Interaction of Urea with *p*-Nitrophenol

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Urea(U) can abstract H^+ ion from *p*-nitrophenol (PNP) forming a hydrogen bonded ion pair (proton-transfer complex $PNP^- \cdots H^+U$) of 1 : 1 stoichiometry with a formation constant 0.42 at 303 K. Infrared spectral measurements of the uronium phenolate and uronium nitrate have supported that the proton transferred from PNP is attached to the oxygen center of the amide. The needle shaped light yellow urea–PNP adduct is fairly stable under ordinary conditions decomposing at 398 K. The standard free energy, enthalpy, and entropy of formation determined from spectrophotometric and calorimetric methods have been found to be 3.62 kJ mol^{-1}, −13.30 kJ mol^{-1}, and −57.5 J mol^{-1} K^{-1}, respectively at 303 K.

Recent studies have indicated that urea can significantly affect the hydrogen ion activity of strong acids in aqueous medium.[1–4] It has been pointed out that the oxygen atom of the amide provides the preferential binding site for the hydrogen ion. Earlier X-ray, IR, and NMR studies have also supported that the binding of urea and strong acids occur at the oxygen rather than the nitrogen center of the amides.[5,6] However, studies on the interaction between urea and weak acids are rare and the nature of the species formed consequent to this is not specifically known. We have observed that urea can affect the dissociation of *p*-nitrophenol, PNP ($pK=7.15$ at 25 °C) whereas *p*-nitrosalicylic acid, PNSA ($pK=10.33$ at 25 °C) remains unaffected; a relatively strong base like ethylenediamine can abstract H^+ ion from PNSA yielding a hydrogen-bonded ion pair or proton transfer complex (PTC).[7,8] The formation of PTC is the result of directionally specific interaction and because of much greater charge separation its formation is favored in polar media.[9] The spectrophotometric method is incapable of differentiating between an ion pair and the PTC, therefore, the spectrum of the PTC is the same as that of the ion of the conjugate base of the weak acid.[10] We have assumed that the above arguments are valid in our acid-base system of PNP and urea. Our objective has been to study the interaction between PNP and urea using spectrophotometric, conductometric, and calorimetric methods. It will be seen that the spectral results support PTC formation rather than dissociated ionic species. The energetics of the above interaction has been presented. Besides, the urea–PNP adduct has been prepared and characterized by IR and NMR methods with reference to the nitrate adduct of the amide.

Experimental

Materials. The urea and *p*-nitrophenol used were described earlier.[3,4,8] Nitric acid used was of Anala R grade, E. Merck, Germany. Doubly distilled conductivity water of specific conductance ca. 1.5 μS cm^{-1} was used for the preparation of solution.

Methods. Spectrophotometric measurements were taken in a Carey 17D spectrophotometer in 1 cm cuvettes. Infrared spectra were taken in KBr pellets in a Perkin–Elmer Model 297 Infrared spectrophotometer. About 1.0 mg of the finely ground sample was intimately mixed with approximately 100.0 mg of dried potassium bromide powder in a mortar and pestle. The mixture was then pressed in a special die at 10000 pounds per square inch to yield a transparent disk. The disk was then held in the instrument beam for spectroscopic examination. A JEOL FT NMR FX-100 was used for NMR spectral measurements. Approximately 3.0 mg of the sample dissolved in 0.3 ml of $CDCl_3$ was used for the measurements at 100 MHz with TMS as internal standard. Conductivity measurements of aqueous PNP and PNP–urea solutions were taken with a JENWAY, U.K. conductometer in a cell of cell constant 1.02 in a thermostated bath at 303 K.

Preparation of Adducts: To prepare uronium-nitrophenolate, the amide and the PNP mixed in 1 : 1 mol ratio was dissolved in a small amount of water and allowed to stand in a beaker at low temperature (283 K) overnight. Fine needle shaped light yellow crystals were found to appear at the bottom. The product was carefully washed with distilled water, dried under vacuum and stored in a desiccator. The elemental analysis has shown the compound to be of 1 : 1 composition. The compound decomposes at 398 K.

