

IODINE, IODINE MONOCHLORIDE AND BROMINE INTERACTION WITH 1,3,5-TRIAZINE IN CHLOROFORM SOLUTION

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Abstract: The interaction between 1,3,5-triazine as n-donor, with I₂, ICl and Br₂ as σ -acceptor have been studied spectrophotometrically in chloroform at 25 °C. The results obtained for iodine indicate that of the complex [triazineI ^{δ^+} -I ^{δ^-}] is formed through an equilibrium step which is followed by slow conversion to [triazineI⁺I] and a fast reaction with iodine to produce [triazineI⁺I₃], through nonequilibrium steps. The equilibrium and rate constants of the recent reactions were measured. In the case of ICl the formation of [(triazine)₂I⁺ICl₂⁻] by an equilibrium step is confirmed. The stability constant of the resulting complex was evaluated from the computer fitting of the absorbance vs. mole ratio data. The interaction with bromine involves only partial charge transfer which results in a blue-shift and an increase in the molar absorptivity (ϵ) of Br₂. Based on the comparison of the results, it has been concluded that the interactions vary in the order ICl $\gg$ I₂ > Br₂.

Key Words: Spectrophotometry, Iodine monochloride, Iodine, Bromine, Charge-transfer

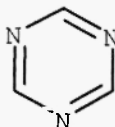
Introduction

The iodine molecular complexes with a wide variety of n-donors have been extensively studied [1-5]. Some of the resulting charge transfer complexes have shown interesting physical properties [2-5]. Moreover, some attentions have been attributed to halogens and interhalogens [6-8]. However, it seems that the studies on interhalogens are considerably less than the iodine ones. On the other hand, although the comparative studies of halogens and interhalogens would be more informative, much research has been done separately. Thus, more investigations on halogens other than iodine and also comparative studies would be needed. To develop our pervious investigations on molecular complexes [9-18], we report here the results of our study on the interaction between I₂, ICl and Br₂ with 1,3,5-triazine in chloroform solution.

Experimental

Reagent grade iodine (Merck) was sublimed and stored in a desecrator over P₂O₅. Iodine monochloride, bromine and 1,3,5-triazine (all obtained from Merck company) with highest purity were used as received. Tetraethylammonium chloride (TEACl) was prepared from tetraethylammonium chloride-monohydrate (Merck). Before use, molecular sieves dried the corresponding solution.

1,3,5-Triazine

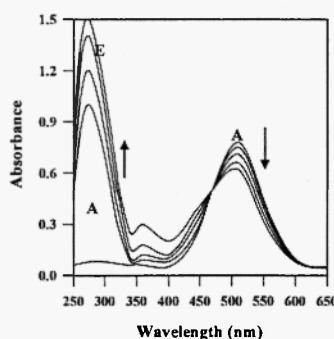


All UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer and absorbance measurements were made with a Philips PU875 spectrophotometer at 25 $\pm$ 1°C.

In order to obtain UV-Vis spectra, 3 mL of 1.85 $\times$ 10⁻⁴ M iodine, 8.0 $\times$ 10⁻³ iodine monochloride and 9.60 $\times$ 10⁻⁵ M bromine were transferred into 1.00 cm quartz cell and titrated with a concentrated solution of 1,3,5-triazine by a 100- μ L Hamilton syringe. Each spectrum was recorded immediately after the titrant addition. The same procedure was followed for absorbance measurement.

Results and Discussions

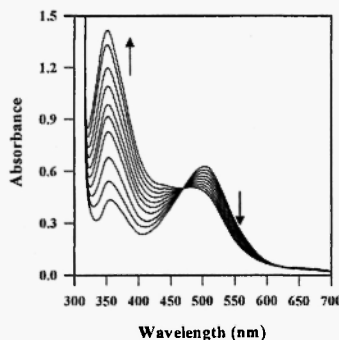
A. Iodine: The absorption spectra of 8.73×10^{-4} M iodine solution in the presence of 0.00, 0.098, 0.159, 0.245 and 0.358 M solutions of 1,3,5-triazine are shown in Figures 1A-1E, respectively. As it can be seen, upon addition of triazine to iodine solution, i) a well defined isosbestic point is observed at 475 nm, ii) the intensity of iodine band at 510 nm decreases and iii) two new bands are appeared at 275 and 364 nm. The observation of an isosbestic point along with the decrease in the intensity of iodine band indicates that triazine and iodine have a simple complexation equilibrium [19]. On the other hand, the absorption maxima at 275 and 364 nm are characteristic of the formation of triiodide ion in the form of contact ion-pair. So, the appearance of these bands shows that triiodide is the final complexation adduct [10-13].



