

# Complexes of the Picolinium Ion and Picolinic Acid with Cresol Red

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A spectrophotometric analysis of acidified aqueous solutions of picolinic acid and cresol red indicator suggests the existence of two complexes. Both the picolinium ion, a moderately strong acid, and picolinic acid, a weak acid, form complexes with the negative basic cresol red indicator species. The equilibrium constants for the formation of these complexes at 25 °C are  $5.3 \pm 0.6$  and  $1.6 \pm 0.3$ , respectively. The existence of complexes of moderately strong acids with indicators has been known for some years. However, complexes between a weak acid and an indicator appear not to have been previously reported.

It has been recognized for some time that some moderately strong acids ( $pK < 2$ ) form complexes with acid–base indicators.<sup>1</sup> Specifically, the protonated forms of such acids interact with the basic indicator species to form complexes whose spectral properties are similar to those of the protonated indicator. These complexes can have a dramatic effect on the values of the acid dissociation constants derived from the spectrophotometric data. As an example, consider an aqueous solution of trichloroacetic acid ( $0.1 \text{ mol dm}^{-3}$ ) and cresol red (*o*-cresolsulfonephthalein) indicator ( $\sim 10^{-5} \text{ mol dm}^{-3}$ ). The ionic strength of the solution is adjusted to  $0.25 \text{ mol dm}^{-3}$ . The pH of the solution is controlled by the trichloroacetic acid.

The pH of the solution can be estimated by measuring the absorbance of the indicator. This estimate relies on a calibration experiment that measures the indicator absorption as a function of pH. These data can be used to calculate the indicator acidity constant  $K_{\text{HIn}}$  and molar absorptivities  $\epsilon_{\text{In}}$  and  $\epsilon_{\text{HIn}}$  for the basic and protonated forms of the indicator. Using these parameters, a simple calculation provides the pH of the trichloroacetic acid mixture. For the specific solution described in the previous paragraph,  $[\text{H}^+]$  is found to be essentially identical ( $\pm 1\%$ ) to the concentration of the trichloroacetic acid, suggesting that trichloroacetic acid is completely dissociated. Since the value of  $pK_{\text{a}}$  for this acid is approximately equal to 0.5, this result is clearly fallacious.

The failure of the spectrophotometric method to account for the dissociation properties of trichloroacetic acid (HTCA) arises from two factors. First, the formation constant of the acid–indicator complex  $\text{HTCA}\cdot\text{In}^-$  in the reaction  $\text{HTCA} + \text{In}^- = \text{HTCA}\cdot\text{In}^-$  is comparable to the formation constant of  $\text{HIn}$  in the reaction  $\text{H}^+ + \text{In}^- = \text{HIn}$ . Second, the spectral properties of  $\text{HTCA}\cdot\text{In}^-$  are similar to those of  $\text{HIn}$ . These factors suggest that the basic form of the indicator cresol red does not distinguish between an aqueous  $\text{H}^+$  ion and an  $\text{H}^+$  ion associated with trichloroacetate ion.

Trihaloacetic, dihaloacetic, and squaric acids exhibit similar complexation behaviors in the presence of the indicators cresol red, picric acid, and 4-phenylazodiphenylamine.<sup>2</sup> All of these complexes involve the electrically neutral species of the pH controlling acid. Because the electrical charge of the complexing entities is likely to

influence the complexation interactions, we thought that it would be informative to study the complexation behavior of a cationic acid species.

For the cationic acid, we chose the picolinium ion, the protonated form of picolinic acid (1-pyridine carboxylic acid), denoted here as  $\text{HP}^+$ . Picolinic acid itself will be denoted P. The temperature dependence of the acid dissociation constant of the ion ( $\text{HP}^+ = \text{H}^+ + \text{P}$ ) has been obtained recently from a pH potentiometric method using similar experimental conditions as those of the present work.<sup>3</sup> At 25 °C, the dissociation constant for  $\text{HP}^+$  is approximately 0.15. Cresol red, which is chemically stable and readily soluble in aqueous solution, is a suitable indicator. Picolinic acid, the basic species, is a sufficiently weak acid ( $pK \sim 5.3$ ) so that its dissociation can be neglected.

