

## Short Communication

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### The photochemical reaction between ferrocene and iodine

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Some years ago, Russian workers reported on the reaction between iodine and ferrocene in benzene solution [1]. They showed that the reaction, giving ferricenium tri-iodide as the ion pair, proceeded towards an equilibrium that was attained virtually within a matter of minutes. The forward reaction was quoted as being first order in ferrocene and second order in iodine, but the mechanism proposed involved as a first and presumably rate-determining step the process



(where the symbol Fn denotes a molecule of ferrocene and  $\text{Fn}^+$  a ferricenium ion) which would appear not to require that the reaction be second order in iodine.

However, it has been noted [2] that, when a solution of ferrocene and iodine in benzene is illuminated by light causing dissociation of the iodine molecules, then the reaction to form ferricenium tri-iodide is displaced from its normal position of equilibrium. Thus a preliminary study of photochemical effects on this system was carried out to clarify how the results might relate to the thermally initiated reaction.

#### 1. Experimental

The ferrocene was Reagent grade, twice re-sublimed under vacuum, and the iodine was AnalaR grade, re-sublimed. Solutions used in flash photolysis experiments were made up just before use from stock solutions of ferrocene and of iodine in AnalaR benzene.

The flash photolysis system, previously described [3], had a custom-made cylindrical quartz cell of internal diameter 1.5 cm and 20 cm path length with a coaxial filter compartment. Within the reflector, the cell was fixed between two flash tubes fired in parallel and the analysing light from a stabilized xenon arc lamp was directed down the axis of the cell, then through a glass filter to the grating monochromator and photomultiplier tube whose output was displayed on a storage oscilloscope.

## 2. Results and discussion

When a solution in benzene, nominally  $5 \times 10^{-4}$  mol dm $^{-3}$  in ferrocene and  $2 \times 10^{-4}$  mol dm $^{-3}$  in iodine, was flashed with distilled water in the filter compartment, 60  $\mu$ s after the flash onset (when the intensity of the scattered light had diminished sufficiently to allow accurate absorbances to be measured) an appreciable increase in absorbance was detected at 625 nm. This was obviously attributable to an enhanced concentration of ferricenium tri-iodide effected by the flash. The absorbance appeared to be constant over a period of milliseconds but the sharp increase was found to decay over a period of a few seconds. Another flash of the same energy minutes later was found to reproduce the absorption change of the original, which indicated that meaningful data could be obtained by the repeated flashing of a single solution at intervals of a few minutes, with systematic changes in the experimental parameters.

One solution of iodine and ferrocene in benzene was degassed by five cycles of freeze-pump-thaw [4] in a bulb attached to the cell assembly, after which it was sealed off under vacuum. It was found that all the absorbance changes observed at various wavelengths and various flash energies with this degassed solution could be reproduced when it was again equilibrated with air. This indication that the presence of oxygen in the solution did not interfere with the reaction observed meant that degassing was unnecessary.

By varying the wavelength setting of the monochromator it was found, as shown in Fig. 1, that the maximum increase in the absorbance was close to 630 nm. Above 700 nm the increase was minimal and at about 577 nm the change in absorbance changed sign and became increasingly negative down to 560 nm which, because of the increasing absorbance due to molecular iodine, was the lower limit of observation. The decrease observed at these shorter wavelengths obviously arose from the diminished concentration of iodine accompanying the increased concentration of the tri-iodide.

When the filter compartment of the cell was filled, not with water but with a solution of  $2 \times 10^{-4}$  mol dm $^{-3}$  aqueous benzoic acid, which would intercept almost all the light below 295 nm, the absorbance changes at each wavelength were scarcely decreased, indicating that the light causing the reaction was almost exclusively of wavelength greater than 300 nm and that it was not being absorbed by the ferrocene. It is well known that excitation of I $_2$  in the band at around 520 nm causes its dissociation to I atoms and so the following mechanism may be proposed:



An alternative fate of I atoms would be recombination:



