

## STANDARDIZATION OF THE POTASSIUM FERRIOXALATE ACTINOMETER OVER THE TEMPERATURE RANGE 5 - 80 °C

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### Summary

The quantum yield of ferrous ion formation on irradiation at 313 nm is constant and has a value of 1.24 in the temperature range 5 - 80 °C. At temperatures above ambient the samples should be deoxygenated to eliminate reoxidation of Fe<sup>2+</sup> by O<sub>2</sub>. At 80 °C there is a competing thermal reduction producing Fe<sup>2+</sup> which is first order in ferrioxalate.

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### 1. Introduction

There is considerable interest in the measurement of the activation parameters of photochemical reactions [1], but the short lifetimes of excited states and the high rates of excited state reactions make such measurements difficult. In some cases the rates can be measured directly using a flash photolysis apparatus containing a thermostatted cell [2] or can be obtained from the emission intensities as a function of temperature [3]. However, when rate constants are obtained indirectly from the measurement of quantum yields, the experimental procedure is more complicated. This is due to the fact that the most common method of obtaining quantum yields is through the use of a carousel apparatus and a chemical actinometer which is not calibrated for different temperatures. This has necessitated the use of a collimated light source, a beam splitter and two irradiation chambers, one of which is maintained at ambient temperature while the other is varied.

A chemical actinometer calibrated over a wide range of temperatures would greatly simplify the experimental procedure and allow data to be obtained from any carousel located in a constant-temperature bath. Although the transformations already studied [4] can be used as an actinometer, these systems do not lend themselves to general use and it would be valuable to know the temperature dependence of an actinometer in general use. Of the many actinometers available, the most frequently used is the ferrioxalate type. It has the advantages of high sensitivity and excellent wavelength response, it is easy to use and has recently had its capacity improved [5]. It is also the primary standard against which most other actinometers are

measured and is the most accurate of the chemical actinometers. We therefore decided to measure the quantum yield of ferrous ion production as a function of temperature.

## 2. Experimental details

A potassium ferrioxalate solution (0.006 M) was prepared, irradiated and analysed according to the literature procedure [6]. A Coleman-Perkin-Elmer 139 spectrophotometer was used for the analyses. A 450 W medium pressure Hanovia mercury lamp was used for all irradiations. The emission from this lamp was filtered by passing it through a 0.5 cm solution of  $1.00 \times 10^{-3}$  M potassium chromate and a Corning 7-54 filter to isolate the 313 nm mercury line. The experimental apparatus consisted of the lamp and two carousels located at equal distances from the lamp. Each carousel was placed in a constant-temperature bath containing a Pyrex window. The irradiations were performed using 3 ml of the sample in Pyrex test tubes of outside diameter 13 mm. The ratio of the light intensities at the two carousels was measured by irradiating ferrioxalate at ambient temperature in both and comparing the quantity of  $\text{Fe}^{2+}$  produced. The ratio was found to be 1.00. It was rechecked at various times during the experiments and was found to remain unchanged. Since it is known [7] that the quantum yield of ferrioxalate reduction is constant in the temperature range 22 - 32 °C, the temperature of the reference carousel bath was not controlled but was allowed to vary during the irradiation. It was found that the temperature of this bath did not exceed the temperature range of known quantum yield. In each case blanks were subjected to the same treatment and analysis, the only difference being that they were not irradiated. Conversions were limited to 2% in the linear range of the actinometer response.

In some cases oxygen was removed by passing water-saturated nitrogen gas through the solutions for 15 min and then stoppering the test tubes.

Except where noted the same potassium ferrioxalate solutions were used in the thermal studies and were maintained at constant temperature in a Lauda K4R constant-temperature bath which controlled the temperature to within  $\pm 0.1$  °C.

## 3. Results and discussion

The quantum yield of  $\text{Fe}^{2+}$  production at various temperatures was measured relative to the known value [6] at 22 °C in the temperature range 5 - 80 °C. The results are shown in Table 1. As can be seen the quantum yield is constant. It was found that at 80 °C there was a thermal reaction which produced  $\text{Fe}^{2+}$  and that only 25% of the  $\text{Fe}^{2+}$  produced was due to the photochemical reaction at the lamp intensity used. The quantum yield at 80 °C represents only the portion of  $\text{Fe}^{2+}$  generated photochemically. No thermal reaction was detected at 60 °C.

TABLE 1

Quantum yield for the production of  $\text{Fe}^{2+}$  from potassium ferrioxalate

$T$ ( $^{\circ}\text{C}$ )	Quantum yield
5	$1.27 \pm 0.04$
22	$1.24 \pm 0.02^{\text{a}}$
40	$1.25 \pm 0.04$
60	$1.28 \pm 0.04$
80	$1.24 \pm 0.04$

<sup>a</sup>Reference temperature.

At lower light intensities the thermal process could easily swamp the photochemical process so it was decided to study the thermal reaction. (A study of the disappearance of  $\text{Fe}^{2+}$  at lower temperatures is reported in ref. 8.)

