Summary

It is shown that the Bower-Barff protective coating, produced by the action of steam on iron at about 700° with subsequent cooling in air, is built up of layers of ferrous oxide, magnetite and ferric oxide, arranged in this order (the order of oxidation) upon the iron base. The thicknesses of these layers are estimated to be of the order of 10^{-2}, 2×10^{-4} and 2×10^{-5} cm., respectively. The data on which the above conclusions are based are the positions and intensities of lines on powder photographs taken with molybdenum, iron and copper $K\alpha$ x-rays. The iron and copper $K\alpha$ x-rays penetrate the coating to different depths and give information about different parts of its structure because their wave lengths are, respectively, a little greater and a little less than the critical-absorption wave length of the iron which forms the greater part of the coating.

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[Contribution from the Chemical Laboratory of Princeton University]

THE ACTION OF LIGHT ON THE FERROUS-FERRIC: IODINE-IODIDE EQUILIBRIUM

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Sime time ago, in a paper with the same title, Rideal and Williams[2] described measurements of the quantum yield of the reaction $2Fe^{++} + I_3^- \longrightarrow 2Fe^{+++} + 3I^-$ occurring in light of wave length 5790 Å. A dark equilibrium mixture was used, being about 0.016 N with respect to iodine. The rate of change of the iodine titer in light was approximately unimolecular and the authors, calculating accordingly the initial velocity of the photochemical reaction and measuring the absorbed light energy, came to the conclusion that one molecule of iodine reacted on the absorption of one quantum of green light by the complex I_3^- ion. The spectral sensitivity of the reaction was studied by means of different light filters as light sources, an incandescent and a mercury lamp being used. A distinct maximum of sensitivity for the reaction was observed in the region 6500–5000 Å., no reaction occurring in the light 4000–5000 Å. The authors connected these facts with the known critical potential of the iodine molecule, 2.34 v., corresponding to a wave length of 5300 Å. This supposed pronounced maximum of sensitivity is, however, rather improbable, as the continuous absorption of the tri-iodide ion extends increasingly from red far into the ultraviolet region of the spectrum. The writer has, therefore, repeated and extended the experiments of Rideal and Williams, obtaining different results.

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[2] Rideal and Williams, *J. Chem. Soc.*, **127**, 258 (1925).

The solution was prepared exactly as by Rideal and Williams, the iodine concentration increasing in a week to a steady value of 0.0173 *N*. One part of this solution afterwards was diluted with four parts of water and it showed after a few days a steady iodine concentration of 0.0031 *N*. This solution will be referred to as the dilute solution. The reaction vessel with plane-polished quartz ends (34 × 34 mm.) had a volume of 9.35 cc. As light source a Krohmeyer water-cooled mercury lamp[3] was used. The light filters were the following. (1) For the line 5465 Å., the Wratten filter N77, transmitting besides this line a little of the yellow and red mercury lines. (2) For 4360 Å., a cuprammonium sulfate solution and one of quinine. Besides the line 4360 only traces of 4070 Å. were transmitted. (3) For 3660 Å. a nickel oxide glass, transmitting only light of this wave length in noticeable amounts. The reaction vessel was placed behind light filters and was standing directly behind a diaphragm 30 × 30 mm. in area. The lamp was 28 cm. distant from the diaphragm. The absorbed light energy was measured by means of a Moll thermopile covering 314 sq. mm. and standing 30 mm. behind the diaphragm. The energy absorbed by the iodine was calculated from the deflections of the galvanometer when (a) the vessel filled with solution and (b) the vessel filled with water were interchanged, these measurements being made before and after each experiment.

With all three wave lengths, measurable reaction velocities were obtained. Table I represents the results. As the light intensity of the lamp varied slightly from experiment to experiment, the constants *K*, calculated by the formula $K = (1/t)ln[a/(a-x)]$, were divided by the absorbed energy expressed in centimeters' scale deflection, the average values for each wave length and equal time of experiment being given in the table. The energy actually absorbed was the equivalent of 6 cm. scale deflection for the light 5460 Å.; 2 cm. for 4360 Å. and 3.5 cm. for 3660 Å.

TABLE I

REACTION VELOCITY PER UNIT OF ENERGY ABSORBED

Wave length, Å.	Time of illumination, min.	$K, \frac{\text{Moles in 1000 cc.}}{\text{sec.}} \times 10$
5460	30	4.15
5460	120	3.20
4360	60	3.76
4360	120	2.85
3660	30	3.54
3660	60	3.39
3660	120	2.61
	Dil. solution	
3660	30	17.5

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[3] The Laboratory is indebted to the Hanovia Chemical and Manufacturing Company for the use of this lamp, as also for the nickel oxide glass filter.

