

Mutual determination of Iron and Tropolone

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Mutual determination of Iron and Tropolone*

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Synopsis

It has been known that tropolone reacts with iron to give green and brownish red complexes. It was found that the green complex is formed in the presence of excess iron, while the latter, in the presence of excess tropolone. The green complex shows a broad absorption band with its maxima at 435 and 582 m μ . The maximal color develops over the acidity range from 0.05 to 1 N. The formation of the brownish red one is complete over the pH range from about 1.3 to 8.5 and it shows the absorption peaks at 425, 550 and 595 m μ .

The composition of the green complex is 1:1. That of red one is considered to be 1:3. The formation constant of the green complex is evaluated to be 1.0×10^{11} .

These complexes are utilized in the mutual determination of iron and tropolone. Beer's law is valid for both complexes at the wavelength of maximum absorbancy and iron and tropolone have been determined up to 0.07 γ /ml and 1.0×10^{-5} M/l respectively.

I. Introduction

Iron added to tropolone makes a characteristic color development which has been used for the detection of tropolone. However, the coloration of green or red in certain cases under different conditions, tends to result in confusion and little has been known about its chemical nature. It was confirmed by the authors that the green color is obtained in the presence of excess of iron, whereas it turns red as the concentration of tropolone increases. Even in an excess of tropolone, however, the solution gives a green color in rather strongly acidic solution.

The coloration can be used for a photometric determination of iron (III) and tropolone. In particular, for the determination of the former, tropolone has proved to be as sensible as the Nitroso-R salt.

An investigation was therefore made to study the variables involved in the determination of iron and tropolone. The compositions of the two complexes and the formation constant of the green complex were also evaluated from the photometric data.

Spectrophotometers used were Hitachi EPB-U and EPU-2 type. All pH measurements were made by means of Beckman glass electrode assembly.

II. Absorption spectra of tropolone-iron (III) complexes

The green complex is soluble in water, whereas the brownish red one is soluble in benzene or alcohol and gives a stable solution, but is difficultly soluble in water.

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Figure 1 shows the spectral absorption curves of green complex in aqueous solution. The absorption maxima were found at 582 and 435 $m\mu$ in the visible range. Green complex was stable over the wide range of acidity covering from

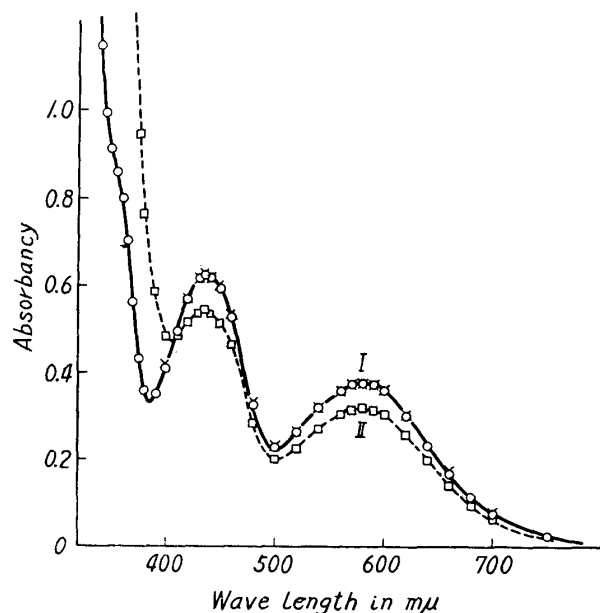


Fig. 1. Absorption spectra of green complex
 $\text{Fe}(\text{ClO}_4)_3$: 3.7×10^{-3} M/l
 Tropolone: 2.8×10^{-4} "
 Curve I —○— HClO_4 : 0.52N, —×— HClO_4 : 0.05N
 II —□— HCl : 0.4N

0.05 to 1N. In hydrochloric acid or perchloric acid solution, the color intensity differed from each other. It may be considered that this discrepancy is due to a different kind of co-ordinated ligands to iron atom besides a tropolone molecule. In hydrochloric acid solution, absorption band of ferric chloride was observed to overlap in a range below 440 $m\mu$.