The nitric acid adduct was prepared in the following way. In 1 mol dm^{-3} solution of urea, 1 mol dm^{-3} nitric acid solution was slowly added. Fine crystals of uronium nitrate were formed and settled at the bottom. The crystals were separated, washed with distilled water for a number of times and stored in a desiccator. Elemental analysis confirmed the adduct to be of 1 : 1 composition. It decomposes at 423 K (lit, value[11] 425 K).

Spectrophotometeric Measurements: Solutions of PNP and urea were prepared in a number of test tubes at constant concentration of the former (10^{-4} mol dm^{-3}) and variable concentrations of the latter from 0.05 to 6.0 mol dm^{-3}. They were placed in a constant temperature thermostated water bath at 303 K for 1 h. The spectra of the solutions were then recorded in the spectrophotometer in the wavelength range 250—450 nm at 303±0.02 K.

Conductance Measurements: The conductances of PNP at concentrations 1,2,4,6,8, and 10 mmol dm^{-3} in water as well as in 8 mol dm^{-3} aqueous urea were measured at 303 K. The conductance of the urea solution was also measured and the value subtracted from each set of the PNP–urea mixtures to compensate for the urea effect on ion transport.[1]

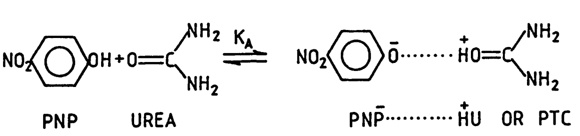
Calorimetric Measurements: The enthalpy of the urea–PNP interaction was determined in a Tronac 458 Isoperibol Calorimeter at 303 K. The calibration of the calorimeter was checked by measuring the heat of neutralisation of HCl with NaOH. In an actual run, urea solution was added into PNP solution keeping the final stoichiometry at least 1 : 100 and the heat liberated was determined at five urea concentrations. The heat of dilution of both the urea solution as well as the PNP solution were also determined and subtracted from the above heat of interaction to calculate the enthalpy following the procedure described elsewhere.[12,13] Since the base was directly added into the aqueous solution of PNP from a syringe in a water bath outside the Dewar flask, the heat of the interaction was calculated from the overall temperature change and the heat capacity determined after the introduction. The reported enthalpy refers to the extrapolated to zero urea concentration. The estimated standard deviation in the enthalpy value was ±0.7 kJ mol^{-1}.

Results and Discussion

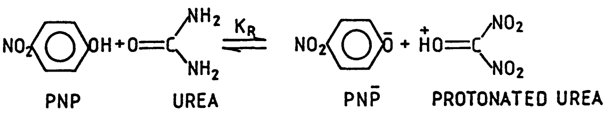
The 1 : 1 stoichiometry of the reaction has been supported by the elemental analysis data of the prepared uronium *p*-nitrophenolate. The ^{1}H NMR spectrum of the PNP–urea adduct indicates the presence of the aromatic group as two double doublets centerd at δ=8.12 and 6.98 characteristic of a para substituted phenyl ring. The ^{1}H NMR spectrum of PNP and tetramethylurea[14] showed similar characteristics. In addition, the methyl proton signals appeared at δ=2.84 as a singlet. The signals were in the ratio of 1 : 3 indicating the formation of a 1 : 1 adduct. Analogically we consider that the PNP–urea adduct was also of 1 : 1 mol ratio.

The specific conductance–concentration plot in Fig. 1 suggests specific interaction between PNP and urea. Simple reduction in conductance[15] by the association of the dissociated H$^+$ ion as evidenced in the cases of HCl and HOAc (acetic acid) is not solely contributing to the ion transport phenomenon. A distinct departure is evidenced at higher PNP concentrations. A specific association of the migrating species PNP$^-$ and UH$^+$ is anticipated which is regarded as the hydrogen-bonded ion pair.

