NMR study on the three component solution containing STPP, Urea and Hydrogen Peroxide

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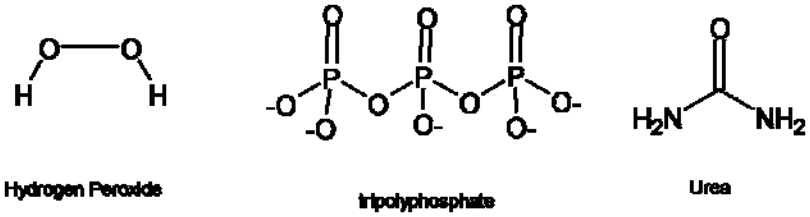
1.0 Introduction

NMR spectroscopy has long been used to analyse sodium tripolyphosphate since the first reported case in the late 1970's [1]. This current study utilises 1D ^{31}P, and ^{1}H nmr to investigate the intermolecular interactions of the three component system containing, sodium tripolyphosphate, urea and hydrogen peroxide.

Urea has long been known to enhance the bleaching effect of peroxide; the crystal structure of the active percarbamide has previously been determined [2]. This investigation seeks to determine the relationship between the STPP, urea and peroxide in solution.



The ^{31}P nmr of STPP is shown in Figure 1, the central phosphorus resonating as a triplet centred at -20.25 ppm, with the two outer phosphorus atoms being equivalent and appearing as a doublet centred at -5.25 ppm. The smaller peak at -6.00 ppm, which integrates for one fifth that of the main peaks is most likely that of the hydrolysed product, pyrophosphate.

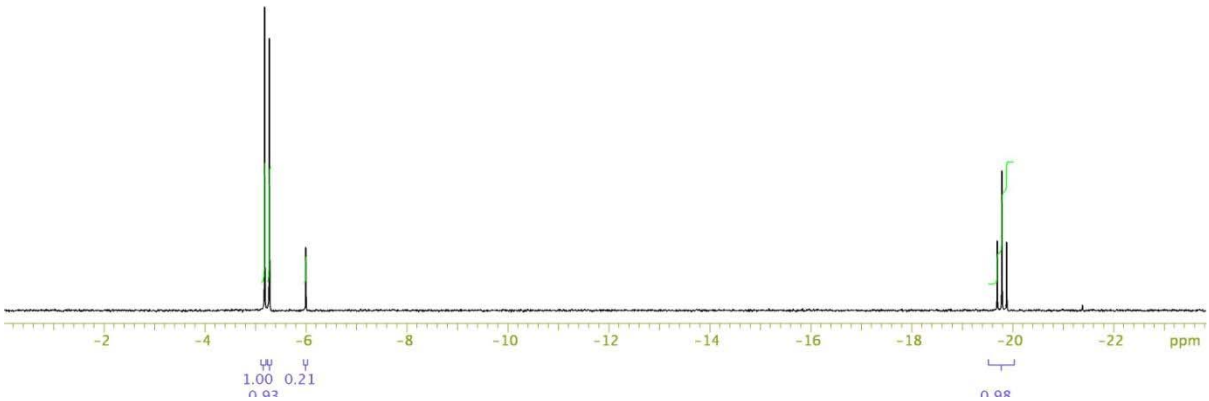


Figure 1. ^{31}P NMR of STPP as supplied. Sample was prepared to contain approx. 10 mgs / ml in D_2O.

As this investigation was carried out in solution, any interactions occurring with STPP will be illustrated with a slight spectral shift in any / all of the peaks as the electronic environment of the phosphorus nuclei are altered. This is illustrated in Figure 2, which shows a direct comparison of STPP and the IRT Sample 2 containing STPP: Urea: Peroxide (35 % in H_2O) 19.22 : 15.42 : 65.36 (%w/w/w). It can be observed from this spectrum that all of the ^{31}P signals are shifted upfield

relative to STPP. This suggests that either the H_2O_2 or urea (or both) are interacting with the STPP, affecting the electronic environment surrounding the phosphorus atoms resulting in a change of chemical shift. The second observation arising from the combined spectra was that all three phosphorus atoms are affected as all peaks were observed to move upfield.

Figure 2 suggests that there is an intermolecular interaction between the STPP and either one or both of the remaining two components. In an attempt to ascertain a possible structure for this three component adduct a systematic series of NMR titrations were performed.

