

CHEMICAL REACTION HAZARDS ASSOCIATED WITH THE USE OF SODIUM BOROHYDRIDE
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Sodium borohydride is a highly energetic reducing reagent often used as a solution in water or alcohol. In competition with the desired reaction, aqueous sodium borohydride undergoes hydrolysis. The hydrolysis exotherm is capable of raising a 20w/w% aqueous solution to the boil in little over one hour together with an associated gassing rate of about 1000L of hydrogen gas/hr/L reagent.

Addition of a small amount of sodium hydroxide has been found to significantly reduce the rate of hydrolysis.

Sodium borohydride hydrolysis reduction hydrogen

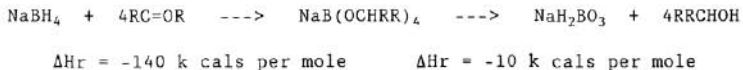
INTRODUCTION

Sodium borohydride is a commercially available reagent which is used with increasing frequency on a manufacturing scale for the selective reduction of organic molecules. A number of factors mitigate in choosing this reagent over other, more traditional reducing agents.

Use of sodium borohydride facilitates the reduction of, for example, aldehydes and ketones to primary and secondary alcohols respectively. The reagent is selective in that the reduction can be carried out in the presence of esters, nitriles, unsaturated aliphatic species etc. without adverse affect.

Sodium borohydride is readily soluble in water and alcohols, with water providing the most usual medium in which the reagent is used on a manufacturing scale.

Each mole of sodium borohydride is capable of reaction with up to four moles of the substrate and the reaction is highly energetic.



Heat of reaction for the reduction of a ketone to a secondary alcohol is about -150 k cal/s per mole of sodium borohydride. The reaction is usually

accomplished in two steps. Initially sodium borohydride reacts with the substrate to generate a borate intermediate and the heat of reaction associated with this step is about -140 k cal per mole. The borate intermediate is hydrolysed, usually by addition of acid, to liberate the corresponding secondary alcohol and the heat of reaction for this step is about -10 k cal per mole. Neither of the steps involves generation of a gaseous species.

HAZARDS OF THE DESIRED REACTION

As shown above, the desired reaction, ie reduction of a ketone using sodium borohydride, is extremely exothermic. The reaction has therefore been characterised using a heat flow calorimeter to determine whether reaction occurs readily or if accumulation could lead to a potential hazard.

The reaction has been examined at 25°C under isothermal conditions in a well stirred power compensation heat flow calorimeter. The reactor was placed inside an oven which was held at the same temperature as the reactor contents. A fixed cooling load was applied to the reactor and an electrical immersion heater was used to maintain the reactor contents at the required temperature. The external heater power demand is recorded and any drop in power demand represents the reaction exotherm.

In the isothermal experiment, 20 w/w% aqueous sodium borohydride was charged at a fixed rate over 150 minutes to an aqueous solution of a ketone. Partway through the addition, ie after about 45 minutes, there was a ten minute interruption to the addition.

Figure 1 shows the experimental raw data which were recorded throughout the duration of the reaction, ie sample temperature, weight of 20 w/w% aqueous sodium borohydride charged, external power demand, and gas evolution. It can be seen that exothermicity commenced immediately with the addition, ie there was an immediate drop in supplied external heater power demand when the addition commenced.

Figure 2 shows the process power output versus time profile. On our scale of operation, process power output rapidly reached about 15 watts and remained at this value until the addition was interrupted whereupon process power output ceased immediately. Upon resuming the addition (at the original rate) exothermicity commenced immediately and again was about 15 watts.

When the required stoichiometric amount of aqueous sodium borohydride had been charged, process power output returned quickly to the baseline value, ie after addition of 19.0 g of 20 w/w% aqueous sodium borohydride (0.10 g mole) to 0.4 g mole of ketone. In accord with the above equation, one mole equivalent of sodium borohydride was required per four moles of ketone. Heat of reaction was found to be -137 k cal per mole of sodium borohydride and no gas was evolved.

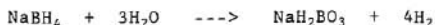
Conversion of the borate intermediate to liberate the secondary alcohol was by addition of concentrated hydrochloric acid to the batch at 25°C under isothermal conditions. The experiment was carried out in the heat flow calorimeter and the experimental raw data is shown in figure 3.