The rate of  $\text{Fe}^{2+}$  formation at  $80^{\circ}\text{C}$  was monitored for the  $0.006\text{ M}$  ferrioxalate solution. Figure 1 shows that samples which had been deoxygenated follow first-order kinetics while samples containing oxygen gave lower yields and a greater deviation from the best straight line. Apparently oxygen is reoxidizing some of the  $\text{Fe}^{2+}$  generated. It should be noted that these conversions are very small and that the data fit second-order, third-order or even zero-order kinetics equally well. To ascertain the order of the reaction, the initial rate of production of  $\text{Fe}^{2+}$  (pseudo zero order) was

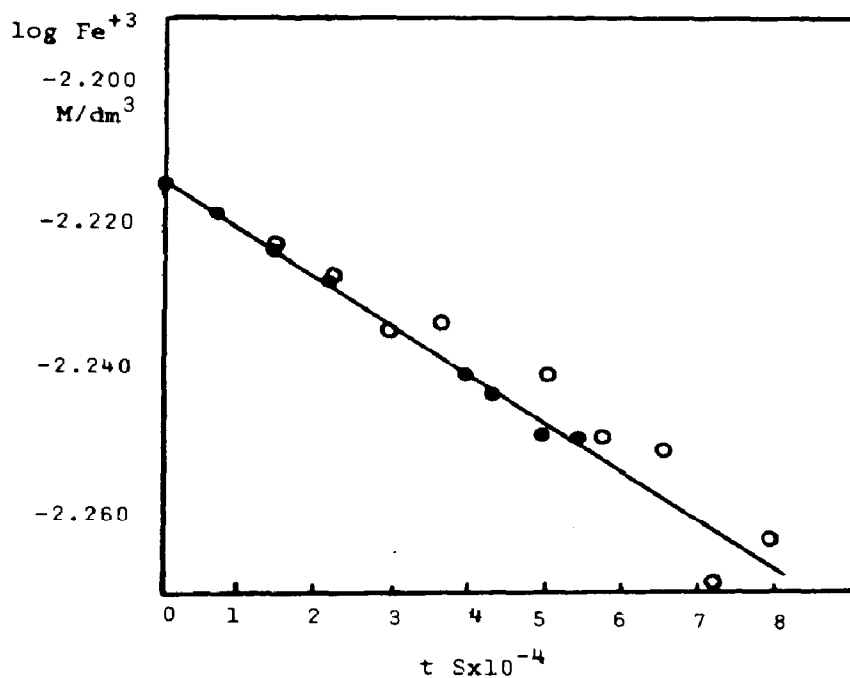


Fig. 1. Plot of  $\log [\text{Fe}^{3+}]$  against time for the thermal reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  at  $80^{\circ}\text{C}$ : ●, reaction in the absence of oxygen; ○, reaction in air.

measured as a function of the initial concentration. The points (at five concentrations of  $\text{Fe}^{3+}$  from 0.006 to 0.15 M) fit a straight line showing that the reaction is first order in ferrioxalate. The slope gives a rate constant of  $(1.44 \pm 0.02) \times 10^{-6} \text{ s}^{-1}$ . It is preferable to use a lower concentration of ferrioxalate (e.g. 0.006 M) at 80 °C to reduce the effect of the thermal reaction. The light intensity for 0.006 M  $\text{Fe}^{\text{III}}\text{OX}_3$  should be  $6 \times 10^{12}$  photons  $\text{s}^{-1}$  per millilitre of solution in the sample in order for the rate of the photochemical reaction to equal that of the thermal reaction.

In all cases the conversions obtained were small so that except at 80 °C the effect of oxygen on the reoxidation of  $\text{Fe}^{2+}$  was found to be negligible. However, it seemed reasonable to assume that reoxidation could be important at higher conversions and/or longer irradiation times. In an attempt to determine the importance of reoxidation, two sets of solutions of 0.006 M ferrioxalate, one of which had been deoxygenated, were irradiated. The conversion was allowed to attain 3% (5 min irradiation) and the tubes were then maintained for 2 h at the same temperature (40 °C) before analysis. The deoxygenated solution gave an  $\text{Fe}^{2+}$  titre of  $(1.62 \pm 0.03) \times 10^{-4}$  M while the untreated solution gave only  $(1.35 \pm 0.03) \times 10^{-4}$  M. Evidently the oxidation reaction is important even at 40 °C.

#### 4. Conclusions

The quantum yield of  $\text{Fe}^{2+}$  formation in the irradiation of potassium ferrioxalate at 313 nm is independent of temperature in the range 5 - 80 °C. Samples should be deoxygenated to eliminate the reoxidation of  $\text{Fe}^{2+}$  by atmospheric oxygen. At 80 °C there is a competing thermal reduction producing  $\text{Fe}^{2+}$  which is first order in ferrioxalate and has a rate constant of  $(1.44 \pm 0.02) \times 10^6 \text{ }^\circ\text{C}^{-1}$ .

At 80 °C the actinometer must be accompanied by a blank so that the thermal reaction can be subtracted from the total yield.

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