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Assay of the Insensitive High Explosive 3-Nitro-1,2,4-triazol-5-one (NTO) by Acid-Base Titration

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Abstract: The insensitive high explosive 3-nitro-1,2,4-triazol-5-one (NTO) is a weak acid (pK_a 3.76) due to the labile N–H bond. The weakly acidic character of this compound is exploited for its assay by aqueous acid-base titration. The NTO sample was dissolved in water and the resultant solution was titrated against 0.07 N NaOH solution using phenolphthalein as indicator. Regular batch samples were assayed by this method and the results were compared with those obtained by the HPLC method. The aqueous acid-base titration method was found to be suitable for the quality control of the product.

Keywords: NTO, purity, acid-base titration, HPLC, quality control

Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) is receiving attention in the field of high energy materials (HEMs) as one of the important insensitive high explosives (IHEs). Its performance in terms of detonation is comparable with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), however it is far less sensitive than RDX. Lee *et al.* [1, 2] first published the study of NTO as a high explosive material. Since then, the R&D work on NTO has been continuously pursued with great interest in process development and scale up to pilot plant scale [3-6], as well as evaluation of its properties [7-10] and performance [11-15]. This laboratory

is also establishing the manufacturing technology at pilot plant scale [14-18]. This demands a good analytical method for assaying the product. Analysis of NTO by high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) has been reported in the literature [19, 20]. The reported methods are dependent upon the use of expensive instruments. Moreover, these methods are more appropriate for the analysis of explosive mixtures containing NTO as one of the components rather than production batch samples.

This paper describes a simple and rapid method for the assay of actual batch samples by acid-base titration. NTO is a weak acid (pKa 3.76) due to the labile N–H bond [3]. The weakly acidic character of this compound is exploited for its assay by an aqueous acid-base titration method.

Materials and Methods

Chemicals

All of the chemicals used were analytical (AR) grade from M/s Merck Ltd., Mumbai, India. Distilled water was used for the preparation of aqueous solutions.

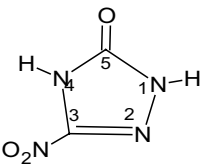
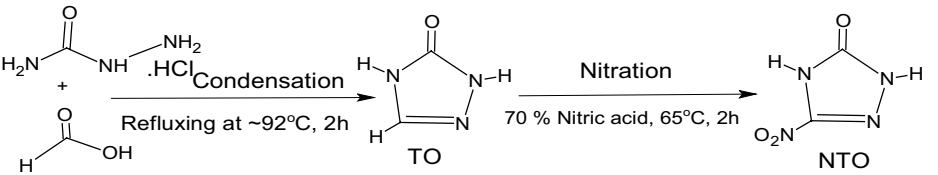


Figure 1. Chemical structure of NTO.

NTO samples were obtained from batches carried out in this laboratory at bench scale (500 g/batch). It was synthesized in a two step process viz. condensation of semicarbazide hydrochloride with formic acid to give the intermediate 1,2,4-triazol-5-one (TO), followed by the nitration of TO to NTO (Scheme 1). The crude NTO thus obtained was dissolved in hot water (80 °C) and crystallized by cooling crystallization. The crystallized sample was used as a production batch sample. As no standard NTO sample was available, one batch sample was crystallized three times from hot water and a few, well defined NTO crystals were isolated and crushed to a powder. This powdered NTO sample was used as the standard (purity 99.9%).



Scheme 1. Synthetic route to NTO.

Titration method

Preparation and standardization of the titrant (0.07 N sodium hydroxide solution in water)

The titrant (0.07 N NaOH solution) was prepared by dissolving 2.8 g sodium hydroxide flakes in water in a 1000 ml volumetric flask and making up to the mark with water. The solution was standardized [21] using the primary standard potassium hydrogen phthalate (well dried), using phenolphthalein indicator, prior to analysis of the NTO.

Analytical method for the assay of NTO by aqueous titration

NTO powder (200 to 250 mg) was weighed accurately and transferred into a conical flask (250 ml). Distilled water (150 ml) was added and the mixture was warmed on a hot plate, with occasional swirling, to dissolve the NTO, resulting in a yellow solution. The solution was then cooled to room temperature and a few drops of phenolphthalein indicator solution were added to it. This solution was titrated against standard 0.07 N NaOH solution and the end-point was indicated by a sharp colour change from yellow to wine red. The burette reading (Vs) was noted. A blank titration was also carried out without NTO. The blank (V_b) usually consumes 0.05 ml of titrant.