## Materials

Samples of picolinic acid and cresol red were obtained from the Aldrich Chemical Co. and used without further purification. Picolinic acid samples were analyzed to be 99.6–99.8% by alkometric titration. Even concentrated solutions of the acid were water white. All other materials were reagent grade.

## Spectrophotometric Measurements

All the spectrophotometric data were obtained using Beckman Acta CIII spectrophotometers equipped with thermostated cell holders. In each series of experiments, two independent solutions of the indicator were prepared, and two different spectrophotometers were used. Both instruments were adjusted to 516 nm,  $\lambda_{\text{max}}$  for  $\text{HIn}$ , and both were set to provide a 1 nm band-pass. The 1.000 cm quartz cuvette was fitted with a temperature probe. Special care was taken to ensure thermal equilibration. On the basis of repeated measurements on several solutions carried out at different times, we determined that the standard deviation in the absorbance data,  $\sigma$ , was approximately 0.002 A.

## Determination of the Indicator Parameters

The indicator parameters  $K_{\text{HIn}}$ ,  $\epsilon_{\text{HIn}}$ , and  $\epsilon_{\text{In}}$  were determined from measurements using two separate sets of solutions. These two sets were prepared from separate stocks of concentrated solutions of cresol red, HCl, and KCl.

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The first set consisted of eight solutions, each containing  $4.5 \times 10^{-5}$  mol dm<sup>-3</sup> cresol red. The concentration of H<sup>+</sup> in the eight solutions ranged from  $3 \times 10^{-5}$  mol dm<sup>-3</sup> to 0.25 mol dm<sup>-3</sup>. The ionic strength of each solution was adjusted to 0.25 mol dm<sup>-3</sup> with KCl. The absorbances ranged from 0.08 A to 1.7 A. The temperature was maintained at 20 °C. The second set consisted of six solutions with H<sup>+</sup> concentrations similar in value to those in the first set, but with the concentration of cresol red set equal to  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup>. Experiments with this second set were performed at five temperatures ranging from 18 °C to 43 °C. The absorbances ranged from 0.04 A to about 0.9 A.

The absorbance versus composition data were fit to the following set of model equations:

$$K_{\text{In}} = \gamma_{\text{H}}\gamma_{\text{In}}[\text{H}^+][\text{In}^-]/\gamma_{\text{HIn}}[\text{HIn}] \quad (1)$$

$$C_{\text{In}} = [\text{HIn}] + [\text{In}^-] \quad (2)$$

$$A = \epsilon_{\text{In}}[\text{In}^-] + \epsilon_{\text{HIn}}[\text{HIn}] \quad (3)$$

where  $\gamma$  and  $\epsilon$  are the ionic activity coefficients and molar absorptivities, respectively. The activity coefficients were obtained from the extended Debye–Huckel equation using the temperature-dependent  $A$  and  $B$  coefficients given by Robinson and Stokes.<sup>4</sup> The sizes of the H<sup>+</sup> and In<sup>-</sup> ions were estimated to be 0.9 nm and 1.2 nm, respectively.

The optimized values of the three indicator parameters  $K_{\text{In}}$ ,  $\epsilon_{\text{In}}$ , and  $\epsilon_{\text{HIn}}$ , were calculated using the Levenberg–Marquardt algorithm as implemented by Press et al.<sup>5</sup> This algorithm minimizes the goodness-of-fit parameter  $X^2$ , defined by

$$X^2 = \sum [A(\text{obs}) - A(\text{calc})]^2/\sigma^2 \quad (4)$$

where  $\sigma$ , the uncertainty in the absorbance measurements, was set equal to 0.002 A.

In each regression, the value of  $X^2$  was less than or equal to the number of degrees of freedom, indicating a good fit of the data to the mathematical model. The values of  $K_{\text{In}}$  obtained from the second set of solutions increased monotonically as a function of temperature, ranging from 0.0514 at 18.5 °C to 0.0592 at 43.1 °C. The value of  $K_{\text{In}}$  at 20 °C obtained from the first set of solutions was 0.0517, in excellent agreement with the results from the second set. The standard error estimates of the  $K_{\text{In}}$  were all less than 1% of their values. The values of the  $\epsilon_{\text{HIn}}$  decreased by about 4% over the temperature range from  $4.9 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> to  $4.7 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> and had relative uncertainties of about 0.4%. Values of  $\epsilon_{\text{In}}$  showed a similar temperature dependence. They decreased from about  $1.7 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> to  $1.6 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> with similar uncertainties.