Absorption spectra of 8.73×10^{-4} M of pure iodine solution (A) and its mixture with 0.098 (B), 0.159 (C), 0.245 (D) and 0.358 M (E) 1,3,5-triazine.

Figure-1

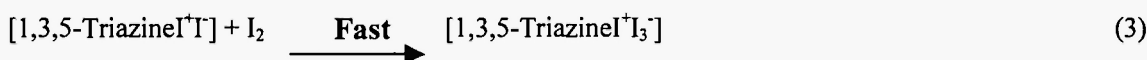
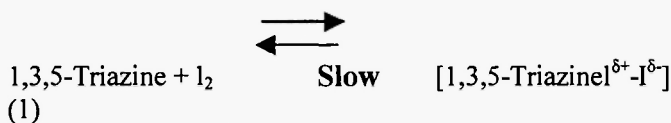
Figure-2 shows the absorption spectra of 8.73×10^{-4} M of iodine solution in the presence of 0.245 M of 1,3,5-triazine. The spectra have been recorded in time intervals of 2 minutes. The gradual increase in the intensity of the 364 nm band is accompanied by the simultaneous decrease of 510 nm band. These phenomena can be described by a reaction leading to the formation of triiodide ion, which involves iodine consumption. During the course of reaction, the isosbestic point at 475 nm is maintained. Thus, it can be concluded that the kinetic behavior is in accord with the initial equilibrium reaction.



Absorption spectra of 8.73×10^{-4} M of iodine solution in the presence of 0.245 M 1,3,5-triazine in time period of 2 min.

Figure-2

According to above results, it can be said that 1,3,5-triazine and iodine have fast pre equilibrium followed by a nonequilibrium reaction. This produces triiodide through consumption of iodine. The corresponding equations are suggested as follows:



The suggested mechanism can be confirmed by two similar works which were done for pyridine-I₂ system [20] and the reaction of tetrabutylammonium iodide and I₂ that produce triiodide ion as a product [21].

To evaluate the stability constant of the resulting molecular complex (Eqn. 1), the decrease in the intensity of iodine band immediately after addition of 1,3,5-triazine was followed. It should be noted that, the concentration of [1,3,5-TriazineI^TI] is negligible at this stage. Thus, it can be assumed that only a simple equilibrium exit. The formation constant, K_f, was determined according to the following procedure. The formation constant of the complex is equal to:

$$K_f = [1,3,5\text{-TriazineI}^{\delta+}\text{-I}^{\delta-}] / [\text{I}_2][1,3,5\text{-Triazine}] \quad (4)$$

The equilibrium concentration of free iodine is equal to:

$$[\text{I}_2]_{\text{eq}} = [\text{I}_2]_0((\text{Abs})_{\text{eq}}/(\text{Abs})_0) \quad (5)$$

The equilibrium concentrations of other species are:

$$[1,3,5\text{-TriazineI}^{\delta+}\text{-I}^{\delta-}]_{\text{eq}} = [\text{I}_2]_0 - [\text{I}_2]_{\text{eq}} \quad (6)$$

$$[1,3,5\text{-triazine}]_{\text{eq}} = [1,3,5\text{-triazine}]_0 - [1,3,5\text{-TriazineI}^{\delta+}\text{-I}^{\delta-}]_{\text{eq}} \quad (7)$$

The combination of Eqs. 4-7 yield:

$$K_f = \frac{1 - [(\text{Abs})_{\text{eq}}/(\text{Abs})_0]}{[(\text{Abs})_{\text{eq}}/(\text{Abs})_0]([1,3,5\text{-Triazine}]_0 - [\text{I}_2]_0(1 - [(\text{Abs})_{\text{eq}}/(\text{Abs})_0]))} \quad (8)$$

The results of K_f, from four experiments are 0.67, 0.70, 0.72 and 0.68 M⁻¹, respectively. The average of formation constant is 0.69±0.02 M⁻¹. The good agreement between the results indicates that the approximations are valid.

In order to investigate the kinetics of triiodide formation, the absorbance of 364 nm band was monitored as a function of time at 25°C. The absorbance changes were found to be adopted with a first order kinetics [22]. The rate constant was obtained from the slope of the corresponding linear Ln(A_t/A₀) vs. t plot (Figure-3) that is k = 0.07±0.01 s⁻¹.