Calculation:

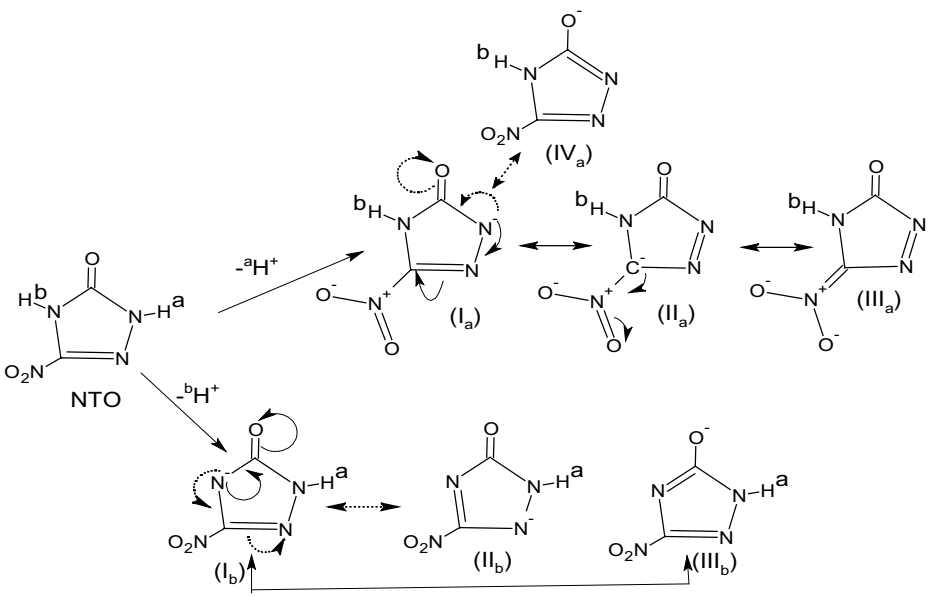
$$\% \text{ Purity of NTO} = \frac{(Vs - Vb) \times N \times 13.0}{m}$$

where: V = burette reading (ml), N = normality of sodium hydroxide solution, m = mass of the sample (g).

Results and Discussion

There are two ionisable hydrogen atoms in the NTO molecule. These are at positions N(1) and N(4) (Figure 1). The hydrogen at N(1) is more acidic than

that at position N(4). It has been reported by previous workers [10, 13, 14, 22] that the hydrogens in both positions can be ionised to form different NTO salts. However, under a mild basic environment, the hydrogen at position N(1) only is ionisable. This can be explained from the basic concept of acid-base theory of weak, organic, acidic molecules with respect to the stability of the corresponding conjugate base. The conjugate base obtained by the ionization of H^a of NTO gives four canonical structures due to the extra delocalization of the negative charge by the –R group NO_2 (Scheme 2). By contrast, ionization of H^b, gives only three canonical structures, and, moreover, there is no scope for delocalization of the negative charge by the NO_2 group in these canonical structures. Thus, the former conjugate base is more stable than the latter. Hence, NTO has a single ionisable hydrogen (H^a) and behaves as a monobasic acid.



Scheme 2. Connonical structures of the conjugate bases of NTO by ionisation of two acidic protons (H^a & H^b).

The acidic character of NTO has been exploited in the present assay method. Generally, weak organic acids are titrated by a non-aqueous titration method. Earlier, Nandi *et al.* developed a non-aqueous titration method [23] for the assay of another important, insensitive, high explosive, 1,1-diamino-2,2-dinitroethene (FOX-7). However, in the case of NTO, the acidity of the molecule (pKa = 3. 76) is found to be sufficient to allow acid-base titration in

an aqueous medium. The selection of the indicator for this titration is crucial to realizing a sharp colour change at the end-point. We tried several indicators for this titration. Phenolphthalein was found to be the best one. Other indicators, such as methyl orange and methyl red, were found to be unsuitable (due to interference from the NTO colour). Sample weights in the range 200-250 mg and a titrant concentration of ~0.07 N gave burette readings of 22-28 ml, and this was found to be suitable for the desired accuracy and precision. Due to the poor solubility of NTO in water at room temperature, warming of the solution is essential for dissolution of solid NTO prior to titration. NTO samples were assayed by this aqueous titration method and the results are presented in Table 1. Normal batch samples showed a purity of ~99.2%, whereas the standard sample showed a purity of 99.6%.

Table 1. Assay results of NTO samples by aqueous acid-base titration

Sample	No. of replicates	Avg. purity (%)	STDEV (σ)
1	3	99.2	0.07
2	4	99.3	0.09
4	2	99.5	0.05
3	3	99.4	0.08
5	4	99.4	0.04
Standard NTO	3	99.6	0.06

As discussed above, NTO is synthesized by a two step process [2, 3]: condensation of semicarbazide hydrochloride with formic acid to give the intermediate 1,2,4-triazol-5-one (TO) which is then nitrated to NTO using 70% nitric acid as the nitrating agent (Scheme 1). Crude TO obtained from the condensation reaction contains acidic impurities which are removed by crystallization from hot water. The purified TO was subjected to the nitration reaction using 70% nitric acid as the nitrating agent. The nitration process gives crude NTO which is dissolved in hot water (80 °C) and crystallized by cooling crystallization. Crystallized NTO was used as a batch sample.