The agreement between the values of  $K_{\text{In}}$  at the two different indicator concentrations, the smooth temperature dependence of each of the regression parameters, and the appropriate values of  $X^2$  indicate that the simple model of eqs 1–3 accurately describes the behavior of cresol red in solutions containing HCl and KCl.

### Complexes of Picolinic Acid with Cresol Red

We prepared 10 solutions each containing cresol red, picolinic acid, and HCl. The concentration of cresol red in each solution was  $2.5 \times 10^{-5}$  mol dm<sup>3</sup>. The concentrations of picolinic acid ranged from 0.15 to 0.4 mol dm<sup>-3</sup>, while those of HCl ranged from 0.1 to 0.25 mol dm<sup>-3</sup>. The ratio of moles of HCl to moles of P ranged from about 0.3 to 1.3.

The ionic strength was adjusted to 0.25 mol dm<sup>-3</sup> with KCl. The pH of one of the solutions was adjusted to 4.0 with KOH. The absorbances, which ranged from 0.04 A to 0.7 A, were determined with the same spectrophotometer and the same temperature range used to determine the indicator parameters.

A second set of 12 solutions, all at 20.0 °C, contained  $4.5 \times 10^{-5}$  mol dm<sup>-3</sup> cresol red. The molar ratios HCl/P were similar to those of the first set, but the concentrations of these components were somewhat lower. The values of the absorbance were between 0.08 A and 1.3 A.

The regression analysis of the absorbance versus composition data using a “classical” model in which the primary species are HP<sup>+</sup>, P, H<sup>+</sup>, HIn, and In<sup>-</sup> (no complexes present) gave poor values of  $X^2$ . In addition, the value of  $K_{\text{HP}}$ , the picolinium ion dissociation constant, obtained from the regression was clearly different from, smaller by a factor of 2, the pH potentiometric estimate of  $K_{\text{HP}} = 0.15$  mentioned above. The potentiometric result was obtained under experimental conditions very similar to those employed in this work, and the calculations used the same estimates of the activity coefficients. Consequently, we concluded that the classical model cannot be used for a spectrophotometric study of this system.

To proceed, we observed that, in the range from 400 nm to 600 nm, the spectra of solutions containing HCl and cresol red are almost identical (though not superimposable) to those containing HCl, picolinic acid, and cresol red. All the spectra consist of two broad peaks. One peak, centered at approximately 435 nm, results from the absorption of both HIn and In<sup>-</sup>. The appearance of this peak is independent of whether P is present. The other peak, centered at approximately 516 nm, results almost entirely from the absorbance of HIn. Unlike the peak at 435 nm, the peak at 516 nm is shifted approximately 1 nm to longer wavelengths in the presence of P. A series of HCl–cresol red mixtures displays a well-defined isospeptic point. However, a similar series containing P showed a very small displacement of the isospeptic point with varying concentration of both HCl and P. These observations suggest the existence of at least one complex between one or more of the picolinic acid species and the indicator.

To allow for the effect of these possible complexes, we adjoined the following two equations to our model to describe the equilibria  $\text{P} + \text{In}^- = \text{P}\cdot\text{In}^-$  and  $\text{HP}^+ + \text{In}^- = \text{HP}^+\cdot\text{In}^-$

$$K_{\text{PIn}} = \gamma_{\text{PIn}}[\text{P}\cdot\text{In}^-]/\gamma_{\text{P}}\gamma_{\text{In}}[\text{P}][\text{In}^-] \quad (5)$$

$$K_{\text{HPIn}} = \gamma_{\text{HPIn}}[\text{HP}^+\cdot\text{In}^-]/\gamma_{\text{HP}}\gamma_{\text{In}}[\text{HP}^+][\text{In}^-] \quad (6)$$