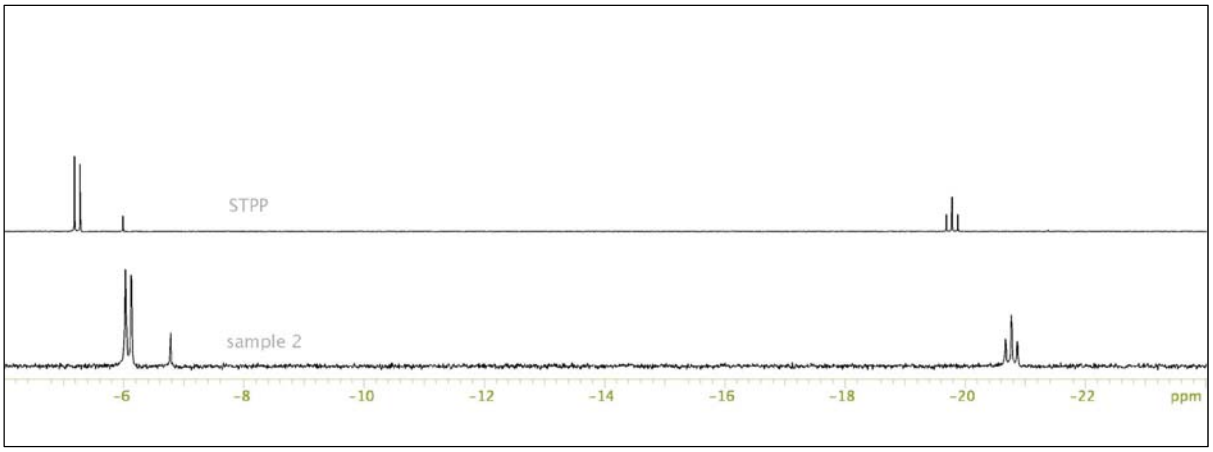


Figure 2. Overlaid ^{31}P NMR spectra of STPP and Sample 2. Samples prepared to contain approx. 20 mgs /ml in D_2O.

2.0 NMR titrations using ^{31}P NMR.

Based on the composition of a previously received sample from ICT ltd containing the constituents STPP, Urea and hydrogen peroxide in a 20.95: 17.14: 61.91 (% w/w/w) ratio, various NMR samples were prepared to allow for variation within the three components.

Experiment 1 kept the amount of STPP and Urea constant while varying the amount of H_2O_2 present in the samples. The spectra are displayed in Figure 3a with Figure 3b showing expanded areas of interest.

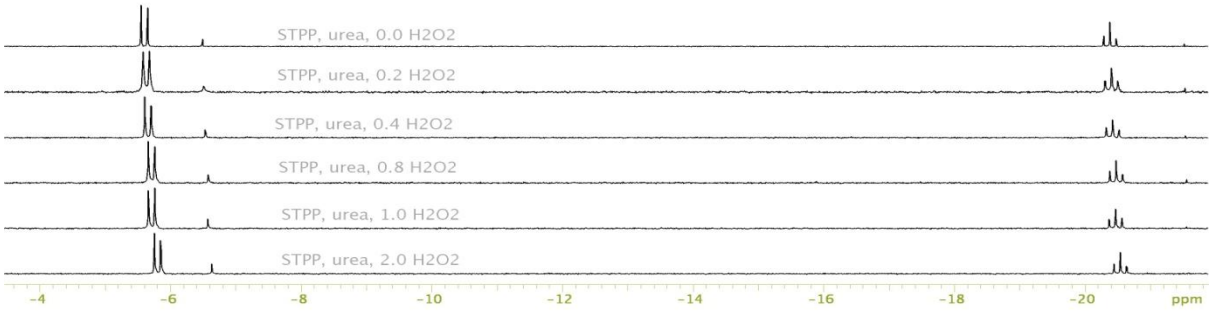


Figure 3a. ^{31}P nmr spectra for the various samples with varying peroxide content.

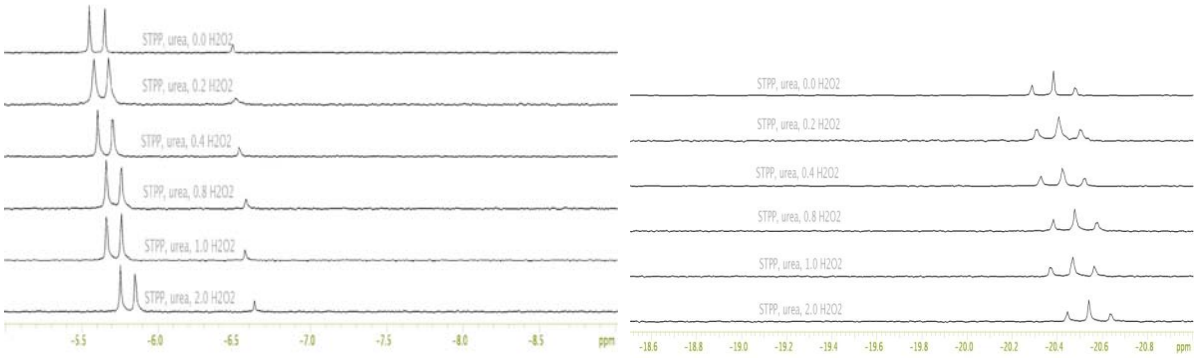


Figure 3b. Expansion of Figure 3a showing regions of interest.

It can be observed from Figure's 3a and 3b that the chemical shifts have been moved upfield upon increasing H_2O_2 concentration, suggesting that the hydrogen peroxide is interacting directly with either the STPP or with an STPP:Urea adduct. A similar experiment was carried out to allow for the analysis of Urea. Figure's 4a and b show the ^{31}P NMR spectra when STTP and H_2O_2 concentrations were fixed while the concentration of urea was varied.