Possible impurities in NTO samples are not reported in the literature. Zbarsky *et al.* [24] isolated a by-product (N-nitro-1,2,4-triazol-5-one) which is formed by N-nitration of TO, but due to its instability, it isomerizes to NTO (Scheme 3) during the hot water crystallization [24]. There is a further possibility of the formation of 2,4-dihydro-2,4,5-trinitro-3H-1,2,4-triazol-5-one (DTNTO, Figure 2) due to further nitration of NTO at other positions [25]. However, the presence of such an impurity in the NTO samples (synthesized by the above mentioned method) was not observed (confirmed by HPLC analysis). It is

envisaged that unconverted TO may be incorporated in the NTO sample, as a major impurity in the case of incomplete nitration. Hence, it was imperative to check for the interference of TO in the above titration method. Thus, the titration was also carried out with accurately weighed (150-200 mg) TO samples (water crystallized).

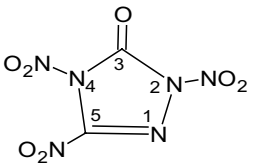
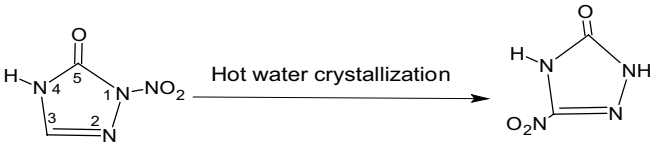
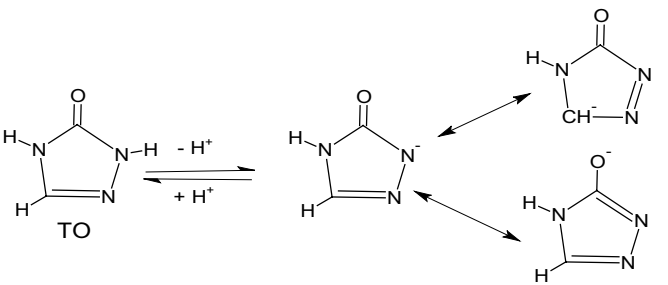


Figure 2. Chemical structure of DTNTO.



Scheme 3. Isomerization of N-nitro-1,2,4-triazole-3-one.

TO too has a labile N−H bond due to stabilization of its conjugate base by the carbonyl group (Scheme 4) and thus, it behaves as a weak acid [8]. However, the acidity of TO was found to be too low to permit titration in the aqueous medium. Thus, TO was not found to respond in this aqueous acid-base titration. However, water crystallized TO (1st crop) did show some consumption of titrant (~5 ml of 0.07 N NaOH solution) in the titration (appearance of a light pink colour at the end-point). This is due to neutralization of free acids (HCl and formic acid) present in the TO sample. These acidic impurities are incorporated in the sample from the TO preparative process. They are largely removed during the crystallization of crude TO from hot water. However, a certain percentage of hydrochloric acid (<7%) forms a stable salt with TO which is not removed by water crystallization. On further analysis of TO sample by argentometric titration (Metler Autotitrator, DL55; Electrode DM141-SC; sample (1 g) dissolve in 1 M nitric acid solution and titrated against 0.02 M $AgNO_3$ solution), it was revealed that the samples contained ~7% chloride impurity.



Scheme 4. Acid-base properties of TO.

Thus, NTO batch samples containing TO as an impurity can be assayed correctly by this aqueous, acid-base, titration method. However, the presence of mineral acids (HCl and HNO_3) in the NTO sample will give a positive interference (mol. wt. of HCl (36.5) is much smaller than that of NTO (130)). The argentometric analysis of a few NTO batch samples revealed that there is hardly any chloride impurity (<0.5 %) present in these products.

The assay values of NTO samples were found comparable with those obtained by an in-house developed HPLC method (Shimadzu; Column: C18; mobile phase: 18% acetic acid in methanol; flow rate: 1 ml/min; sample: 100 ppm in the mobile phase; injection volume: 0.1 µl). HPLC analysis gave a single peak at retention time 3.38 min for NTO. The typical purity values for three batch samples are shown in Table 2. The purity value obtained from the HPLC method was found to be marginally lower (by <1%) than that from the titration method. This may be due to positive interference by mineral acid impurities (HCl and HNO_3) present in the sample or to human error involved in the aqueous titration method.

Table 2. Assay results of NTO samples by the HPLC and acid-base titration methods

Sample	% Purity of NTO	
	HPLC method	Acid-base titration method
1	98.6	99.2
2	98.8	99.3
3	99.0	99.5
Standard NTO	99.5	99.6

Conclusion

The acidic character of NTO was exploited for its assay by aqueous acid-base titration. No interference from the precursor TO (possible impurity) is observed in this titration method. The method is simple and economical. However, the presence of free mineral acid impurities in the sample gives positive interference in the analytical value when compared to the assay value obtained by the HPLC method. This titration method may be adopted as a quality control tool for NTO manufacture. It may also be used to estimate acidic impurities present in the precursor TO.

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