One mole equivalent of acid per mole of borate intermediate was required to complete the reaction. The reaction was found to be much less exothermic than the preceding stage and the heat of reaction was found to be -9.3 k cals per mole of borate intermediate, see figure 4. Again no gas was evolved.

From a chemical reaction hazards viewpoint, both steps of the desired reaction can be readily controlled. Both reactions occur readily and no accumulation of reagents is apparent. By adjustment of the addition rate of aqueous sodium borohydride, the batch temperature can be maintained at the required set temperature in balance with the available vessel cooling capacity. In the event of cooling failure or loss of agitation the addition can be stopped and as shown in figure 1 process power output would cease immediately.

HAZARDS OF THE UNDESIRE D REACTION

Under certain conditions, for example if the substrate is heavily substituted, hydrolysis of sodium borohydride, producing sodium borohydrate and hydrogen, can compete with desired reaction, ie:



$$\Delta\text{Hr} = -58 \text{ k cals}$$

Heat of reaction for complete hydrolysis of sodium borohydride is about -58 k cals per mole and four moles of hydrogen are liberated per mole of sodium borohydride, ref. 1.

A typical concentration for use of aqueous sodium borohydride on a plant scale is about 20 w/w%. At this concentration calculation shows that complete hydrolysis of one litre of aqueous sodium borohydride could raise the batch temperature by up to about 337 K and would evolve about 635 litres of hydrogen gas.

The solubility of sodium borohydride in water is reported to be 55 g per 100 ml, ref. 2. The maximum temperature rise and volume of hydrogen to be liberated from hydrolysis of such a strength solution would be correspondingly higher.

The rate of hydrolysis of aqueous sodium borohydride, ie the rate of heat evolution and rate of gassing, has been examined under various conditions.

When the reaction was examined under isothermal conditions, 20 w/w% aqueous sodium borohydride was agitated at 25°C in a heat flow calorimeter. Heat evolution and gassing were monitored continuously and the results are shown in figure 5.

The evolved gas was collected in 100 ml aliquots and each aliquot is shown as a step increase in figure 5. Gassing, of hydrogen, occurred at a near linear rate for the duration of the test and was equivalent to about two litres of hydrogen evolved per hour per litre of reagent. The rate of hydrolysis, as judged by the rate of gassing assuming four moles of gas are to be evolved from hydrolysis of one mole of sodium borohydride, was found

to be low, ie about 0.25 % per hour.

Figure 5 shows that there was no significant heat evolution during the hydrolysis, ie there was no change to the amount of energy supplied by the applied electrical immersion heater and required to maintain the batch at the set temperature.

This experiment shows that if the temperature is maintained at 25°C the rate of hydrolysis is extremely low and provided the small amount of hydrogen produced is adequately and safety vented no hazard will occur. However for plant operation it is necessary to determine the consequence of sodium borohydride solutions being present in uncooled storage vessels and / or the occurrence of cooling failure.

The hydrolysis of 20 w/w% aqueous sodium borohydride was therefore examined under low heat loss, adiabatic, conditions in a Dewar reactor.

The equipment consists of a Dewar flask fitted with an internal thermocouple, gas vent/recorder, and agitator. The reactor is surrounded by an electrical fanned oven, the temperature of which is controlled to be coincident with the reactor contents temperature. As exotherms occur in the reactor, the oven temperature responds to the reactor temperature and minimises any heat losses to the environment.

Heat losses to the Dewar reactor and ancillary equipment absorb 5-15 % of the total heat evolved and any exotherm will be abated to this extent. The abatement value is comparable to that expected for many plant scale jacketed reactors.

Charging of solid sodium borohydride to water was found to be mildly exothermic and generation of the 20 w/w% solution raised the batch temperature by about 5 K, see figure 6.

Continuation of the experiment under adiabatic conditions showed that the rate of hydrolysis increased dramatically when the reagent was held under adiabatic conditions.