When the molar ratio of iron to tropolone was five, the formation of the green complex was completed. Thus, absorbancy remained constant until 13.3 times of iron (III) was added to tropolone.

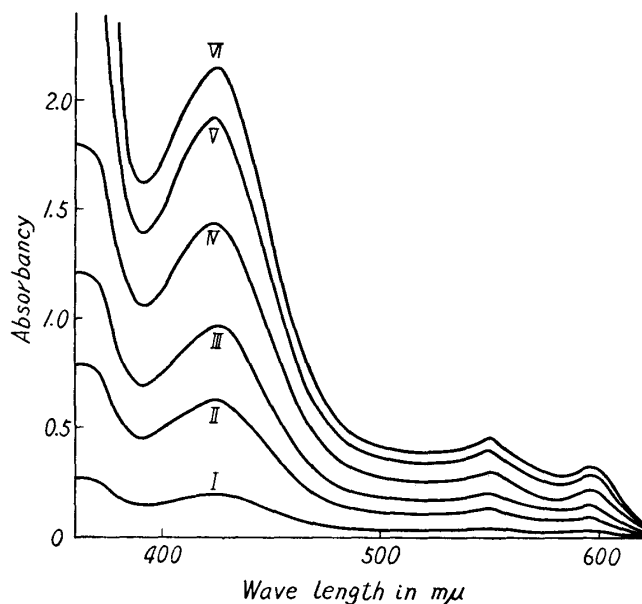


Fig. 2. Absorption spectra of brownish red complex
 $\text{Fe}(\text{ClO}_4)_3$: 1.4×10^{-4} M/l, HClO_4 : 0.05N
 Curve I Tropolone 1.68×10^{-4} M/l
 II " 2.52 "
 III " 3.15 "
 IV " 3.78 "
 V " 5.04 "
 VI " 25.2 "

The absorption spectra of the brownish red complex in benzene solutions is illustrated in Figure 2. The absorption maxima were found at 425, 550 and 595 $m\mu$ in the visible range. As is shown in the figure, each curve at various molar ratios of tropolone to iron (from 1.2 to 18) showed a good similarity. Accordingly, it may be concluded that there is only one kind of the complex to exist.

The readings on benzene solution remained constant within the pH range from 1.3 to 8.5. Hydrogen ion concentration was adjusted after the tropolone was added so as to avoid the hydrolysis of iron (III).

As is described above, the green complex is soluble in water and is not extracted with benzene,

whereas the brownish red one is extracted in benzene and is difficultly soluble in water. Fortunately, since both complexes were soluble in 40 per cent alcoholic solution, this medium was used for the determination of the composition of two complexes by a molar ratio method. The concentrations of ferric perchlorate and perchloric acid were kept at 1.4×10^{-4} M/l and 0.05N respectively. With an increase of the concentration of tropolone, absorbancy increased linearly until a molar ratio reached 1:1. Above there curved line was obtained and thus the composition of the complexes could not be determined.

Consequently, iron and tropolone was made to react in an aqueous solution at various ratio. Then the brownish red complex was extracted with benzene after the equilibrium in the solution was attained. The results are shown in Fig. 3.

In the figure, the absorbancy in an aqueous phase increased linearly until the molar ratio was 1:1, whereas that in a benzene phase first appeared when the ratio exceeded 1:1. From this fact the composition of the green complex may be considered to be 1:1. The mark ● in the figure is the data obtained from the calibration curves in Fig. 6, assuming the corresponding amount of tropolone was converted entirely to the green complex. These marks took