The absorbance is now given by

$$A = \epsilon_{\text{In}}[\text{In}^-] + \epsilon_{\text{HIn}}[\text{HIn}] + \epsilon_{\text{PIn}}[\text{P}\cdot\text{In}^-] + \epsilon_{\text{HPIn}}[\text{HP}^+\cdot\text{In}^-] \quad (7)$$

The values of  $K_{\text{In}}$ ,  $\epsilon_{\text{HIn}}$ , and  $\epsilon_{\text{In}}$  are those obtained from the regressions on the indicator data. The sizes of the HP<sup>+</sup> and P·In<sup>-</sup> ions were estimated to be 0.6 nm and 1.4 nm, respectively.

The regression analysis determined the optimized values of the thermodynamic equilibrium constants  $K_{\text{HPIn}}$  and  $K_{\text{PIn}}$  and the molar absorptivities  $\epsilon_{\text{HPIn}}$  and  $\epsilon_{\text{PIn}}$ . The results of our calculations appear in Table 1. The molar absorptivities are not listed, since their values depend on the actual indicator concentrations, which are only approximately known. We do provide the dimensionless parameters  $\epsilon_{\text{HPIn}}/$

**Table 1. Thermodynamic Formation Constants and Relative Molar Absorptivities for the Complexes HP<sup>+</sup>·In<sup>-</sup> and P·In<sup>-</sup>**

<i>t</i> , °C	<i>X</i> <sup>2</sup> /d.f.	<i>K</i> <sub>HPIn</sub>	$\epsilon_{\text{HPIn}}/\epsilon_{\text{HIn}}$	<i>K</i> <sub>PIn</sub>	$\epsilon_{\text{PIn}}/\epsilon_{\text{HIn}}$
Series 1: 10 solutions, <i>C</i> <sub>In</sub> = 2.5 × 10 <sup>-5</sup> mol dm <sup>-3</sup>					
18.5	0.6 <sup>a</sup>	5.7 ± 0.6 <sup>b</sup>	0.31 ± 0.07	1.8 ± 0.3	0.042 ± 0.006
25.0	0.5	5.3 ± 0.6	0.29 ± 0.08	1.6 ± 0.3	0.044 ± 0.007
29.3	0.6	5.1 ± 0.6	0.30 ± 0.08	1.6 ± 0.3	0.042 ± 0.009
35.9	0.3	4.8 ± 0.6	0.30 ± 0.09	1.5 ± 0.4	0.044 ± 0.008
43.1	0.3	4.1 ± 0.6	0.25 ± 0.11	1.2 ± 0.3	0.043 ± 0.010
Series 2: 12 solutions, <i>C</i> <sub>In</sub> = 4.5 × 10 <sup>-5</sup> mol dm <sup>-3</sup>					
20.0	0.8	6.7 ± 1.3	0.43 ± 0.09	2.4 ± 0.6	0.040 ± 0.002

<sup>a</sup> *X*<sup>2</sup> divided by the number of degrees of freedom. <sup>b</sup> Uncertainties are central 68.3% confidence intervals obtained using Monte Carlo simulation (see text).

$\epsilon_{\text{HIn}}$  and  $\epsilon_{\text{PIn}}/\epsilon_{\text{HIn}}$ , whose values are independent of *C*<sub>In</sub>. These parameters compare the absorptivities of the two complexes with those of the protonated indicator species. The uncertainties given in the table represent central 68.3% confidence intervals of the parameters. They were derived from Monte Carlo calculations (normally distributed uncertainties; *N* = 1000,  $\sigma$  = 0.002 Å).

Using the values of the equilibrium constants given in Table 1 and the equations for the equilibrium constants and for the mass balance relationships, we find that both the HP<sup>+</sup>·In<sup>-</sup> and the P·In<sup>-</sup> complexes constitute a significant fraction of the total indicator concentration. As an example, we calculate the distribution of the various cresol red species in a mixture consisting of equal concentrations (0.25 mol dm<sup>-3</sup>) of HCl and picolinic acid. We find the following distribution of species: [HIn]/[In<sup>-</sup>]/[HP<sup>+</sup>·In<sup>-</sup>]/[P·In<sup>-</sup>] = 0.4:0.3:0.2:0.06. At higher ratios of picolinic acid to HCl, the proportion of P·In<sup>-</sup> increases and its concentration can exceed that of HP<sup>+</sup>·In<sup>-</sup>.