As expected the rate of heat evolution and of gassing increased significantly as the reagent temperature increased, see table below:

temperature	rate of temperature rise	rate of gassing
25°C	4K per hour	20L per hour per litre of batch
50°C	50K per hour	120L per hour per litre of batch
75°C	240K per hour	510L per hour per litre of batch

Figure 7 shows the sample temperature and gassing rates over the temperature range 25°C to about 75°C. It can be seen that under low heat loss conditions the hydrolysis exotherm is capable of raising the reagent solution from ambient temperature to the boil in little over one hour. At this temperature the rate of gassing will be in excess of 1000 litres per hour per litre of 20 w/w% aqueous sodium borohydride.

PREVENTION OF THE UNDESIRED HYDROLYSIS REACTION

The adiabatic Dewar experiment shows that for plant operation the use of sodium borohydride solutions could lead to an extremely hazardous runaway reaction. The fast rate of the runaway reaction coupled with release of highly flammable hydrogen gas makes emergency relief venting an unattractive option as a basis of safety and if chosen would have to be fitted to all vessels which could contain the borohydride solution. Alternative methods for preventing the undesired hydrolysis reaction were therefore examined.

It was found that addition of sodium hydroxide, at 1 w/w% on weight of batch, was found to dramatically reduced the rate of hydrolysis. Figure 8 illustrates the effect of making a charge of sodium hydroxide, at 1 w/w%, to a 20 w/w% aqueous solution of sodium borohydride undergoing hydrolysis at about 50 to 60°C.

Before making the sodium hydroxide charge, the 20 w/w% aqueous sodium borohydride was self heating at a rate of about 70 K per hour and the rate of gassing was equivalent to about 150 litres of evolved gas per hour per litre of batch. After addition of sodium hydroxide, the rate of self heating fell to about 7 K per hour and the rate of gassing fell to be equivalent to about 5 litres of hydrogen evolved per hour per litre of batch.

The reduced rate of hydrolysis upon addition of 1 w/w% sodium hydroxide can be explained by consideration of the batch pH. Before addition of base the 20 w/w% aqueous sodium borohydride solution was at a pH value of about 10. After addition of 1 w/w% of sodium hydroxide the batch pH increased to about 12.

CONCLUSIONS

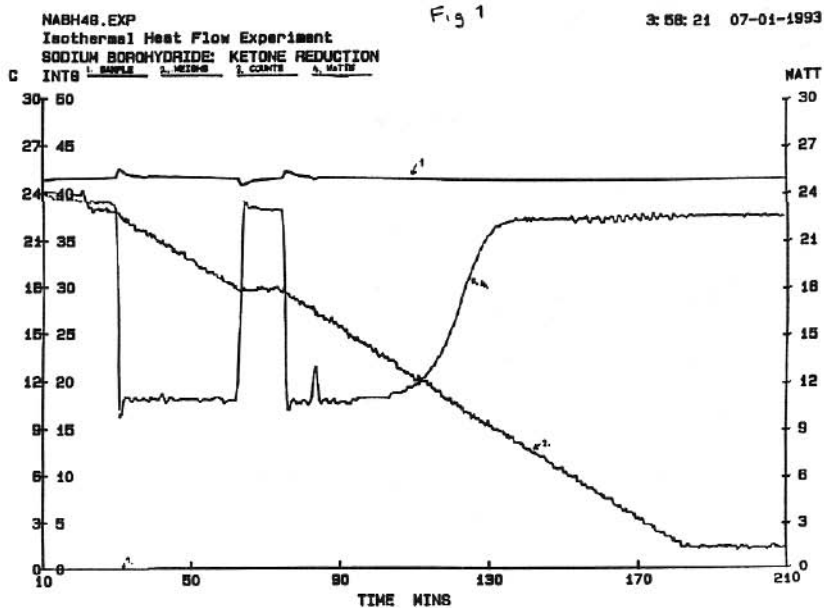
Reductions involving sodium borohydride have been found to be extremely exothermic with a heat of reaction of about -150 k cals per mole of sodium borohydride. The reaction proceeds rapidly at 25°C with no problems of accumulation in a well stirred reactor.

The undesired side reaction involving the hydrolysis of the sodium borohydride solution was found to be slow at 25°C. However under low heat loss conditions, for example in storage vessels or on cooling failure, a violent runaway reaction can occur. For a 20 w/w% aqueous solution the rate of batch temperature rise at 75°C was found to be 240 K per hour with an accompanying rate of hydrogen release of 510 litres per hour per litre of solution.