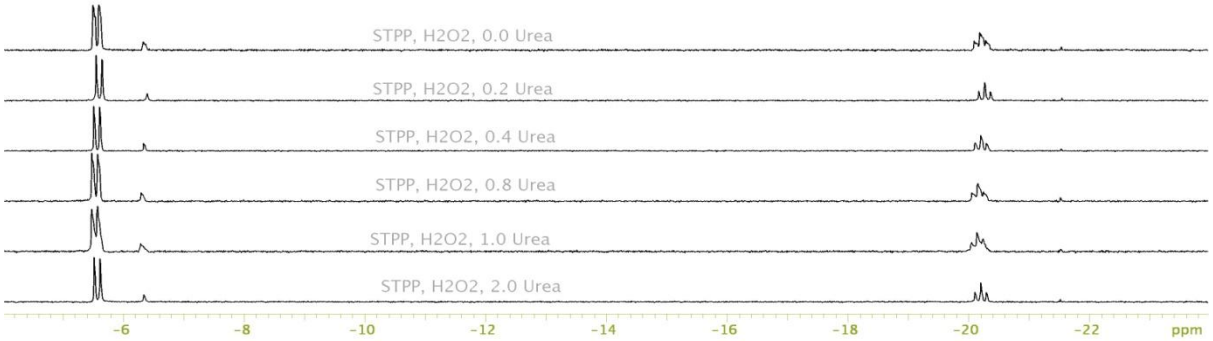


Figure 4a. ^{31}P NMR spectra when STPP and H_2O_2 concentrations remain constant and urea concentration varies.

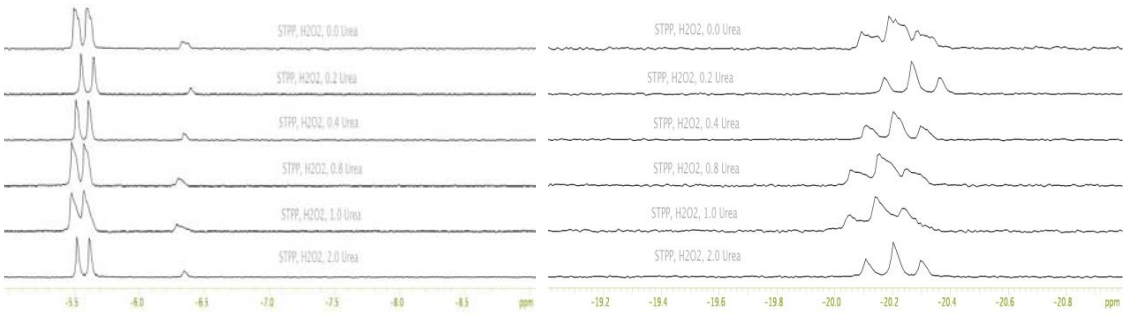


Figure 4b. Expansion of Figure 4a showing regions of interest.

From Figures 4a and 4b it can be observed that there is an absence of any substantial movement in the phosphorus signals upon increasing urea concentration suggesting there is a limited interaction between urea and STPP. However, when the titration was carried with simultaneous addition of both hydrogen peroxide and urea to a fixed STPP concentration (Figures 5a and b), the upfield shift of the phosphorus signals was once again apparent. This would indicate that the STPP is interacting with only the hydrogen peroxide, or possibly the more stable carbamide peroxide.

Figure 5a. ^{31}P nmr spectra showing the simultaneous addition of both H_2O_2 and Urea to a fixed STPP concentration.

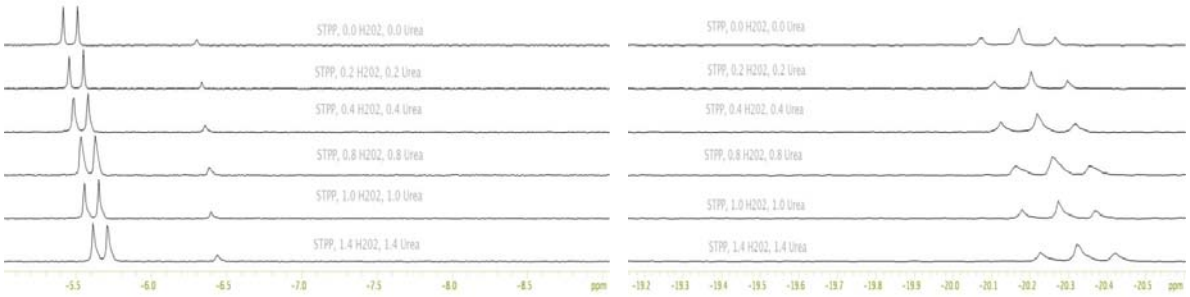


Figure 5b. Expansion of Figure 5a showing regions of interest.

