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Application of thermal analytical techniques in development of a safe and robust process for production of triacetoxyborohydride (STAB)

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Abstract

The thermal hazards associated with the original procedure to produce sodium triacetoxyborohydride (STAB) from the reaction of $NaBH_4$ with glacial acetic acid were identified using various thermal analytical techniques. A substantial amount of $NaBH_4$ reagent accumulated at the end of the addition. As a result, a large heat spike occurred in the subsequent temperature ramp, which had the potential to initiate STAB decomposition and to generate a significant amount of non-condensable gases. Moreover, this rapid heat release was also accompanied by a rapid and uncontrollable generation of hydrogen gas from consumption of the accumulated $NaBH_4$. Evaluation of the reaction kinetics provided the fundamental information needed to develop a safe and robust process. The current procedure, utilizing a solution of $NaBH_4$ in DMAC, provides sufficient control of the heat and hydrogen gas release rates to reduce the processing hazard and eliminate the requirement for specially rated equipment for charging the $NaBH_4$ solids to the reactor.

Keywords: Thermal hazard; Exothermic; Decomposition; Sodium triacetoxyborohydride; RC1 Calorimeter

1. Introduction

Commercial powdered triacetoxyborohydride (STAB) is expensive and contains traces of $NaBH_4$ which has adverse effects on one of the reactions using STAB at Merck Co., Inc. The STAB reagent is also expensive and single-sourced at commercial scale. To overcome these challenges, Merck developed a procedure to produce STAB in *N*,*N*-dimethylacetamide (DMAC). Granular $NaBH_4$ was charged portion-wise into an acetic acid/DMAC solution at −10 °C followed by warming the reaction mixture to 22 °C and aging. This procedure is called the "in situ" STAB formation as the resulting solution was used directly in the subsequent reaction.

Although the process objectives were accomplished, the original procedure posed several safety concerns due to accumulation of $NaBH_4$, an unstable STAB product, a large heat of reaction and rapid rates of heat and hydrogen gas generation. The Operational Hazard Evaluation Laboratory (OHEL) at Merck used various thermal analytical tools, including the RC1 Calorimeter, Differential Scanning Calorimetry and the Reactive System Screening Tool, to assess the thermal hazards associated with the original process and to study the reaction kinetics. These studies led to the development of a safe and robust process while maintaining the process objectives. The revised process used a solution of $NaBH_4$ in DMAC and a higher reaction temperature (15 °C versus −10 °C). The new procedure also eliminated the requirement for specially rated equipment for charging $NaBH_4$ solids to the reactor.

Formation of STAB from sodium borohydride ($NaBH_4$) and glacial acetic acid (HOAc) is described in Eq. (1). Three moles of hydrogen gas are generated for every mole of $NaBH_4$ consumed to form STAB. Both $NaBH_4$ and STAB react violently with water forming hydrogen gas as a by-product

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according to Eqs. (2) and (3).

$$NaBH_4 + 3CH_3COOH \xrightarrow{DMAC} \underset{(STAB)}{NaBH}(OOCCH_3)_3 + 3H_2(g)\uparrow \quad (1)$$

$$NaBH_4 + 2HOH \rightarrow NaBO_2 + 4H_2(g)\uparrow \quad (2)$$

$$NaBH(OOCCH_3)_3 + HOH \rightarrow NaBOH(OOCCH_3)_3 + H_2(g)\uparrow \quad (3)$$

2. Experimental

2.1. Experiment 1 – the original process

The original process was studied in a Mettler RC1 Calorimeter to evaluate any thermal hazards associated with this process. DMAC was first charged to the RC1 Calorimeter and cooled down to −10 °C followed by the glacial acetic acid charge. After the dissolution exotherm, granular sodium borohydride (10–40 mesh particle size) was charged to the HOAc/DMAC solution at −10 °C. The sodium borohydride charge was done in 30 small portions at 3 min intervals to mimic the continuous solids charge over 90 min or ∼1 kg/min at the factory scale. The batch temperature was then ramped to 22 °C at 1 °C/min and aged overnight for reaction completion. Due to calibration requirements for the RC1 Calorimeter, the mixture after the $NaBH_4$ charge had gone through an additional 50 min age at −10 °C prior to the temperature ramp. Stream samples also were taken from the RC1 run for thermal and hazards testing, including differential scanning calorimetry (DSC) and Reactive System Screening Tool (RSST) testing.