It has been found that the addition of 1 w/w% of sodium hydroxide dramatically reduces the rate of this runaway hydrolysis and can be used to improve the safety of plant operations involving sodium borohydride solutions.

REFERENCES

1. Davis, RE, Bromels, E, and Kibby CL, JACS 1962(84), 885-892.
2. CRC Handbook of Chemistry and Physics; CRC Press Inc. 1986, page B-141.



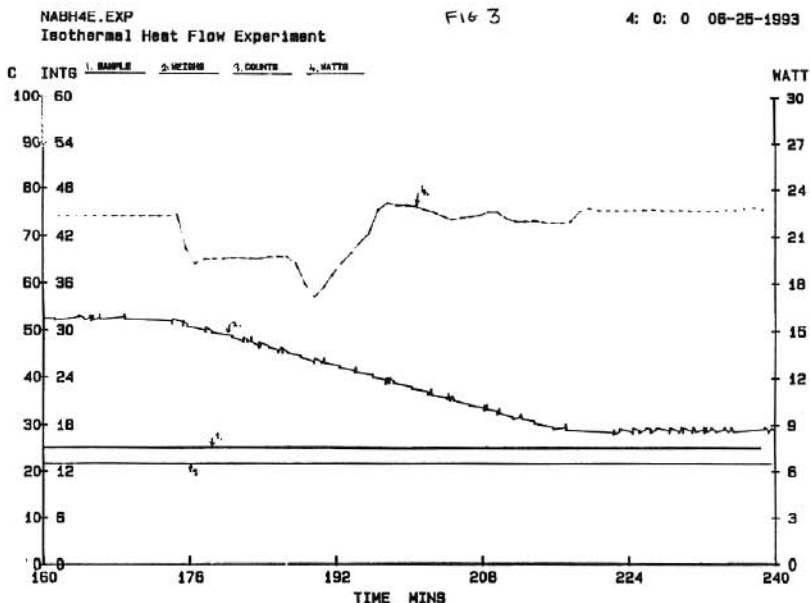
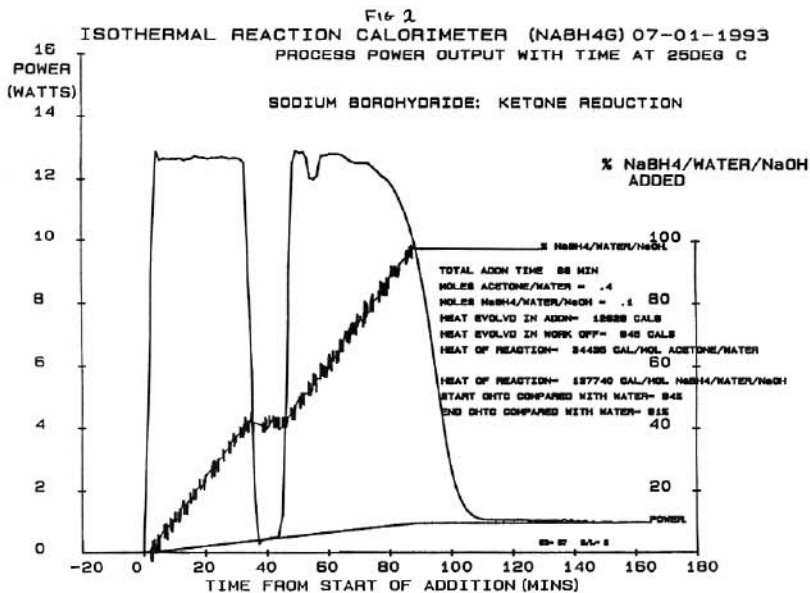
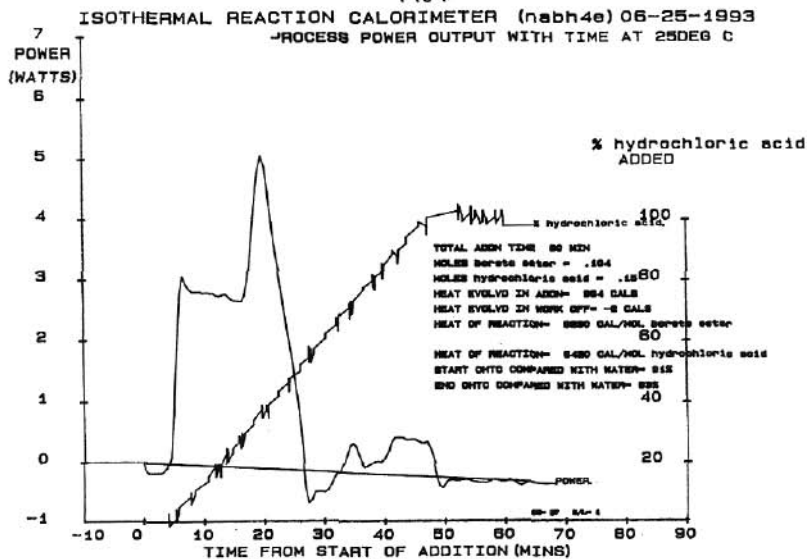