The interaction between PNP and urea may end up into the following equilibria.



(1)



(2)

The spectra of the PNP–urea mixtures reveal decrease in the 315 nm band of the parent nondissociated PNP molecule with concomitant increase in the intensity of the 405 nm band of the phenolate anion or the PTC (Fig. 2). The reaction can thus be spectrophotometrically monitored recording the absorbance at 405 nm where PNP does absorb insignificantly. The spectra show a sharp isosbestic point at 345 nm indicating simultaneous existence of two species in equilibrium. The absorbance contributed by the self-dissociation of PNP is minor; it has been subtracted from the absorbance of all the solutions in the presence of urea to eliminate the effect. It has been established earlier[7] that both *p*-nitrosalicylate anion and the hydrogen-bonded ion pair between the said anion and protonated ethylenediamine have the same absorption maxima at 414 nm. The *p*-nitrophenolate anion (PNP$^-$) and the ion pair between PNP$^-$ and the protonated urea UH$^+$ are considered also to absorb maximum at the same wavelength,[8] 405 nm. From fundamental considerations and following the line

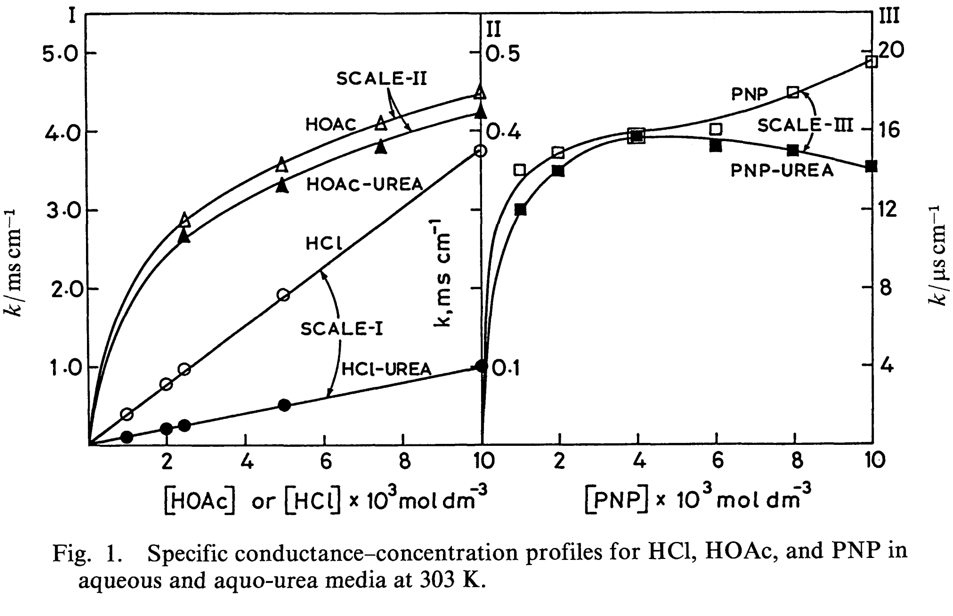


Fig. 1. Specific conductance–concentration profiles for HCl, HOAc, and PNP in aqueous and aquo-urea media at 303 K.

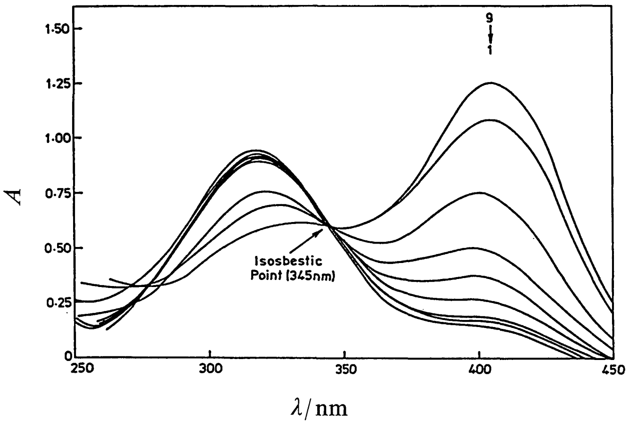


Fig. 2. Spectra of 0.1 mmol dm^{-3} PNP in aqueous urea environment at 303 K. Curves 1 to 9 are at 0, 0.05, 0.1, 0.3, 0.6, 1.0, 2.0, 4.0, and 6.0 mol dm^{-3} urea.

