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SHORT NOTE ON NON-EXPLOSIVE DISTILLATION OF HN_3

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Hydrazoic acid is prepared by reacting 50% H_2SO_4 or 75% H_3PO_4 with 13% NaN_3 followed by the distillation of the solution near boiling temperature. In a typical distillation 50% H_2SO_4 or 75% H_3PO_4 is added dropwise to the NaN_3 solution maintained near boiling temperature [1–4]. A small amount of NaOH is added to the NaN_3 solution so as to avoid an explosion which Kemp [5] stated is due to high concentration of HN_3 during distillation. Recently, Kemp [5] has prepared HN_3 free from SO_4^{2-} impurities by passing nitrogen through the distillation apparatus 30 minutes before and during the process of distillation. He also reports that the distillation proceeds safely near boiling temperature.

In an attempt to prepare SO_4^{2-} free $Zn(N_3)_2$ by following the method recommended by Kemp a violent explosion occurred immediately after distillation while we were trying to remove the receiving flask containing $Zn(N_3)_2$ solution. In a further distillation, another explosion occurred while we were adjusting one of the quick-fit joints during distillation of HN_3. In each case the explosion resulted in serious injuries to the research workers. The reason for the explosion was not apparent but the temperature of distillation and the concentration of HN_3 were unlikely causes, since the distillation was carried out in accordance with the method of Kemp [5].

To investigate the cause of explosion, the distillation was carried out several times under different conditions of temperature and pressure. A modification was made in the technique of Kemp to record the temperature of NaN_3 solution during distillation. This was achieved by fusing a capillary containing a Pt – Pt 13% Rh thermocouple to the distillation flask in such a way that the tip of the thermocouple was in the solution. In order to avoid any reaction between the thermocouple and the reactants of distillation and HN_3 produced, the thermocouple tip was covered by fusing a very small amount of glass at that end of the capillary. The distillation set-up had facilities for nitrogen flow and for evacuation.

The distillation of HN_3 was carried out several times at 92° in an atmosphere of nitrogen and at 75° under reduced pressure of nearly 10^{-2} mm. The results are given in Table 1.

Explosion was not observed when no NaOH was added to the NaN_3 solution. The yield of HN_3 was quantitative even when the distillation was carried out at

Table 1

S/N	Rate of addition of 50% H_2SO_4 or 75% H_3PO_4 drops/minute	Distillation conditions		Adjustment on joints	Explosion
		Temp., °C	atm.		
1.	6, 10, 14, 18 or spontaneous addition of acid	92	Nitrogen	NO	NO
2.	6, 10, 14, 18 or spontaneous addition of acid	92	Nitrogen	YES	YES
3.	6 10, 14, 18 or spontaneous addition of acid	75	Reduced Pressure 10^{-2} mm	NO	NO
4.	6, 10, 14, 18 or spontaneous addition of acid	75	Reduced Pressure 10^{-2} mm	YES	YES

reduced pressure. Since explosion was neither observed at the elevated temperature of 92° nor with very rapid addition of 50% H_2SO_4, we concluded that the temperature of distillation and high concentration of HN_3 was not the cause of explosion. However, the observation that making a slight adjustment to any quick-fit joint did then result in explosion suggested that the frictional energy due to the turning of the joints was sufficient to initiate explosion in the HN_3 solution condensed between the joints.

HN_3 was also produced by reacting a thick paste of $Zn(N_3)_2$ deposited on a nickel spatula with 50% H_2SO_4 at about 60 °C and a little scratching of the paste then resulted in a very violent explosion. Since $Zn(N_3)_2$ does not explode upon scratching at that temperature, this experiment confirmed that a little frictional energy at high temperature was sufficient to cause a violent explosion in HN_3. The explosion of HN_3 upon shaking its 50% solution has been reported [6] and it may be somewhat similar to the explosion observed during distillation.

From the series of experiments reported here it may be concluded that the distillation is non-explosive if trapping of HN_3 between the quick fit joints can be prevented. This may be done by applying grease to all joints and this also facilitates adjustments to the joints without explosion if required during the distillation. Another observation was that the distillation would also go to completion if left overnight after addition of 50% H_2SO_4 or 75% H_3PO_4.

It is felt that this information is of importance for the safety of those working with metallic azides, particularly when distillation of HN_3 has to be carried out for the preparation.

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