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The Thermal Runaway of a Hydrogen-Transfer Reaction

Andrew V. West* and Chris P. Newman

Process Research and Development, Quest International, Ashford, Kent TN24 OLT, United Kingdom

Abstract:

A thermal runaway is reported which occurred during the conversion of an unsaturated alcohol to the saturated ketone via internal hydrogen transfer. An unexpected and extremely rapid rise in temperature and pressure was observed when the reaction was run at production scale. The vessel was able to withstand the pressure generated, and no injury or damage resulted. The possible causes of this incident are considered here. It should be noted that whilst the rate of a hydrogenation reaction can generally be controlled by the rate of addition of hydrogen, this may not be the case where the possibility of internal hydrogen transfer exists, whether by design or unintentionally. Unsaturated alcohols are perhaps less obvious, although they are very good examples of molecules where such a possibility exists. Our pre-scale-up reaction hazard assessment protocol now considers this point specifically.

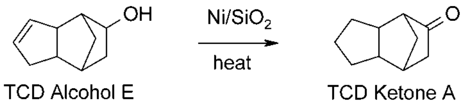
Introduction

We bring to the attention of the readers of this journal the potential hazards associated with the scale-up of hydrogen-transfer reactions. This stems from an incident that occurred some while ago involving such a reaction.

For commercial reasons a large amount of an intermediate was required in a short time scale. The decision was taken to satisfy demand for this material by producing a large batch utilising a process that had already been run on a small production scale. An improved process was to be developed for future use.

The incident related to the transformation of tricyclo[5.2.1.0^{2,6}]dec-4-en-8-ol (TCD Alcohol E) to tricyclo[5.2.1.0^{2,6}]decan-8-one (TCD Ketone A) via an internal hydrogen transfer (Scheme 1). The reaction was carried out in the presence of a nickel catalyst at elevated temperature. In both the laboratory and small-production facility (at 200 kg scale) at Quest this reaction was very slow, requiring a relatively high loading of catalyst (10% w/w), temperatures in excess of 170 °C, and approximately 30−40 h to go to completion. When the reaction was carried out at 1.3 tonne scale, an extremely rapid temperature rise was observed (after several hours of heating with no significant rise in the measured temperature of the reaction mixture, although there is a question as to whether the heating system was functioning correctly during this period), accompanied by pressurisation of the reactor. The reactor being used was a pressure vessel (chosen to reduce the emission of volatiles) and thus was able to withstand the pressure generated. Neither injury to personnel nor material release was caused by this incident.

Scheme 1. **Transformation of the TCD Alcohol E to TCD Ketone A by internal hydrogen transfer**



This chemistry had been carried out many times previously, both at laboratory- and small-production scale (up to 200 kg) without incident. The scale-up of the reaction had been rigorously assessed: indeed trials had been carried out at greater than 210 °C specifically looking for decomposition or hazardous side reactions. All previous work on this reaction suggested that the overall rate is governed by the rate of dehydrogenation of the alcohol, which is slow and requires elevated temperature. However, when the reaction was carried out on a larger scale, a highly exothermic event became apparent at 145 °C. The contents of the reactor self-heated extremely rapidly, over approximately 1−2 min, to a temperature in excess of 200 °C (the exact temperature is not known, as it was above the upper limit of the sensors being used). This was accompanied by pressurisation of the reactor to 8.2 bar. Analysis of the contents of the reactor, by gas chromatography after the event, showed the reaction products to be as expected and the degree of conversion to be 90%.

As a result of this incident, the process concerned was modified to preclude uncontrolled internal hydrogen transfer, by derivatisation of the alcohol functional group. It is not possible to discuss details of these modifications here for commercial reasons. This modified process has since been run safely.

Discussion

At the time of this event, the necessary resources and equipment to fully investigate it to today's standards did not exist within Quest, although some calculations were made using the approach suggested by van Krevelen.[1] This uses group contributions to estimate the Gibbs free energy of formation of organic compounds and hence can be used to estimate a value for the Gibbs free energy of a reaction. This work suggested that the hydrogen-transfer reaction is thermodynamically favoured in the temperature range of interest and that elevated temperature favours it further. Whilst this approach can be used with the overall hydrogen-transfer reaction, it is now felt that the lack of an entropy term for hydrogen precludes its use for looking at the separate dehydrogenation or hydrogenation steps.

Since this incident a dedicated group has been established within Quest to investigate chemical reaction hazards and

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* To whom correspondence should be addressed. E-mail: andy.west@questintl.com.

(1) Van Krevelen, D. W.; Chermin, H. A. G. *Chem. Eng. Sci.* **1951**, *2*, 66.