2.2. Experiment 2 – kinetic study

The heat flow from the first RC1 run, along with the thermal data, indicated several safety concerns associated with the original procedure. The significant accumulation of sodium borohydride at the end of its addition resulted in large and rapid rates of heat release and hydrogen gas generation during the temperature ramp to 22 °C. This heat excursion has the potential to initiate STAB decomposition as determined by DSC and RSST studies.

The second RC1 run was designed to study the effects of temperature and physical form of $NaBH_4$ on the reaction rate and to provide fundamental information for the development of a safe procedure for scale-up. To collect the kinetic data, small portions of either $NaBH_4$ powder or granular $NaBH_4$ (10–40 mesh) were charged to a solution of HOAc in DMAC at 0, 10, and 20 °C. The same laboratory scale as Experiment 1, similar size portions of each solid were charged. The heat flow was allowed to come back to the base line between additions. Each addition was ∼3% of the total $NaBH_4$ charge. The amount of $NaBH_4$ charged to the reactor at the end of the kinetics study was stoichiometrically equivalent to ∼20% of the total acetic acid charged. Therefore, acetic acid was in large excess throughout this kinetics study, so that acetic acid consumption would only minimally affect the observed reaction rate. The kinetic data from this experiment were used in assessment of various procedure options. The solution addition process, determined to be the safest, is described in Experiment 3.

2.3. Experiment 3 – the revised process

In this revised procedure, a portion of the total amount of DMAC in the process was used to prepare a 15 wt.% $NaBH_4$/DMAC solution. Glacial acetic acid was charged to the RC1 Calorimeter followed by the remaining DMAC. The composition in the RC1 reactor at this point was 75 wt.% HOAc in DMAC. After the heat of dissolution dissipated, the previously prepared $NaBH_4$/DMAC solution was charged to the reactor at 15 °C at a constant rate in four portions with a syringe pump. The total addition time was 3 h. The 3 h addition was chosen to accommodate the removal capability of hydrogen gas in the factory process. The resulting solution was then warmed up to 22 °C and aged for reaction completion.

3. Results and discussion

3.1. Thermal decomposition of the STAB/DMAC solution

Samples at the end of the $NaBH_4$ charge and after the 22 °C age from the first RC1 run of the original process were taken for thermal characterization studies. As shown in Table 1, the sample after age had lower initiation temperatures and larger sizes of the decomposition exotherms than the sample after the $NaBH_4$ charge as seen by DSC. These data suggested that STAB was relatively less stable than $NaBH_4$. Similar data were obtained with the pure materials. The DSC of the commercial STAB previously showed a rapid decomposition exotherm of 222 J/g at 85 °C, while $NaBH_4$ decomposed at 125 °C at a slower rate with a smaller heat release (Table 1).

DSC analysis of the reaction solution after aging showed two major decomposition exotherms. The first exotherm occurred at a temperature as low as ∼50 °C with 180 J/g. The second exotherm was 42 J/g and occurred at ∼150 °C. Note that the initiation temperature seen by DSC should only be used as an approximation as it is a temperature-driven system. The exothermic activity generally starts at a temperature well below that seen by DSC.