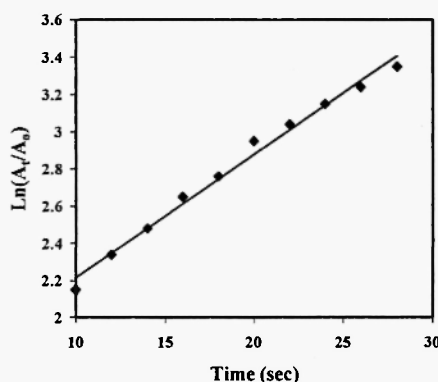
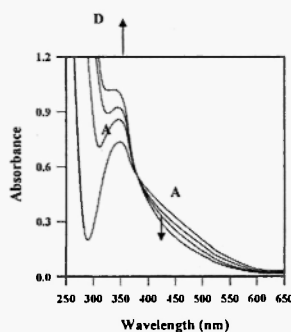
Plot of $\ln(A_t/A_0)$ vs. time for 1,3,5-triazine- I_2 system at 364 nm.

Figure-3

Finally, the conductance of $CHCl_3$, 8.73×10^{-4} M of iodine, 0.358 M 1,3,5-triazine and 8.73×10^{-4} M of iodine in the presence of 0.358 M triazine were measured, giving the values 1.3, 1.3, 12.0 and 13.0 μS , respectively. The small increase in the conductance during complexation shows that the complex is mainly ion pair and there is little free ion in the solution.

B. Iodine monochloride: The absorption spectrum of 5.80×10^{-3} M of ICl is shown in Figure-4A. The spectrum shows a λ_{max} at 350 and a shoulder at 475 nm. The absorption spectra of ICl in the presence of 5.80×10^{-3} M, 1.16×10^{-2} M, 1.74×10^{-2} M and 2.32×10^{-2} M of 1,3,5-triazine are shown in Figures-4B-4D, respectively. The addition of varying concentrations of 1,3,5-triazine to ICl solutions causes an increase in the intensity of 350 nm band along with a blue-shifted in going from A to D. Decrease in the shoulder at 475 nm and the appearance of an isosbestic point at 375 nm were also observed. Such observations indicate that an equilibrium reaction exist between ICl and 1,3,5-triazine.

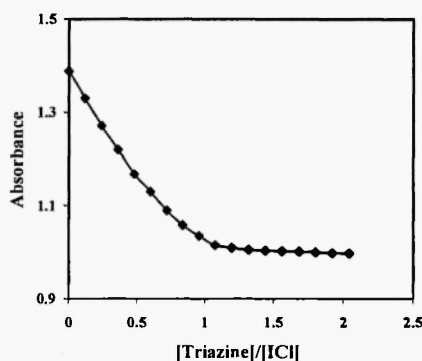
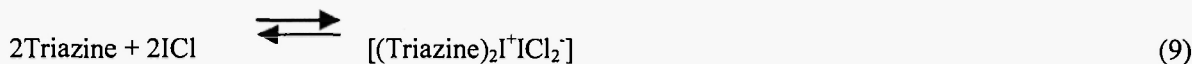


Absorption spectra of 5.80×10^{-3} M of pure iodine monochloride solution (A) and its mixture with 5.80×10^{-3} (B), 1.16×10^{-2} M (C) and 1.74×10^{-2} M (D) 1,3,5-triazine.

Figure-4

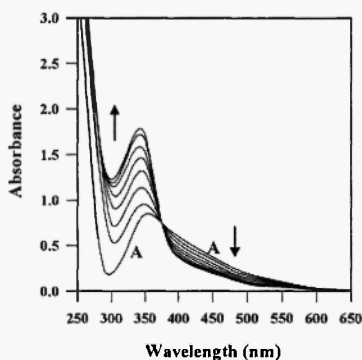
The absorbance vs. 1,3,5-triazine/ICl mole ratio plot [23], obtained at 400 nm (Fig. 5), clearly indicates the formation of 1:1 complex in chloroform solution. On the other hand, the similarity between

the spectra of 1,3,5-triazine-ICl (Figure-4) with that of TEACl-ICl mixtures (Figure-6) proves that identical products were obtained in both cases. The ICl_2^- is the most probable adduct of the interaction between TEACl and ICl. Thus, it can be concluded that 1,3,5-triazine and ICl also produce ICl_2^- . Because of having 1:1 stoichiometry (Figure-5), the following reaction can be suggested.



Absorbance vs. [1,3,5-triazine]/[ICl] mole ratio plot obtained at 400 nm.