To confirm our hypothesis that the above mentioned shifts in the ^{31}P NMR spectra are due to the interaction of H_2O_2 and STTP a titration was performed where the STTP concentration was fixed and increasing amounts of H_2O_2 were added. The results are presented in Figures 6a and b and show the expected upfield shift of the phosphorus signals upon addition of H_2O_2. Conversely, the addition of increasing amounts of urea to a fixed concentration of STPP resulted in spectra (Figure's 7a and b) that were relatively unchanged.

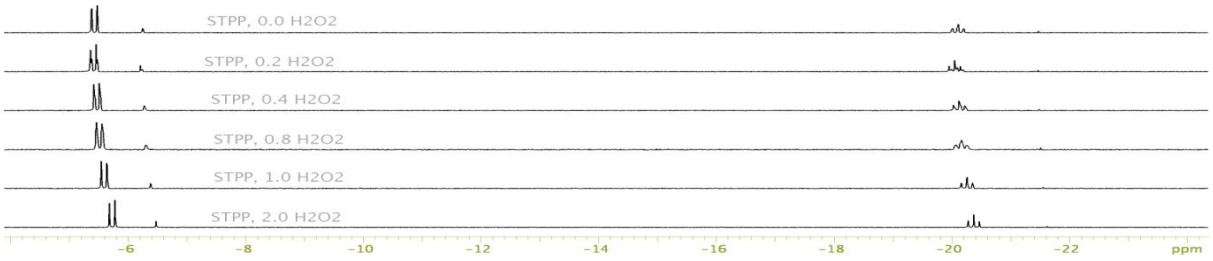


Figure 6a ^{31}P nmr study showing the addition of increasing amounts of hydrogen peroxide to a fixed amount of STPP.

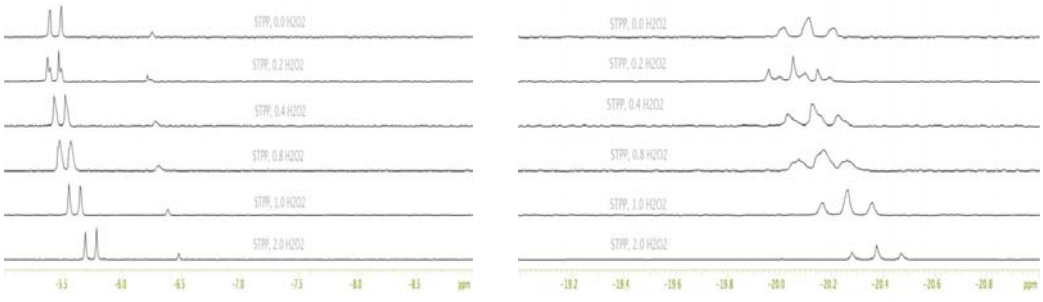


Figure 6b Expansion of Figure 6a showing regions of interest.

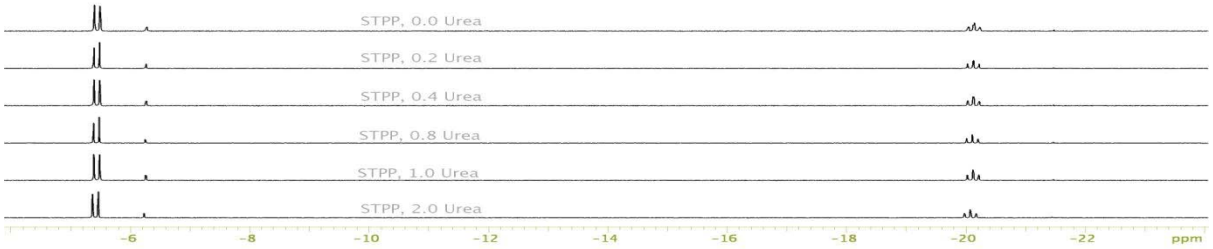


Figure 7a ^{31}P nmr study showing the addition of increasing amounts of urea to a fixed amount of STPP

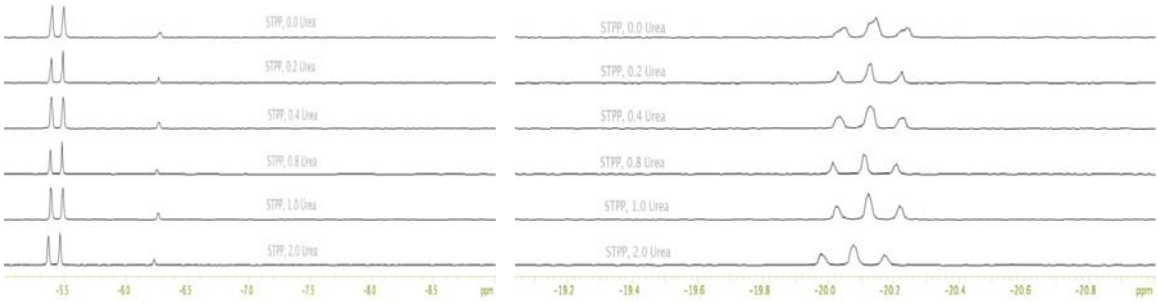


Figure 7b Expansion of Figure 7a showing regions of interest.