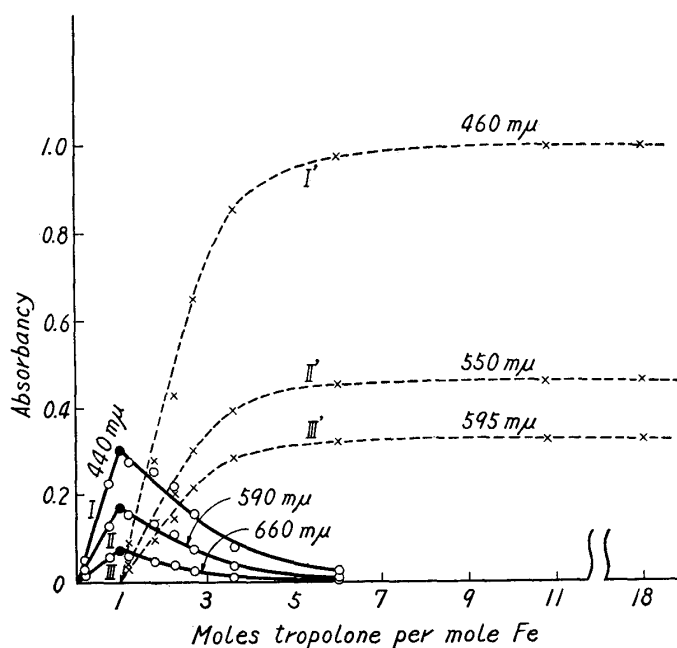


Fig. 3. Effect of ratio of tropolone to iron
 $\text{Fe}(\text{ClO}_4)_3 : 1.4 \times 10^{-4}$ M/l, $\text{HClO}_4 : 0.05$ N
 — aqueous phase, benzene phase

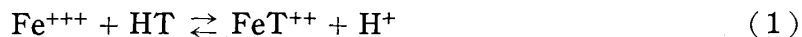
their positions on straight lines of I, II and III. In case tropolone added was 6 times as much as iron in a molar ratio, full color was not obtained in benzene phase and the existence of the green complex was observed. At the molar ratio above 11, any increasing amount of reagent cannot produce further change in color intensity.

The points of crossing of tangent lines of the curves (I', II' and III') were obtained at the ratio 3.4~3.6. Taking into consideration the coordination number of iron (III), it may be considered that the composition of the brownish red complex is 1 to 3.

III. Formation constant of the green complex

Basing on the principle of McConnell and Davidson, and Kruh, etc¹⁾, the formation constant of the green complex was evaluated.

As mentioned above, the green complex is formed according to the following equation as the first step:



and then this 1:1 chelate reacts with more tropolone to form a brownish red one. When an excess of iron (III) ion was added, the brownish red complex thus formed returned to the green complex.

The equilibrium constant, K_1 , of eq. 1 is given by

$$K_1 = \frac{[\text{FeT}^{++}][\text{H}^+]}{[\text{Fe}^{+++}][\text{HT}]} \quad (2)$$

Let the concentration of the green complex formed be x M/l in a solution initially a M/l in iron (III) and b M/l in tropolone.

Then equation 2 leads to

$$K_1 = \frac{x \cdot [\text{H}^+]}{(a-x)(b-x)}$$

If a and b are chosen to be $a = b$, then K_1 may be rewritten as follows:

$$K_1 = \frac{x \cdot [\text{H}^+]}{(a-x)^2} \quad (3)$$

Let ε_{Fe} and ε_g represent the molar absorption coefficients of ferric salt and green complex, and A the total absorbancy of the solution, it follows

$$A = \varepsilon_{\text{Fe}}(a-x) + \varepsilon_g x \quad (4)$$

so that

$$x = \frac{(A - A')}{(\varepsilon_g - \varepsilon_{\text{Fe}})} \quad (5)$$

where A' is the absorbancy of ferric salt first taken, i. e.,

$$A' = a\varepsilon_{\text{Fe}}$$

From equations 3 and 5 it becomes

$$\frac{a}{A - A'} = \frac{1}{\varepsilon_g - \varepsilon_{\text{Fe}}} + \left\{ \frac{1}{(\varepsilon_g - \varepsilon_{\text{Fe}}) \cdot K_1} \right\}^{1/2} \left\{ \frac{[\text{H}^+]}{A - A'} \right\}^{1/2} \quad (6)$$

Now, within the wavelength range measured, ε_{Fe} was substantially equal to zero. Therefore, equation 6 is reduced to

$$\frac{a}{A} = \frac{1}{\varepsilon_g} + \left(\frac{1}{\varepsilon_g \cdot K_1} \right)^{1/2} \left(\frac{[\text{H}^+]}{A} \right)^{1/2} \quad (7)$$

1) H. McConnell, N. Davidson: J. Am. Chem. Soc., **72**(1950), 3614.
P. S. Farrington: *ibid.*, **74**(1952), 966.
R. Kruh: *ibid.*, **76**(1954), 4865.