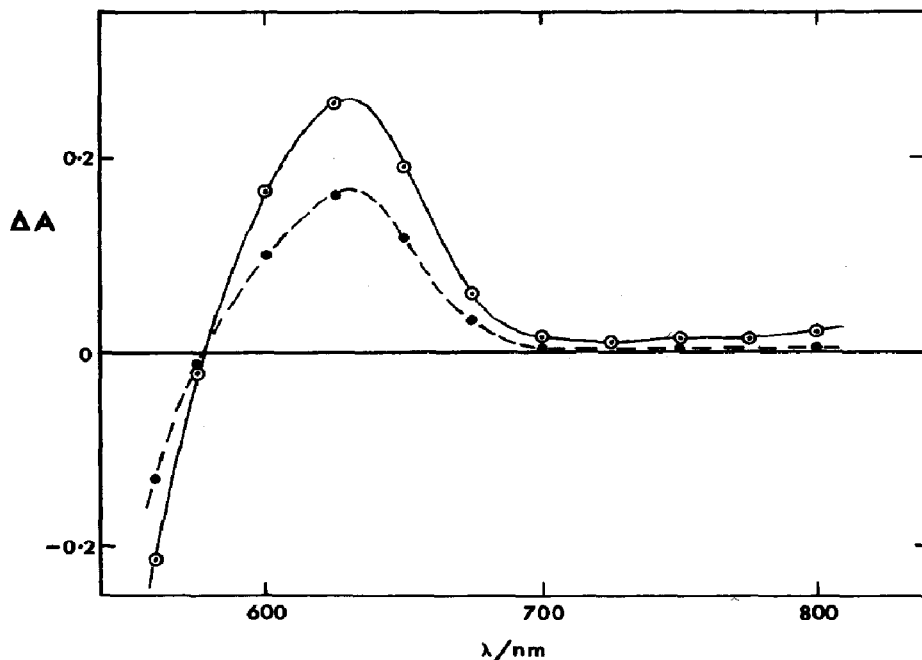


Fig. 1. Absorbance change 0.5 ms after a flash of energy 422 J as a function of wavelength for benzene solutions at 20 °C, nominally  $2 \times 10^{-4} \text{ mol dm}^{-3}$  in  $\text{I}_2$  and (○)  $5 \times 10^{-4} \text{ mol dm}^{-3}$  or (●)  $8 \times 10^{-5} \text{ mol dm}^{-3}$  in ferrocene.

Some experiments were carried out varying the concentration of ferrocene. In this series, the nominal concentration of iodine was constant but, since the concentration of ferricenium tri-iodide present at equilibrium would not be invariant, this would mean that the *actual* iodine concentration would not be strictly constant. However, using for the equilibrium constant of the process



the value of  $174 \text{ dm}^{9/2} \text{ mol}^{-3/2}$  determined in benzene solution by Brand and Snedden [2], it can be shown that the degree of tri-iodide formation is very slight in these dilute solutions so that variations in the actual iodine concentration and thus in the manner of light absorption would be very slight. It was found that at very low ferrocene concentration, the size of the absorbance change at any wavelength varied with the ferrocene concentration, but that when the ferrocene concentration was increased above  $5 \times 10^{-4} \text{ mol dm}^{-3}$ , the absorbance change scarcely increased any further. This suggests that at such ferrocene concentrations, the predominant fate of an iodine atom is reaction (3) rather than reaction (5), so that the product yield can be increased only minimally by increasing the ferrocene concentration. However, at lower concentrations of ferrocene, reaction (3) is no longer predominant.

Variation of the iodine concentration affects chiefly the manner in which the light of the photoflash is absorbed in the solution. For mono-

chromatic light normal to the cylindrical axis, the increment  $dI$  absorbed between  $l$  and  $l + dl$  is proportional to  $ecI_0 10^{-ecI} dl$ , a function which at low concentrations is almost proportional to the concentration  $c$  but which attains a maximum at  $c = (2.303\epsilon l)^{-1}$  [5]. In the present system, the light is not monochromatic nor is it restricted to normal incidence, but for  $I_2$  concentrations in the range  $(1 - 5) \times 10^{-4}$  mol  $dm^{-3}$ , the magnitude of the absorbance changes caused by flashing varied as predicted by the above considerations, taking the effective value of  $l$  as 0.8 cm.

When the energy of the flash was varied, the absorbance change usually altered in the same sense. Under conditions where the ferrocene concentration was large, the absorbance change approximated closely to being proportional to the flash energy, but at low ferrocene concentrations the curve deviated appreciably from direct proportionality. All deviations from linearity may be attributed to the fact that when the flash energy is increased, the iodine atom yield rises in proportion but the extent of reaction (5) increases proportionately more and that of reaction (3) proportionately less. Thus the curvature of the plot is expected to be greater under conditions where the extent of reaction (5) is not negligible in comparison with reaction (3).

A simple mathematical model of the reaction is easily constructed. Assuming that the extent of reaction (*i.e.* formation of ferricenium triiodide) is governed by the occurrence of reactions (2), (3) and (5) and that the concentration of iodine atoms at the end of the flash ( $t = 0$ ) is  $a$  and at time  $t$  is  $a - x$ , then the rate of decrease of the concentration of I atoms is given by

$$\frac{dx}{dt} = 2k_5(a - x)^2 + k_3(b - y)(a - x) \quad (6)$$

where the ferrocene concentration is initially  $b$  and becomes  $b - y$  at time  $t$ . (This equation also embodies the simplifying assumption that all I atoms are formed before any reaction commences.) If the approximation is made that the decrease in the ferrocene concentration is proportionately small so that  $b$  may be substituted for  $b - y$  then the final concentration increase of ferricenium triiodide is given by

$$\Delta [Fn^+] = \int_0^{\infty} k_3 b(a - x) dt = \frac{k_3 b}{2k_5} \ln \left( 1 + \frac{2k_5 a}{k_3 b} \right) \quad (7)$$

If I atoms react predominantly with ferrocene, *i.e.*  $k_3 b \gg 2k_5 a$ , then to a good approximation we may substitute  $z$  for  $\ln(1 + z)$  when  $z$  is very small, and obtain the answer  $\Delta [Fn^+] = a$ . Otherwise, the increase in the product concentration would always be less than this, by a greater amount the larger the ratio  $a/b$ . Thus eqn. (7) explains the dependence of the absorbance changes on both the ferrocene concentration and the flash energy.

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