In summary, the ^{31}P nmr study suggests that STPP directly interacts with hydrogen peroxide with minimal contribution from the urea being apparent. **However, the ^{31}P nmr chemical shifts of polyphosphates have been shown to be sensitive to solution pH**. Therefore we further investigated the effect of solution pH on the ^{31}P nmr spectrum of STPP.

3.0 Effect of pH on the ^{31}P nmr of STPP

Previous examples in the literature have shown that the phosphorous resonances of polyphosphates tend to move upfield with decreasing pH due to the sequential protonation of the phosphate groups [3]. The acid base equilibria of the tripolyphosphate ion is as follows:

It is also known that aqueous solutions of H_2O_2 are acidic. Therefore, to ensure that the changes in chemical shifts observed in the above experiments are due to chemical interactions and not just a change in solution pH several pH titrations were performed.

Using 5M HCl as an acidic solution, small amounts were added to a solution of STPP and the ^{31}P nmr recorded. Figure 8 shows the ^{31}P nmr spectra of STTP solutions at pH's 9.26, 7.94 and 5.77 in

descending order and demonstrates a significant upfield shift of all resonance's upon decreasing pH. This is consistent with effects observed above when increasing amounts of H_2O_2 were added to fixed solutions of STPP. However, to get an indication of the magnitude of the HCl induced changes with respect to the H_2O_2 induced changes we plotted the ^{31}P nmr chemical shift (using the doublet at approx. 6ppm) against solution pH (Figure 9).

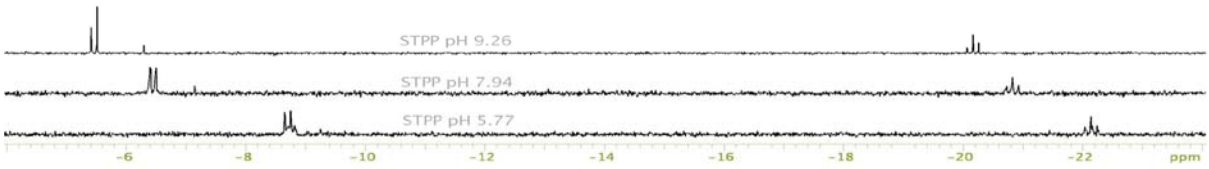
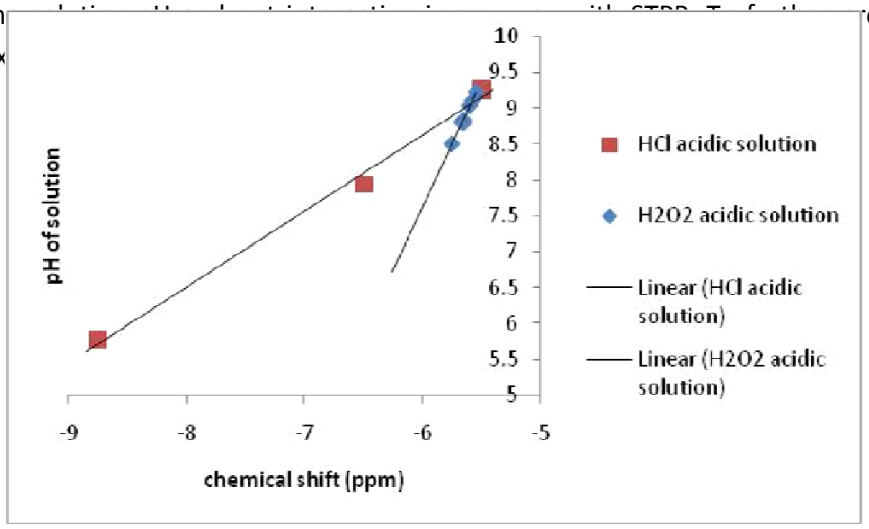


Figure 8 ^{31}P nmr spectra of STTP at various pH controlled by the addition of 5M HCl.

Figure 9 clearly shows that that the magnitude of the HCl induced changes in chemical shift are much more significant than the H_2O_2 induced changes suggesting that there is an interaction between the STPP and H_2O_2 that suppresses the expected change in chemical shift i.e. we would expect the change in chemical shift upon addition of H_2O_2 to be much greater if it was only changing th obe these interactions we ex



Eqs of H_2O_2	Solution pH
0.0	9.24
0.2	9.12
0.4	9.04
0.8	8.84
1.0	8.80
2.0	8.51

Figure 9 Plot of solution pH against ^{31}P nmr chemical shift for (a) solutions of STPP where pH was changed by the addition of 5M HCl (red squares) and (b) solutions of STPP where pH changed with increasing H_2O_2 concentration. Table shows the pH value of solutions containing a fixed amount of STPP and varying amounts of H_2O_2.

4.0 NMR titrations using ^{1}H nmr

Samples were prepared in an identical manner to those used in the ^{31}P nmr study. The ^{1}H nmr of urea is relatively simple and contains only one broad peak centred at 5.65 ppm corresponding to the

four equivalent urea protons. The first titration conducted was to determine the effect of adding hydrogen peroxide on the chemical shift of the urea protons (Figure 10.)