Thus, if the composition of the green complex is 1:1, a plot of a/A against $[(H^+)/A]^{1/2}$ should be a straight line, the intercept being $1/\epsilon_g$ and the slope $(\frac{1}{K_1 \cdot \epsilon_g})^{1/2}$. K_1 can be evaluated from the intercept and the slope.

Then, by changing acidity from 0.7N to 1.8N and keeping the molar ratio of iron (III) to tropolone at 1:1, the equilibrium constant of the green complex was determined from the absorption of an aqueous solution. Ionic strength of the solution remained constant at 2.00 with NaClO_4 . The measurement was made at 19.5~19.7°C. Under the condition the green complex is formed exclusively without any formation of the brownish red one. The absorption spectra of these solutions were quite similar to that of the solution containing large excess of iron (III).

A plot of a/A against $[(H^+)/A]^{1/2}$ are given in Fig. 4 in which a linear relationship is seen at each wavelength. The equilibrium constant K_1 of the green complex was evaluated graphically. It is given in Table 1. As a mean value of K_1 1.0×10^4 was obtained, each value in Table 1 being in accord with one another.

Table 1. Equilibrium constant of the green complex (1)

λ (m μ)	K_1
435	1.0×10^4
440	1.0×10^4
460	1.0×10^4
590	1.2×10^4
aver. 1.0×10^4	

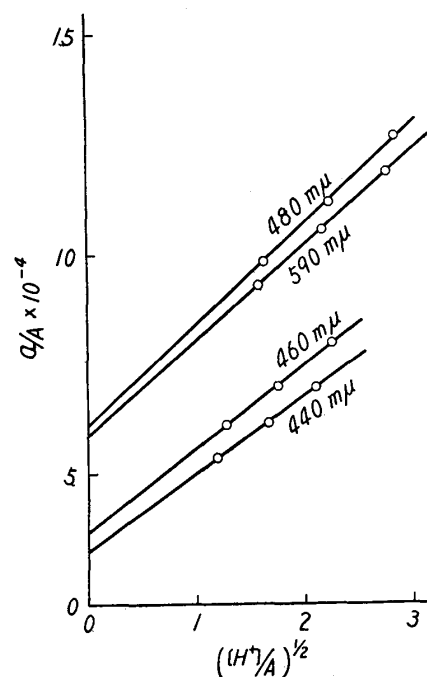


Fig. 4. Graphical determination of K_1
 $\text{Fe}(\text{ClO}_4)_3$: 2.8×10^{-4} M/l
 Tropolone: " "
 pH : 2.0

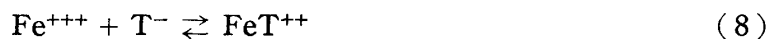
Next, the color development was made by adding 10 times as much of ferric perchlorate to tropolone in molecular ratio and by changing the concentration of perchloric acid from 2.7 to 4.3N. From the absorbancy of the green complex the equilibrium concentration of each component was obtained and the equilibrium constants were calculated and are given in Table 2. The average value obtained

Table 2. Equilibrium constant of the green complex (2)

$[\text{Fe}^{+++}]$ added ($\times 10^{-3}$ M/l)	$[\text{HT}]$ ($\times 10^{-4}$ M/l)	$[\text{HClO}_4]$ (N)	$[\text{FeT}^{++}]$ ($\times 10^{-4}$ M/l)	K_1
1.40	1.40	2.69	1.25	1.8×10^4
"	"	3.20	1.13	1.0×10^4
2.80	2.80	3.31	2.44	0.88×10^4
"	"	4.34	1.96	0.40×10^4
aver. 1.0×10^4				

was also 1.0×10^4 . But the individual constants in Table 1 are in better accord with one another than those in Table 2.