of arguments presented earlier,[7,8] the following Eqs. 3 and 4 can be derived for the above-mentioned Eqs. 1 and 2, respectively,

$$C_{PNP}/A = 1/\varepsilon + (1/K_A\varepsilon^2)\,1/C_u \qquad (3)$$

and

$$C_{PNP}/A = 1/\varepsilon + (1/K_R\varepsilon^2)\,A/C_u \qquad (4)$$

where C_{PNP} and C_u are the stoichiometric concentrations of the p-nitrophenol and urea respectively, A is the absorbance of the solution at 405 nm, ε is the molar extinction coefficient of the absorbing species and K_R and K_A have significance as defined above. Since dilute solution of PNP has been used and urea is a neutral molecule, the activities of the species arising in solution are considered equal to their concentrations. The validity of Eq. 3 is examplified in Fig. 3, where a nice straight line plot is observed between C_{PNP}/A and C_u^{-1} with a correlation coefficient 0.9996 (curve 1). The ε_A and K_A derived from the slope and the intercept are $(1.78\pm0.08)\times10^4$ dm^3 mol^{-1} cm^{-1} and 0.24 ± 0.01 dm^3 mol^{-1} respectively. The value of ε of the phenolate ion[16] has been reported to be 18330 dm^3 mol^{-1} cm^{-1} at 303 K. It is seen in the figure that the results very poorly fit Eq. 4. Extrapolation of the curved course (curve 2), however, yields the same intercept as produced by the curve 1, which ought to be so because the values in both the equations refer to the same species. The good correlation of the experimental results with Eq. 3 speaks in favor of the said PTC formation (Eq. 1) rather than replacement reaction (Eq. 2). From pH measurements we have reported the association constants of H$^+$ ion of HCl with urea to be 1.42—5.38 at 310 K in the urea concentration range of 0.5—6 mol dm^{-3}. The PNP$^-\cdots$UH$^+$ PTC formation constant is 0.24 dm^3 mol^{-1} at 303 K, the interaction is weaker than H$^+$ ion binding with the amide.

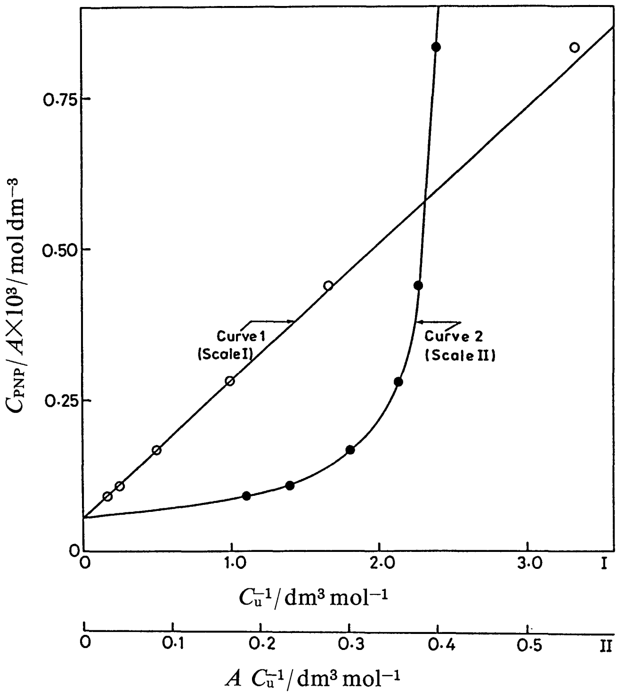


Fig. 3. C_{PNP}/A versus C_u^{-1} and C_{PNP}/A versus A/C_u plots for testing the validity of Eqs. 3 and 4 and the evaluation of the equilibrium constant, K_A and the molar extinction coefficient, ε of the complex at 303 K.