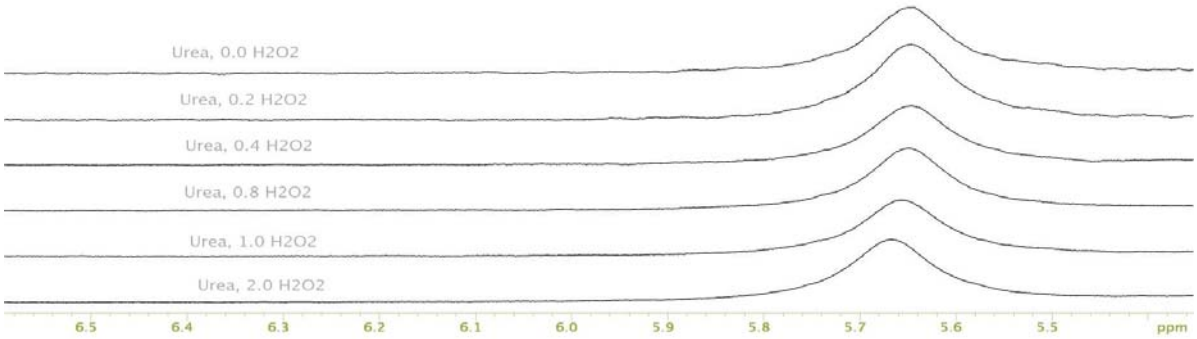


Figure 10 ^{1}H nmr spectra showing the addition of increasing amounts of H_2O_2 to a fixed concentration of Urea.

As can be observed from Figure 10, only a minor downfield shift was observed in the urea protons from 5.65 to 5.69 ppm upon increasing amounts of hydrogen peroxide. ^{1}H nmr spectroscopy is not expected to be as sensitive to changes in chemical shift when compared to ^{31}P spectroscopy as the spectral range is much greater in ^{31}P nmr due to the increased number of orbital's present in phosphorus relative to hydrogen. This shift, although minor, would indicate a hydrogen bonding interaction between the urea and hydrogen peroxide.

However, when increasing amounts of H_2O_2 was added to a fixed amount of Urea and STTP a distinctly different spectrum was observed (Figure 11). Here, a marked upfield shift was observed in the urea protons from 5.65ppm to 5.5 ppm. This suggests the electronic environment of the urea protons is significantly altered in the presence of STPP and H_2O_2.

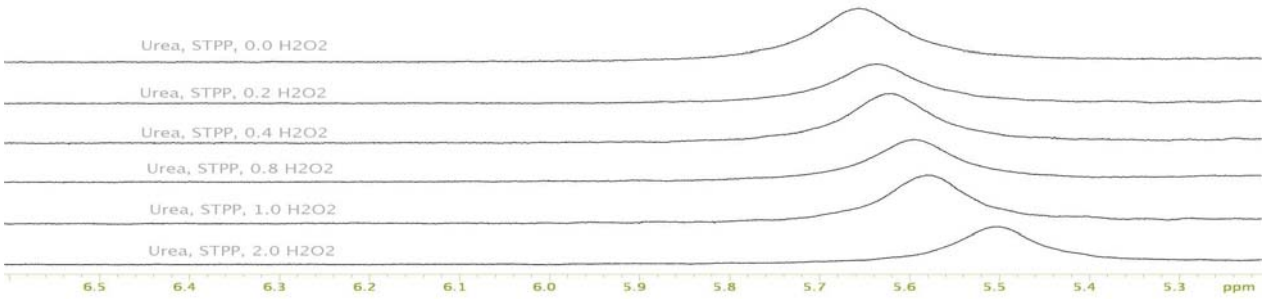


Figure 11 ^{1}H nmr spectra showing the addition of increasing amounts of H_2O_2 to a fixed concentration of Urea and STPP.

In contrast, in the ^{1}H nmr spectrum of a solution containing only Urea and STPP the chemical shift of the urea protons are unchanged at 5.65 ppm (observed by comparing the top spectrum in Figure 10 to that in Figure 11). This is consistent with the phosphorus study where the addition of urea to STPP had no effect on the chemical shift of the phosphorus nuclei.

5.0 pH Titrations

To determine the effect of solution pH on the ^{1}H nmr spectra of Urea a pH titration was performed. Figure 12 shows the ^{1}H nmr spectra of urea at pH's 8.20, 1.51 and 1.08 in descending order. As can be observed from Figure 12 the proton signals disappear completely at low pH, possibly due to deuterium exchange. However, when an identical amount of acid was added to a solution of Urea with STPP present (Figure 13) the pH of the final solutions were much higher and the proton signal was apparent. This suggests the STPP acts in a buffering capacity minimising the effect of the HCl addition. More importantly, it also confirms that the H_2O_2 induced changes shown in Figure 11 are real and are not in any way due to changes in solution pH. Figures 14a and 14b show the change in chemical shift of the urea protons as a function of solution pH and H_2O_2 concentration, for a solution of urea only (Figure 14a) and for a solution of urea in the presence of STPP.