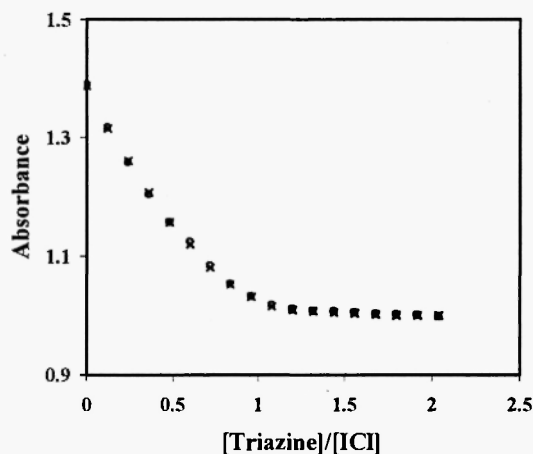
Figure-5



The absorption spectrum of 7.50×10^{-3} M of ICl (A) and its mixture with 4.80×10^{-4} (B), 9.60×10^{-4} (C), 1.44×10^{-3} (D), 1.92×10^{-3} (E), 2.40×10^{-3} (F), 2.88×10^{-3} (G) and 3.36×10^{-3} M (H) of TEACl.

Figure-6

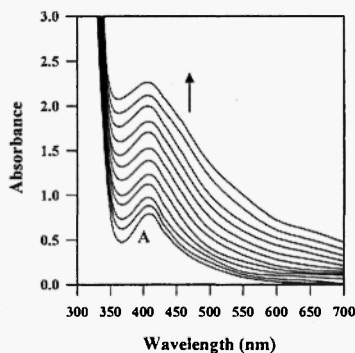
To evaluate the formation constant of the above complex, K_f , from the absorbance mole ratio data, a nonlinear least square curve-fitting program KINFIT was used [24]. The program is based on the iterative adjustment of the calculated values of absorbance to the observed values by using either the Wentworth matrix technique [25] or the Powell procedure [26]. Adjustable parameters are K_f and ϵ , where ϵ is the molar absorptivity of iodine monochloride. The output of KINFIT program comprises the refined parameters, the sum-of-squares and the standard deviation of the data. Fig. 7 shows the resulting computer fit of the absorbance-mole ratio data. As seen, the fair agreement between the observed and calculated absorbances further support the existence of the 1:1 (or 2:2) complexation between triazine and ICl. The $\log K_f$ value by this procedure is 5.4 ± 0.1 .



Computer fit of absorbance vs. Triazine/ICl mole ratio at 400 nm. (x) experimental points and (O) calculated points.
Figure-7

Similar to iodine, in this case a small increase in conductance upon complexation was also observed.

C: Bromine: The absorption spectrum of 9.6×10^{-5} M of bromine in the presence of various quantities of 1,3,5-triazine are shown in Fig. 8. The triazine/ Br_2 mole ratios are 0.0-12, respectively. The absence of isosbestic point indicates that triazine and Br_2 have a nonequilibrium interaction. On the other hand, shift to lower wavelengths and an increase of the intensity of bromine band is observed by stepwise addition of triazine. Perturbation of locally excited transitions has been usually observed [20]. This may be a direct result of the partial transfer of an electron from triazine to an antibonding orbital in the bromine, which can increase the effective size of the acceptor so that the excitation energy was increased [27].



Absorption spectra of 9.60×10^{-5} M of pure bromine solution (A) and at different mole ratios of [1,3,5-triazine]/ $[\text{Br}_2]$ 0.0-12.0.

Figure-8

The increase in molar excitation coefficient of bromine also originates from the increase in effective size. In fact, higher effective size causes a higher absorption cross section, which will increase the ϵ of bromine [28]. Anyhow, the spectra shows that triazine and Br_2 have a weak interaction in which the electronic composition of bromine is somewhat perturbed.

Conclusions

According to the results presented it can be concluded that:

- 1) ICl is a much better acceptor than iodine because of its polar nature, and form a much stronger complex.
- 2) Bromine has the weakest interaction with triazine among the diatomic halogen acceptors.
- 3) The separation of I^+ and Cl^- occur very fast. However, the separation of I^+ and I^- occurs slowly.
- 4) Due to observation of a small increase in conductance, it can be concluded that the complexes of Triazine-ICl and Triazine- I_2 are mostly in the form of ion pair.
- 5) In all cases, the 1,3,5-triazine behaves as an n-donor.

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Received on November 27, 2005