The low initiation temperature of the first decomposition exotherm with respect to the operation temperature of 22 °C was a concern. Therefore, an RSST run of the solution af-

Table 1
Thermal characterization

Sample #	Process			Exothermic activity[a]		
	Sample description	Operating temperature (°C)	Operating condition	Initiation temperature (°C)	Size (J/g)	Heat release rate
1	After charging $NaBH_4$ to the solution of HOAC/DMAC	−10	atm	63	30.1	Rapid
				87	69.5	Slow
				150	34.7	Moderate
				205	3.8	Rapid
2	After #1 warmed up and aged	22	atm	50	177.8	Slow–moderate
				150	41.8	Slow
3	Commercial STAB solids			85	222.6	Rapid
4	Commercial $NaBH_4$ solids			125	24.7	Slow

[a] Exothermic activity was evaluated up to 250 °C in the DSC.

ter aging was carried out to quantify the rates of temperature and pressure increases associated with these exotherms. The RSST data showed a moderate temperature increase rate of 12 °C/min associated with the 50 °C exotherm. However, the rate of temperature increase associated with the 150 °C exotherm was an order of magnitude higher than that from the 50 °C exotherm (166 °C/min). The RSST also measured a moderate pressure increase (14 psi) and a moderate residual pressure (7 psi), indicating formation of non-condensable gases.

3.2. Hazard potentials of the original procedure

The heat flow from the RC1 run of the original procedure is shown in Fig. 1. STAB formation was exothermic with a heat of reaction of −147 kJ/mol of $NaBH_4$. Note that this measured heat also included the dissolution heat of solid $NaBH_4$. The corresponding adiabatic temperature rise was calculated to be 136 °C.

Fig. 2 plots the feed fraction of $NaBH_4$ and the thermal conversion as functions of time. As shown in this figure, a substantial amount of $NaBH_4$ was accumulated during its addition at −10 °C. A thermal conversion of only 63% was achieved at the end of the $NaBH_4$ charge. Due to the calibration requirement of the RC1, the reaction mixture was aged at −10 °C for an additional 50 min prior to warming to 22 °C. During the temperature ramp, a significant heat release was encountered as shown in Figs. 1 and 2. Significant evolution of hydrogen gas was also observed concurrently with this heat release. A thermal conversion of 91% was measured at the end of the 30 min temperature ramp.

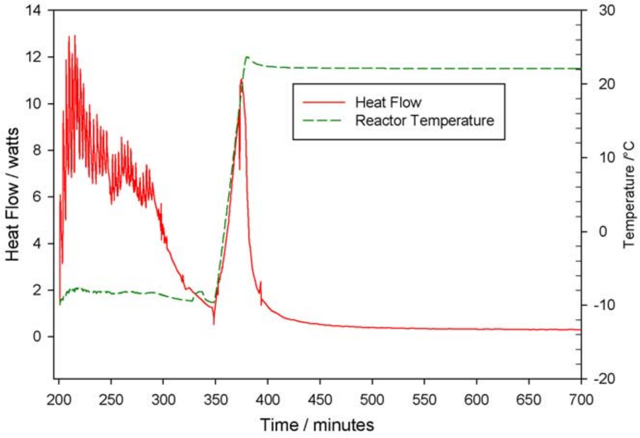

Fig. 1. Heat flow and temperature profile from the granular $NaBH_4$ process.

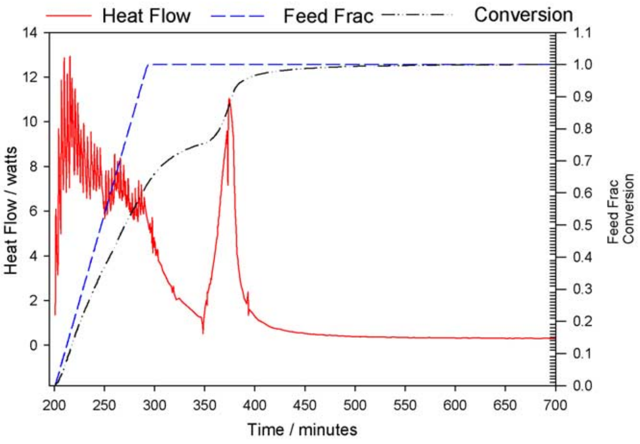

Fig. 2. Heat flow, feed fraction and thermal conversion from the granular $NaBH_4$ process.