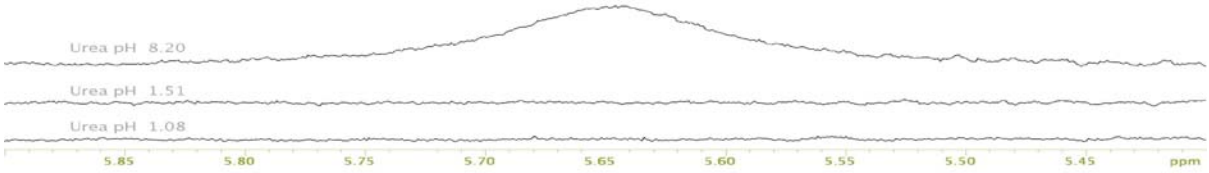


Figure 12. ^{1}H nmr spectra of Urea at various pH values where pH was changed by the addition of 5M HCl. Top spectrum: no HCL added; middle spectrum: $1x10^{-4}$ moles of HCl added to a final volume of 4 mL of Urea in D_2O; bottom spectrum: $3x10^{-4}$ moles of HCl added to a final volume of 4 mL of urea in D_2O.

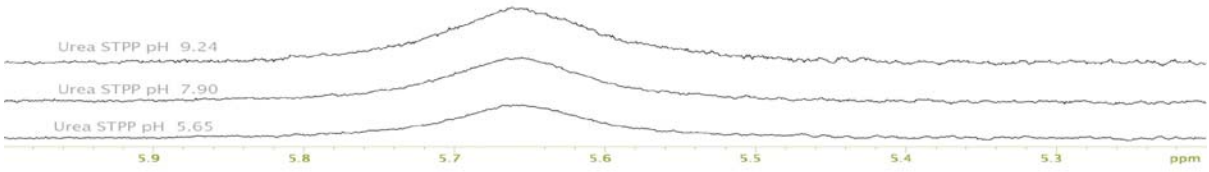


Figure 13. ^{1}H nmr spectra of Urea at various pH values with STPP present. Note the amount of HCl added was identical to Figure 12 for each spectrum the only difference being that STPP was also present in the solution.

Amount of HCl added (moles)	pH of Urea only solution	pH of Urea + STPP solution
0	8.20	9.24
$1x10^{-4}$	1.51	7.90
$3x10^{-4}$	1.08	5.65

Table 2 Showing the final pH of solutions containing Urea only and Urea in the presence of STPP before and after the addition of fixed amounts of HCl.

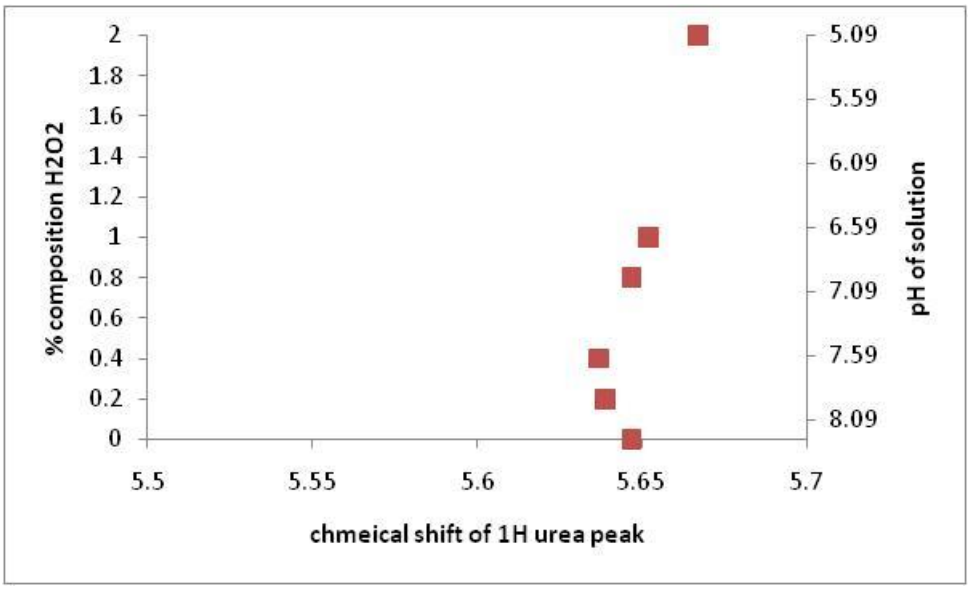


Figure 14a Plot of ^{1}H nmr chemical shift of the urea protons as a function of H_2O_2 concentration and resulting pH