Can the data be described by a simpler model involving a single complex? We performed calculations in which the value of *K*<sub>PIn</sub> was fixed at zero, corresponding to a model with only the HP<sup>+</sup>·In<sup>-</sup> complex, and then performed the analogous calculations with *K*<sub>HPIn</sub> set equal to zero, corresponding to a model with only the P·In<sup>-</sup> complex. For the case in which only HP<sup>+</sup>·In<sup>-</sup> is present, *X*<sup>2</sup> is almost an order of magnitude too large, and more significantly, the optimized value of the molar absorptivity is negative with  $\epsilon_{\text{HPIn}}/\epsilon_{\text{HIn}} = -1.5$ . Clearly, this result is chemically impossible. For the case in which only P·In<sup>-</sup> is present, *X*<sup>2</sup> is more than 2 orders of magnitude too large. We conclude that the model describing the data must include both complexes.

As shown in Table 1, the values of *X*<sup>2</sup>/d.f. (degree of freedom) are always slightly less than unity. These values correspond to rms deviations of 0.001 Å – 0.002 Å between the experimental and calculated absorbance values. The equilibrium constants and relative molar absorptivities from the 10-solution series at 18.5 °C are in good agreement with the values obtained at 20.0 °C using the 12-solution series. As one would expect, the temperature dependence of both the equilibrium constants and extinction coefficient values is smooth.

Our model, containing the two complexes HP<sup>+</sup>·In<sup>-</sup> and P·In<sup>-</sup> depends on the four input parameters: *K*<sub>HP</sub>, *K*<sub>HIn</sub>,  $\epsilon_{\text{HIn}}$ , and  $\epsilon_{\text{In}}$ . We investigated the effect of errors in these parameters. The estimated uncertainty in *K*<sub>HP</sub> is given as 0.002 in ref 3. We added twice this uncertainty to the value of *K*<sub>HP</sub> (a perturbation of approximately 3%) and repeated the regressions. *X*<sup>2</sup> increased only slightly. The optimized values of *K*<sub>HPIn</sub> and  $\epsilon_{\text{PIn}}$  changed by less than 1% while *K*<sub>PIn</sub> and  $\epsilon_{\text{HPIn}}$  were displaced by about 10% and 5%, respectively.

However, even these latter two displacements are smaller than the uncertainties of these parameters.

Since the other three input parameters, *K*<sub>In</sub>,  $\epsilon_{\text{HIn}}$ , and  $\epsilon_{\text{In}}$  were obtained in the same regression procedure, they are not independent quantities. We evaluated the effect of errors in these parameters by first adding to *K*<sub>In</sub> two times its standard deviation. This represents a perturbation of 1.2%. Keeping this parameter fixed, the indicator absorption versus composition data were reevaluated to provide optimized molar absorptivities. It is worth noting that the value of *X*<sup>2</sup>/d.f. increased substantially in these regressions, by a factor of about 3. The perturbed *K*<sub>In</sub> and the molar absorptivities obtained from these regressions were then used as the fixed parameters in the regressions involving the complexes. The four regression parameters *K*<sub>PIn</sub>, *K*<sub>HPIn</sub>,  $\epsilon_{\text{HPIn}}$ , and  $\epsilon_{\text{PIn}}$  were displaced from their optimized values by 10%, 8%, 10%, and 3%, respectively. These changes are too small to affect our analysis. Consequently, we conclude that both complexes, HP<sup>+</sup>·In<sup>-</sup> and P·In<sup>-</sup>, play a role in the picolinic acid/cresol red equilibria.