About 28% of the total thermal conversion would be accounted for during the temperature ramp in a typical process operation, where the 50 min RC1 calibration at −10 °C was not present. Significant evolution of hydrogen gas would occur during this temperature ramp, as three moles of hydrogen gas were generated for every mole of $NaBH_4$ consumed. At a small pilot plant scale, i.e. 12 kg of $NaBH_4$ in a 50-gallon reactor at 80% fill, 28% conversion would generate 267 moles of hydrogen gas or 2412 psi in the head space with an instantaneous generation of hydrogen. The average hydrogen gas flow over the 30 min ramp was calculated to be 200 L/min. Note that the maximum rate of hydrogen gas generation could be much higher than the average flow of 200 L/min based on the heat flow shown in Fig. 1. Dependency of the maximum gas release rate on scale-up was also expected. The rapid and uncontrollable rate and the large amount of hydrogen evolution during the heat-up posed a hazard concern.

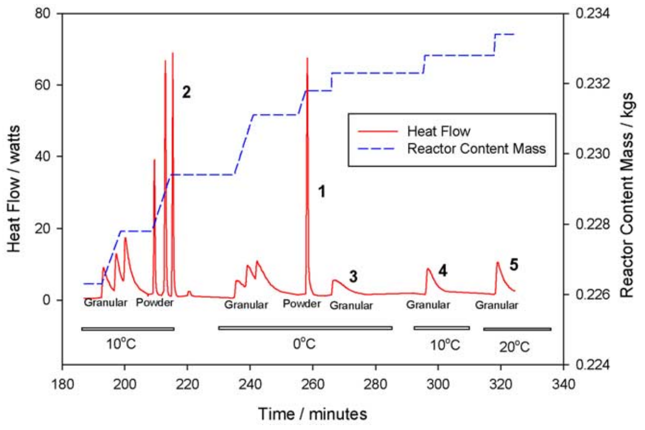

Fig. 3. Effects of temperature and $NaBH_4$ form on apparent reaction rate.

As shown in Fig. 1, a large heat spike occurred during the temperature ramp as a result of consumption of the accumulated $NaBH_4$. This heat release corresponded to a large adiabatic temperature rise of 38 °C, which could have a potential to initiate the 50 °C STAB decomposition exotherm. Consequently, the energy associated with this 50 °C exotherm could have the potential to raise the batch temperature to the initiation temperature of the second STAB decomposition exotherm. As noted previously, moderate generation of non-condensable gases associated with these exotherms was evidenced in an RSST run. The additional pressure and heat generation from the STAB decomposition increased the potential of thermal runaway of the original procedure.

The remaining 9% of thermal conversion was achieved after a 4 h aging at 22 °C. This corresponded to an adiabatic temperature rise of 12 °C, which posed no safety concern.

3.3. Kinetic study results

A kinetic study was performed in the RC1 Calorimeter to provide fundamental information for development of a safer process. Effects of particle size of solid $NaBH_4$ and reaction temperature on the apparent reaction rate were measured.

Fig. 3 shows the heat flow curves for the powder and granular (10–40 mesh) $NaBH_4$ at three temperatures: 0, 10 and 20 °C. The powdered material reacted violently at both 0 and 10 °C (Peaks or Reactions 1 and 2 in Fig. 3, respectively). Therefore, measurements with powder at temperatures higher than 10 °C were not performed. The heat release and hydrogen gas evolution were completed within 1–2 min upon each addition. Due to the rapid hydrogen gas generation, significant foaming occurred causing the volume in the reactor to temporarily increase by ∼20% upon each addition. Venting of such a two-phase system would be difficult and would require a very large vent size for the pilot plant or factory reactor.

Granular $NaBH_4$ reacted very slowly. Depending on the reaction temperature, it took 5–10 min for the heat release and gas generation to stop after each addition. This observation confirmed the severe accumulation of $NaBH_4$ at −10 °C in the original procedure.