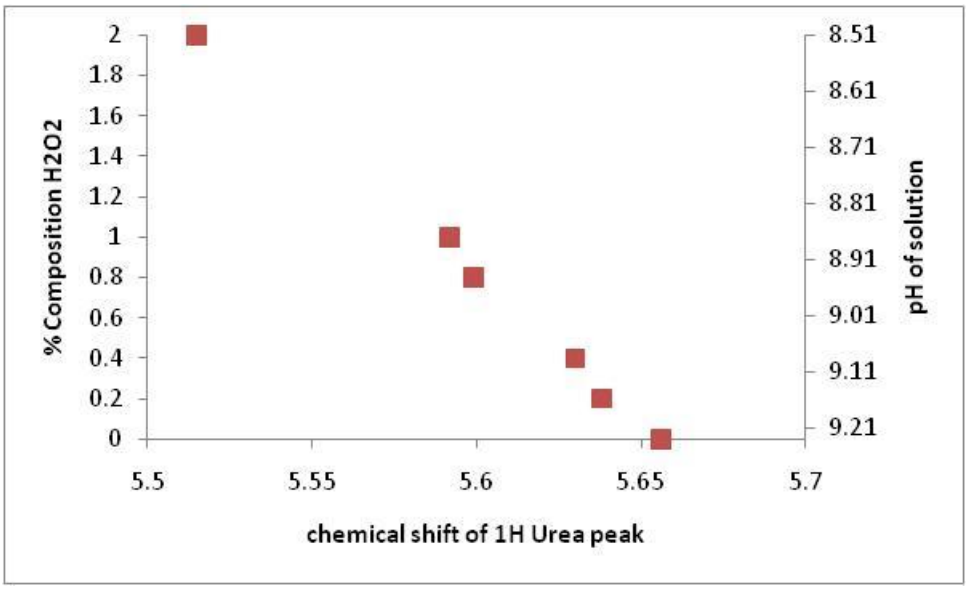


Figure 14b. Same plot as Figure 14a in the presence of STPP.

6.0 Conclusions

The data presented above reveals several interesting interactions of solutions containing Urea, STPP and H_2O_2. These are:

1. The addition of Urea to solutions of STPP has negligible effect on ^{31}P nmr spectrum of STPP suggesting minimal interaction.

2. The addition of H_2O_2 to solutions of STPP cause a significant upfield shift on all signals in the ^{31}P nmr spectrum of STPP suggesting an interaction between these two entities. Although a pH reduction of the solution was observed upon increasing H_2O_2 addition, a pH titration indicated that the magnitude of this shift was not due to pH factors alone.

3. The addition of increasing amounts of H_2O_2 to a solution of Urea alone caused a slight downfield shift in the ^{1}H nmr urea signal. However the addition of increasing amounts of H_2O_2 to a solution of Urea in the presence of a fixed amount of STPP caused a significant upfield shift. These changes were proven to be in no way linked to solution pH.

4. The addition of STPP alone to a Urea solution causes negligible change in the ^{1}H nmr spectrum indicating no direct interaction between the two entities as observed in the ^{31}P nmr investigation.

5. STPP has a profound buffering effect on the three component system.

6. The molar ratio of STPP: Urea: H_2O_2 was calculated as follows:

   %wt/wt STPP: 19.22 ; Urea : 15.42; H_2O_2 (35% solution): 65.36;

   Moles per 100g: STPP= 19.22 / 367 = 0.052;

Urea = 15.42/60 = 0.257;

Peroxide = (65.36x0.35)/34 = 0.673

Therefore molar ratio = **STPP : Urea : H_2O_2 = 1.00 : 4.94 : 12.94**

Based on these conclusions we propose a structure such as that shown in Figure 15 where the STPP interacts strongly with hydrogen peroxide via hydrogen boding but has a minimal interaction with urea. In effect, the hydrogen peroxide functions as a bridge between the STPP and the Urea. Due to the large molar excess of peroxide it is likely that many H_2O_2 molecules decorate the surface of a single STPP molecule and then indirectly interact with Urea. However, due to this large excess of peroxide other participating structures cannot be ruled out.

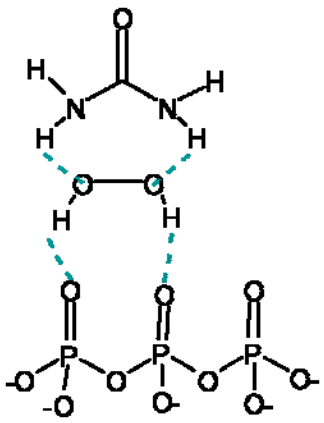


Figure 15 Postulated three component adduct.

Given the fact that STPP is a basic salt we would urge IRT to test other basic salts as an alternative to STPP in order to determine if the bleaching efficiency of the current three component system can be equalled or surpassed. It is our belief that the basic / buffering nature of STPP facilitates the production of O_2 quicker than the two component adduct alone.

References

1. Sojka, S.A.; Wolfe, R. A. *Analytical Chemistry* (**1978**) 50, 585.
2. Lu, C.S.; Hughes, E. W.; Gignere, P. A. *J. Am. Chem. Soc.* (**1941**) 63, 1507.
3. Crutchfield, M. M.; Callis, C. F.; Irani, R. R.; Roth, G. C. *Inorganic Chemistry* (**1962**), 1, 813.