The reactant concentrations used in the experiments

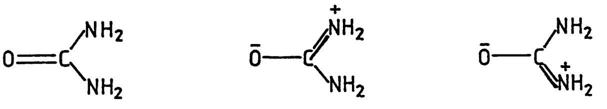
Table 1. Characteristic Infrared Bands of Urea, PNP, Urea–PNP, and Uronium Nitrate

Urea ν/cm^{-1}	PNP ν/cm^{-1}	Urea–PNP[a)] ν/cm^{-1}	Uronium nitrate ν/cm^{-1}	Predominant mode
3400		3400	3400	
				ν_{NH_2} (free)
3500		3500	3500	
	3325			ν_{OH} (H-bonded)
		1690	1700	
1685				$\nu_{C=O}$ stretch
		1650	1670	
1470		1590	1570	ν_{CN} bending
	1590	1590		$\nu_{C=C}$ (skeletal)
	1500	1500	1500	ϕ_{NO_2}
			1380	NO_3^-

a) ν_{CN} for Urea–PNP almost merges with the $\nu_{C=C}$ at 1590 cm^{-1} with a broadening effect.

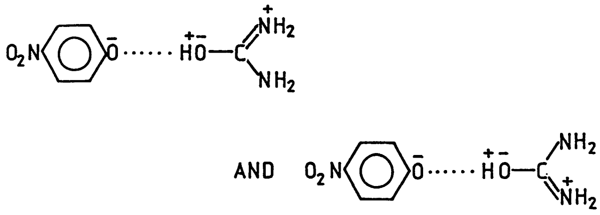
were low, so the thermodynamic parameters herein reported are standard state values. The calorimetric enthalpy of the interaction (ΔH°) has been found to be -13.8 ± 0.7 kJ mol^{-1}. A value of -57 ± 3 J mol^{-1} K^{-1} has been calculated for the ΔS° from the Gibb's equation using the spectrophotometrically obtained standard free energy change ($\Delta G^\circ=3.60\pm0.01$ kJ mol^{-1}). The interaction has an overall order producing effect. The interacted species are stabilized upon complexation, the environmental solvation also adds to the ordering effect.

The characteristic IR bands of urea, PNP, urea–PNP, and uronium nitrate are given in Table 1. The amide has the following resonating structures.[17]


I II III

If linkage of hydrogen occurs through nitrogen then contributions of **II** and **III** will decrease and that of **I** will increase. This results in increase of the CO stretching frequency with a decrease in the CN stretching frequency. If, on the other hand, bonding occurs through oxygen then contribution of **I** decreases, the CO stretching frequency may be affected whereas that of the CN stretching should increase, the NH stretching frequency (3400—3500 cm^{-1}) should remain unaffected.

The bands of free NH_2 at 3400 and 3500 cm^{-1} in urea remain unaffected in urea–PHP and uronium nitrate, supporting noninvolvement of the linking between the nitrogen center of urea with the hydrogen of PNP and HNO_3. The stretching frequency of C=O has been little affected in the adduct whereas that of CN has been affected appreciably; in PNP adduct the shifted band of CN has overlapped with C=C skeletal response of PNP in the spectrum which is, therefore, not distinguishable. The appreciable shift in the stretching frequency of CN and nonaffected NH stretching frequency speak in favor of association of PNP and HNO_3 with the oxygen of urea. The intermolecularly bonded OH of pure PNP has shown a band at 3325 cm^{-1}, which is absent in the urea–PNP adduct indicating free OH to link with the C=O of urea. The following are the possible resonating structures of the 1 : 1 PNP adduct of urea.



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