Then substituting in eq. 2 the value of the dissociation constant of tropolone, which is 1.0×10^{-7} ²⁾, at 20°C and that of K_1 , the formation constant according to the eq. 9 can be calculated and 1.0×10^{11} was obtained as it.



$$k_1 = \frac{[\text{FeT}^{++}]}{[\text{Fe}^{+++}][\text{T}^-]} \quad (9)$$

IV. Mutual determination of iron (III) and tropolone

Next, it was examined whether these complexes were utilized for the determination of iron (III) and tropolone.

Iron from 20 γ to 196 γ as ferric perchlorate was taken and 6.4 mg of tropolone was added. After the pH was adjusted to about 2, the solution was diluted to 50 ml. Then the solution was shaken with 50 ml of benzene. The transmittancy of the brownish red complex in a benzene layer was measured. The result is shown in Fig. 5.

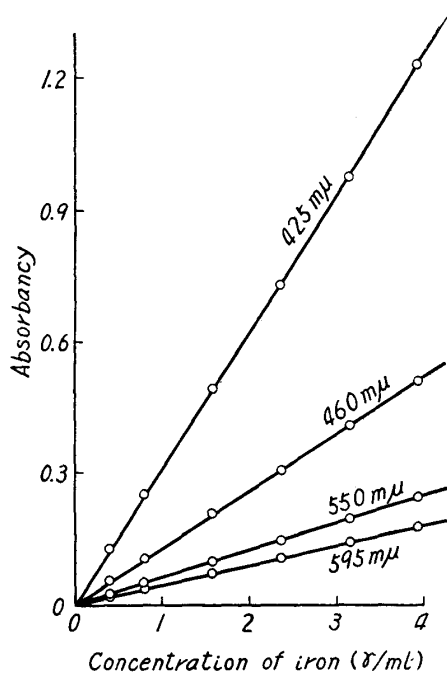


Fig. 5. Absorbance vs. concentration of iron

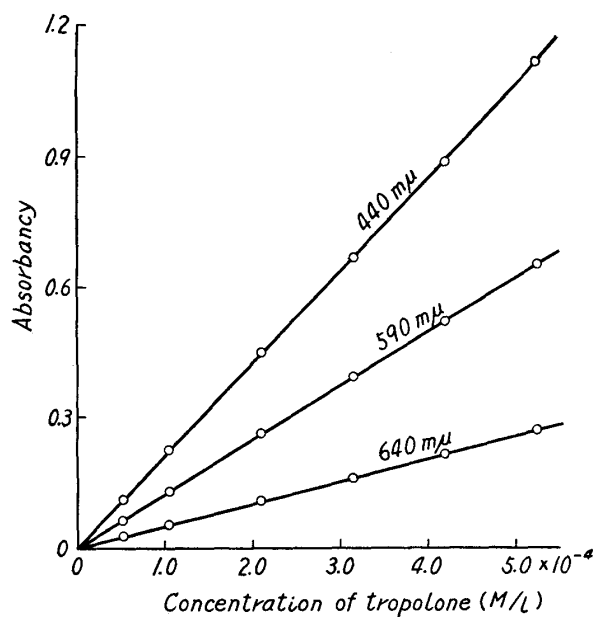


Fig. 6. Absorbance vs. concentration of tropolone

The correlation between the absorbance and the concentration of tropolone was next examined. Spectrophotometric measurements in an aqueous phase were made over a concentration range from 5.25×10^{-5} M/l to 5.25×10^{-4} M/l of tropolone. Concentration of perchloric acid and ferric perchlorate was kept to 0.5N and $2.81 \times$

2) J. W. Cook, A. R. Gibb, R. A. Raphael, A. R. Somerville: J. Chem. Soc. (1951), 503.
P. L. Pauson: Chem.Revs. 55 (1955), 15.

10^{-3} M/l, respectively. The results are shown in Fig. 6. Both complexes were found to obey Beer's law at each wavelength within the range of experiment.

An error, in the measurement, of 0.1 % at 80 % transmittancy reading causes the relative error of about 0.5 % in the determination. Therefore this will be a limit of accuracy.

If this is the case, as little as 0.3 γ /ml of iron and 4.5×10^{-5} M/l of tropolone may be determined satisfactorily.

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