Table 2
Effects of $NaBH_4$ form and temperature on apparent reaction rate

Reaction no.	$NaBH_4$ form	Temperature (°C)	Rate constant (min^{-1})	Half-time (min)	Time at 90% conversion (min)
1	Powder	0	3.55	0.20	0.65
2	Powder	10	4.15	0.17	0.56
3	Granular	0	0.0767	9.04	30.0
4	Granular	10	0.2558	2.71	9.0
5	Granular	20	0.3773	1.84	6.1

The first-order kinetic model was found to fit the heat flow curves well with all the R^2 being greater than 0.97. Note that the reaction rate in this paper only refers to the “apparent” overall rate. Table 2 summarizes the apparent rate constants for the five reactions along with the half-life time and the time to achieve a 90% conversion. The data indicated that the apparent reaction rate increased with the increase in surface area of $NaBH_4$, suggesting that dissolution of solid $NaBH_4$ is the rate limiting step. The rate constant for the powdered material at 0 °C was 46 times higher than that of the granular material at the same temperature.

The temperature dependency of the rate constant for the powdered material was estimated from the rates at 0 and 10 °C and is shown in Eq. (4). The available data suggest weak dependence of the apparent reaction rate on temperature for the powdered material. Temperature had a greater effect on the apparent reaction rate for the granular material as shown in Eq. (5).

$$k_{(\text{powder})} = 57.1 \exp\left(-\frac{E}{RT}\right) \quad \text{and } E = 6.2\,\text{kJ/mol} \tag{4}$$

$$k_{(\text{granular})} = 4.3 \times 10^{7} \exp\left(-\frac{E}{RT}\right) \quad \text{and } E = 45.2\,\text{kJ/mol} \tag{5}$$

where k is rate constant in min^{-1}, T is the reaction temperature in Kelvin degrees, and R is the gas constant.

4. The revised process

The revised process utilized a solution charge of $NaBH_4$ at a slower addition rate (3 h) and a higher reaction temperature of 15 °C to minimize accumulation of $NaBH_4$ (see Section 2 for details). The experiment was un-eventful with no excursion of heat or excessive hydrogen gas generation. Fig. 4 shows the heat flow curve obtained from the RC1 run. The calculated thermal conversion along with the feed fraction of the $NaBH_4$ solution is also included.

As shown in Fig. 4, the heat release was uniformly distributed throughout the addition of the $NaBH_4$/DMAC solution, indicating no accumulation of the reagent. A thermal conversion of 94% was achieved at the end of the addition as

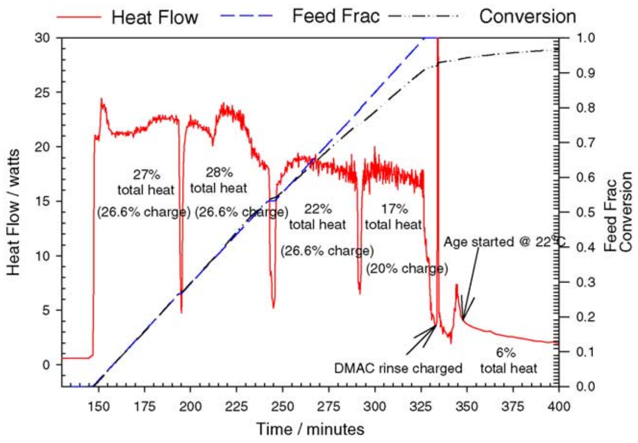

Fig. 4. Heat flow, feed fraction and thermal conversion from the $NaBH_4$ solution process.

opposed to 63% in the original procedure. The heat release during the temperature ramp to 22 °C also was insignificant, thus eliminating the potential of initiating the STAB decomposition exotherms. A similar age time at 22 °C was required to achieve a 99% conversion (∼3.5 h versus ∼4 h).

In addition, the rate of hydrogen gas generation was steady throughout the addition and the temperature ramp. The average flow rate of hydrogen generation was calculated to be about half of that in the original procedure (∼115 L/min versus ∼200 L/min). The lower and steady rate of hydrogen release is beneficial to the Pilot Plant and factory operations/designs.

Other advantages of using the $NaBH_4$ solution include the ease in controlling the addition rate of $NaBH_4$ and the removal of the requirement for specially rated equipment for charging $NaBH_4$ solids to a reactor. These advantages reduce the capital cost to produce STAB.

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