Fig 4



NaBH4B25.EXP
Isothermal Heat Flow Experiment
EXAMPLE

Fig 5

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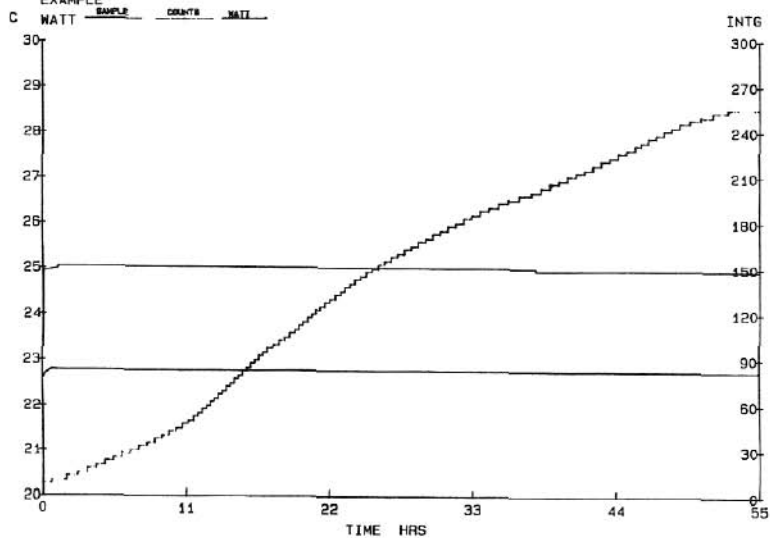


Fig 6

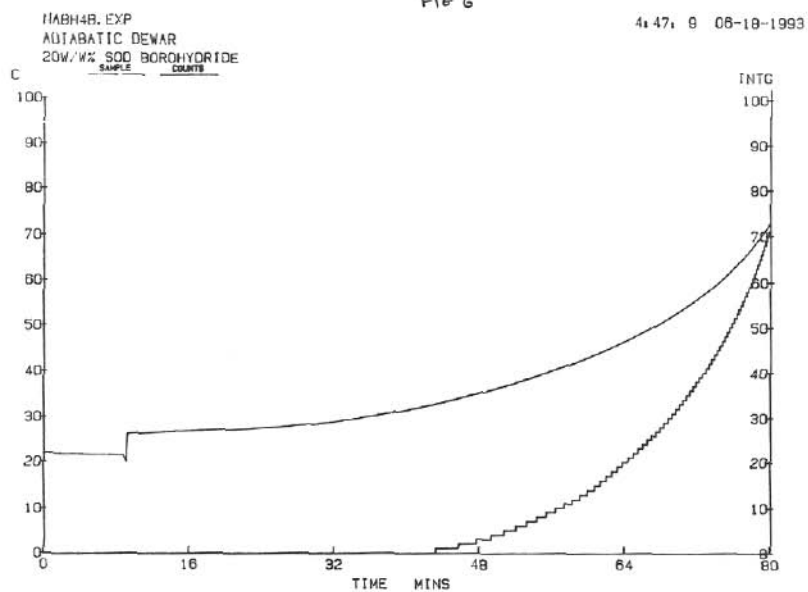


Fig 7