It will be seen from Table I that the unimolecular velocity constant, being inversely proportional to the initial concentration, decreases for longer illumination intervals, indicating evidently that the stationary state, not reached in these experiments, corresponds to a finite and relatively high iodine concentration. However, comparing Table I with values given by Rideal and Williams, we find that for the first hour of illumination, the unimolecular constant is steady enough for the (approximate) calculation of the initial reaction velocity. The constants for the short illumination decrease with decreasing wave length, in the ratio 1:0.9:0.85. Calculating on the other hand the relative numbers of quanta per unit energy, we find for the wave lengths 5460, 4360 and 3660 Å. the ratio 1: 0.8: 0.67. The ratios, being identical well within the experimental errors, strongly support the view that the reaction of iodine with ferrous ions follows the Einstein-Stark equivalence law not only in the light of the wave length 5790 Å. studied by Rideal and Williams, but also, and contrary to their conclusions, in the light 5460, 4360 and 3660 Å. The calibration of the thermopile against a standard lamp[4] gave a value of 1.11×10^{-7} watts per sq. mm. per 1 cm. deflection. Introducing the correction of 3.5% for the reflection of light on the hind quartz plate of the vessel, and assuming that on the illuminated area of 1360 sq. mm. (at 30 mm. distance from the diaphragm) the distribution of light intensity is uniform, an assumption certainly only approximately true, we find the values, given in Table II, of absorbed quanta and reacting molecules of iodine in the initial moments of illumination.

TABLE II

QUANTUM YIELD OF THE REACTION

Wave length, Å.	Absorbed quanta $\times 10^{-14}$	Reacting molecules $\times 10^{-14}$	Ratio Col. 3/Col. 2
5460	4.37	4.07	0.93
4360	3.49	3.69	1.06
3660	2.92	3.48	1.19
3660	2.92	3.12 (dil. solution)	1.07

The determination of the quantum yield was not intended to be a precision measurement; therefore, the corrections were omitted relating to the light intensity distribution on the illuminated area and the variation in light reflection with wave length on the quartz plate protecting the thermopile. This last correction, amounting probably to 5%, would tend to decrease the ratios of Col. 4, Table II, as the standard lamp emits mostly in the red. Altogether, the measurements described show that the reaction follows the equivalence law over a very wide wave-length interval, the quantum yield being independent of the concentrations of the reacting species. At the same time it is shown that the suggested relation to the critical potential of gaseous iodine[2] is highly improbable, the volt equivalent

[4] Calibrated by the Bureau of Standards.

of effective radiation varying from 1.9 (6500 Å.) to 3.4 v. It was shown by Dymond[5] that gaseous iodine is dissociated into atoms only on absorption of radiation of shorter wave length than 5000 Å. (2.48 v.), a normal and an excited atom resulting.

To suggest a similar behavior of the tri-iodide ion, the light-absorbing system in the reaction studied seems to be unjustified. On the other hand, the heat of dissociation of iodine into two normal atoms is only 36,000 cal. (1.5 v.), so that evidently the reaction mechanisms (1) $I_3^- + hv \longrightarrow I_3^-$ (activated); I_3^- (activated) $+ Fe^{++} \longrightarrow Fe^{+++} + 2I^- + I$; $I + Fe^{++} \longrightarrow Fe^{+++} + I^-$; and (2) $I_3^- + hv \longrightarrow I^- + 2I$; $I + Fe^{++} \longrightarrow Fe^{+++} + I^-$ are both possible.

We will not go into a detailed discussion of the probable cause of the wrong observations made by Rideal and Williams. A weak transmission of the light filters used and the large reaction vessel leading to very small changes in the iodine titer may account for them.

Summary

The reaction $2Fe^{++} + I_3^- \longrightarrow 2Fe^{+++} + 3I^-$ has been shown to be sensitive to the following lines in the mercury spectrum: $\lambda = 5460$, 4360 and 3660 Å. This is contrary to earlier results of Rideal and Williams, who found a maximum of sensitivity in the region 6500 – 5000 Å. and no reaction in the region 4000–5000 Å.

An approximate determination of the quantum yield at the three wave lengths indicates a reaction of one molecule per quantum in each case.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, BUREAU OF SOILS]

THE GASOMETRIC DETERMINATION OF NITRIC OXIDE, WITH SPECIAL REFERENCE TO ABSORPTION BY FERROUS CHLORIDE

BY V. N. MORRIS

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During the course of certain experiments involving the use of nitric oxide, the desirability of having available a satisfactory method for the rapid determination of this gas became evident. A search of the literature revealed that the analysis of mixtures of the oxides of nitrogen has been the subject of rather careful investigation and considerable controversy, but the same does not appear to apply to the case of nitric oxide alone.

Various methods for the latter gas, however, have been suggested. Among these are included reduction by glowing copper, oxidation by potassium bromate, hydrogen peroxide, potassium permanganate and

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[5] Dymond, *Z. Physik*, **34**, 553 (1925).