lamp, placed 13 cm. away from the front of the reaction cell. For red light, a 500-watt Osram lamp was employed at a distance of 18 inches, and an additional glass water-cooler was placed outside the box in the path of the beam. The temperature generally rose about 2° during a complete experiment. The thermometer in the box outside the cell was, of course, chiefly affected during the "light" period, but the temperature of the solution inside the cell rose more or less uniformly during both light and dark periods. In any case the results show that any temperature effect was negligible. The filter solutions used are given in the following table. They were far from being monochromatic but, in view of the nature of the experiments, no particular importance was attached to this.

Nature of light.	Filter.
Short ultra-violet (below 265 $\mu\mu$—also visible light).	(*a*) 0·5 cm. N/1600-*p*-nitrophenol. (*b*) 0·5 cm. 0·002% *p*-nitrosodimethylaniline.
Long ultra-violet (365 $\mu\mu$—also some blue and violet).	0·5 cm. 0·0625% acid fuchsine.
Blue-violet (405—436 $\mu\mu$).	(*a*) 0·5 cm. 0·0125% acid fuchsine. (*b*) 0·5 cm. 0·2% quinine sulphate.
Green (500—550 $\mu\mu$).	1 cm. of an alcoholic solution of 2·4% $CoCl_2$ + 2·4% $NiCl_2$ + 0·1% fluorescein (similar to that used by Thomas).
Red (also small amounts of blue and violet).	(*a*) 0·5 cm. 10% ferrous ammonium sulphate. (*b*) 0·5 cm. 0·075% acid fuchsine.

Originally, alternate dark and light experiments, using different fillings in the cell each time, were carried out. The results were very discordant, successive runs on different portions of the same solution sometimes indicating an acceleration in light and sometimes a retardation. The difficulty of accurate control of the rate of dark oxidation of sodium sulphite solutions is well known and has recently been discussed by Rice from a new point of view (*J. Amer. Chem. Soc.*, 1926, **48**, 2099). We therefore altered our procedure and, without removing the solution from the cell, observed its rate of oxidation during successive dark and light periods, removing samples for analysis at the end of each of such periods. Under these conditions, the rate of dark oxidation remained reasonably constant when a particular cell filling was used. The variations in the slopes of the curves for different cell fillings show plainly the impossibility of obtaining conclusive results by the first method. Our data are shown in the figure, where c.c. of 0·1*N*-sodium thiosulphate are plotted against time. Dark periods are shown by continuous, light periods by broken lines. Violet light was used in Expts. 1 and 2, red light in 7 and 8, green in 6, ultra-violet light of long wave-length in 3, and short wave-length ultra-violet light in 4 and 5. In plotting the results of 7 and 8, in order to separate the curves better, 4 c.c. have been subtracted throughout from the actual numbers used in the titrations.

In addition, a few experiments using red light were carried out with an apparatus similar to that of Thomas, the chief changes being that a straight mercury manometer was used, instead of the U-tube type employed by him, and, in addition, that the pipettes were immersed in a thermostat at 25°. The solutions used were aqueous sodium sulphite and ammoniacal cuprous chloride—in both cases red light is said to accelerate the oxidation. Two pipettes were employed and the method of alternate light and dark periods was used. There is no need to give the results in detail. When manometer readings were plotted against time, regular curves were obtained with nothing whatever to indicate any accelerating effect of the red light.

FIG. 1.



Discussion and Conclusions.

It will be seen that, within the limits of experimental error, none of our results indicates any effect of light on the rate of oxidation of aqueous sodium sulphite with the exception of Expt. 4 and (more doubtfully) Expt. 5. In those cases, ultra-violet light of short wave-length was being used, and the work of Mathews and his collaborators (*J. Physical Chem.*, 1913, **17**, 211; 1926, **30**, 414; *J. Amer. Chem. Soc.*, 1917, **39**, 635) has already shown that such light, which falls within the strong ultra-violet absorption band of sodium sulphite, accelerates its oxidation (compare the case of sodium bisulphite or metabisulphite—Baly and Bailey, J., 1922, **121**, 1813; Dietzel and Galanos, *Z. Elektrochem.*, 1925, **31**, 466; Getman, *J. Physical Chem.*, 1926, **30**, 266), This being the case, and taking into account the criticisms of the work of Trautz and Thomas made above, we are of opinion that the effects they observed were due, not to light, but rather to incomplete control of the dark reaction (such as would result from variable diffusion rates or variable amounts of positive catalysts associated with a particular filling or a particular pipette), and that, consequently, their results are probably spurious and cannot be regarded as evidence in favour of the possibility of photochemical retardation.

The above experiments were carried out during 1923. The junior author wishes to acknowledge his indebtedness to the Scientific and Industrial Research Department for a maintenance grant which enabled him to take part in the work.

UNIVERSITY OF LONDON,
KING'S COLLEGE.

[*Received, January* 14*th*, 1927.]