## Discussion

We begin by comparing some of the properties of the HP<sup>+</sup>·In<sup>-</sup> complex with those of corresponding complexes of other moderately strong acids.<sup>2</sup> For the sake of this comparison we note that, for Cl<sub>3</sub>CCO<sub>2</sub>H (p*K* ~ 0.5), the value of the thermodynamic complexation constant with In<sup>-</sup> is approximately 14 near 25 °C. For the somewhat weaker acid, Cl<sub>2</sub>HCCO<sub>2</sub>H, with p*K* ~ 1.3, the complexation constant is approximately 1.0. For both acids, the ratio  $\epsilon_{\text{complex}}/\epsilon_{\text{HIn}}$  is approximately equal to 1.0. This behavior is typical of the polyhaloacids in their complexes with cresol red.

The picolinium ion complexation constant follows the pattern of decreasing complex strength with decreasing acidity. The formation constant for HP<sup>+</sup>·In<sup>-</sup>, approximately 5 at 25 °C, falls between those for tri- and dichloroacetic acids, as does the p*K* of the acid, which is approximately 0.9. However, the color intensity of the HP<sup>+</sup>·In<sup>-</sup> complex, with  $\epsilon_{\text{HPIn}}/\epsilon_{\text{HIn}}$  of about 0.3, is markedly different from those of the corresponding haloacetic acid complexes. This behavior is not unique. Other moderately strong acids also display  $\epsilon_{\text{complex}}/\epsilon_{\text{HIn}}$  values different from unity. For example, for the squaric acid complex of cresol red at 516 nm,  $\epsilon_{\text{complex}}/\epsilon_{\text{HIn}}$  is approximately 0.7.

The P·In<sup>-</sup> complex, which is comprised of the indicator and a weak acid (p*K* near 5.3), is highly unusual. At the present time no other weak acid complexes with indicator species have been reported. In an attempt to rationalize the existence of this complex, we note that the phenomenon of indicator complexation by a moderately strong acid has been interpreted in terms of the structure of the associated forms of the acid. The classical picture had represented the associated acid as a covalently bonded structure. In contrast, it is now believed that the associated form consists, at least in part, of an ion pair involving the anion and a solvated or partially solvated proton.<sup>6,7</sup> The substantially solvated proton in the associated acid is then capable of interaction with In<sup>-</sup>. Because In<sup>-</sup> appears to form a complex with picolinic acid, it seems likely that the acidic proton of this weak acid behaves in a similar fashion. That is, the acidic proton of picolinic acid seems to be available for interaction with In<sup>-</sup>.

In the classical representation, picolinic acid is thought to exist as either one or a mixture of two tautomeric forms involving protonated nitrogen or carboxylate sites. Both these forms feature a covalently and tightly bound proton

not available for interaction with other chemical species. Such a model does not seem to be able to account for the properties of the complexes described here.

We believe that, in aqueous solution, picolinic acid forms an ion pair in which a partially solvated proton is bound or distributed between the two basic sites of the picolinate base. It seems possible that the ion pair provides a bridge for a loose association between the acid and indicator species. The weakness of this interaction is reflected in the values of  $\epsilon_{\text{PIn}^-}/\epsilon_{\text{HIn}^-}$ , which are all approximately 0.04 at 516 nm. The ratio of the molar absorptivities of  $\text{In}^-$  and  $\text{Hin}$  is approximately 0.035 at the same wavelength. That is, the absorptivity of the  $\text{P}\cdot\text{In}^-$  complex is only about 20% greater than that of the uncomplexed  $\text{In}^-$  species. This result seems to suggest that the interaction between P and  $\text{In}^-$  fails to promote the type of structural and electronic alteration in the indicator that is responsible for the color change observed with the  $\text{H}^+$  or  $\text{HP}^+$  species.

This interpretation of our results is clearly conjectural. Nevertheless, whatever the mechanism of the interactions between  $\text{HP}^+$  and P with  $\text{In}^-$ , these interactions result in the formation of the complexes  $\text{HP}^+\cdot\text{In}^-$  and  $\text{P}\cdot\text{In}^-$ . The

latter complex appears to be particularly important. To the best of our knowledge, no similar attraction between a weak acid (e.g., acetic acid or benzoic acid) and  $\text{In}^-$  has been reported. It appears as though the  $\text{P}\cdot\text{In}^-$  complexation involves specific properties of the picolinic acid species that deserve further investigation.

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