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ensure the safety of our processes. The incident itself has been the subject of a retrospective investigation in an attempt to learn from it. The techniques applied to this problem are described later. Unfortunately it has not been possible to recreate this incident in the laboratory; therefore, it has not been possible to determine the course the reaction took experimentally. The reactor being used had previously been cleaned to a mirror finish to assist in meeting clean-down standards. It is thought possible that this process introduced an unknown material that interacted with the catalyst used later, thus altering its activity and possibly causing a lowering of activation energy. However, we have not been able to prove this experimentally.

The incident may be analysed from a theoretical viewpoint. The heats of reaction have been estimated, by various means, and the effects of this heat release on the pressure of the system have been considered.

Two possible hypotheses have been put forward to account for the rapid temperature rise. The reaction concerned is the transfer of hydrogen within the molecule, with the hydrogen liberated by the dehydrogenation of the alcohol hydrogenating the alkene double bond. The first hypothesis is that the dehydrogenation and hydrogenation reactions became uncoupled (previous experience indicated that the dehydrogenation had a higher activation energy than the hydrogenation; this meant that once hydrogen had been liberated, it rapidly reacted with the double bond). The alternative hypothesis is that the combined hydrogen-transfer ran away. These hypotheses are discussed below.

1. The Separate Dehydrogenation and Hydrogenation Reactions. The production reactor was charged with the starting materials, including catalyst, at room temperature and was being heated to its operating temperature when the incident occurred. The heating phase was slower than expected, and it has been postulated that during this time the unsaturated alcohol was dehydrogenating, at least partially (the endothermic nature of the dehydrogenation accounting for the slow heating rate). This is complicated because during this phase there were also some problems with the oil-heating system on the reactor. The resulting hydrogen could have loaded the catalyst (the reactor did not pressurise significantly during this phase). Once a temperature was reached at which the rate of hydrogenation became significant, sufficient heat was generated to increase the rate of both reactions, leading to a thermal runaway.

This hypothesis relies on the activation energy of the dehydrogenation reaction only being lowered. Had the activation energy of the hydrogenation reaction been similarly lowered there would not have been any accumulation of hydrogen.

2. The Combined Hydrogen-Transfer Reaction. The alternative hypothesis considered was that the rates of both the dehydrogenation and hydrogenation reactions were enhanced to the same degree. The reactions proceeded much more rapidly than expected at approximately 145 °C. The heat released was more than could be removed from the reactor, causing a temperature rise, which caused a further increase in rate, and thermal runaway ensued.

Table 1. **Predicted vapour pressure of TCD Ketone A**

temperature [°C]	vapour pressure [bar]
60	0.012
100	0.078
150	0.44
200	1.61
250	4.44
300	10.02
310	11.60
350	19.92
380	28.72

Consideration of the predicted temperature rises as estimated from theory may help distinguish between these two possibilities. Whilst the temperature reached cannot be used directly, as it was above the upper limit of the detectors, we have used it to estimate the vapour pressure of the product. The separate dehydrogenation−hydrogenation hypothesis would result in the release of more heat in the runaway phase than the concomitant hydrogen-transfer reaction. We have estimated the vapour pressure of the product of this reaction, the saturated ketone, at the predicted maximum temperatures (Table 1). It can be seen from these results that the estimated vapour pressure at the predicted maximum temperature for the separate dehydrogenation−hydrogenation case is significantly higher than the 8.2 bar observed. The vapour pressure estimated at the maximum temperature suggested for the combined hydrogen-transfer reaction, however, is in good agreement with the pressure observed.

Whilst this is not conclusive evidence, we feel that it lends credence to the combined hydrogen transfer hypothesis. However, we have not been able to explain the runaway unequivocally.

Experimental Section

This reaction has been studied extensively in the laboratory, in an attempt to recreate the incident. We have not been able to do so.

Differential Scanning Calorimetry (DSC) Studies. The materials concerned were examined by DSC. Samples of the materials concerned and mixtures thereof were subjected to range of test regimes (varying temperature range, heating rate). The effects of possible contaminants (including acid, base, and iron filings) were also tested. The incident could not be recreated in any of these tests. It is possible that the lack of agitation, inherent in this technique, might prevent the catalyst and TCD Alcohol E from interacting.

Autoclave Experiments. In an attempt to simulate the agitated pressure vessel in which the incident occurred experiments were conducted in small, laboratory-scale autoclaves. TCD Alcohol E and catalyst, with and without various possible contaminants, were charged to the autoclave and heated whilst being agitated. Different heating regimes were employed, including heating at full power and a slower heating rate that simulated that observed on the production scale. Again, it did not prove possible to recreate the incident.

It should be noted that it was not possible in the laboratory to exactly recreate the agitation conditions experienced in the full-scale reactor. Since this is a heterogeneous catalysis system, agitation will have an effect on reaction rate; however, it is considered unlikely that this alone explains the extreme difference in behaviour observed in this instance.

Unfortunately, we were unable to recreate the runaway reaction in the laboratory. The intention, had the reaction been reproducible, was to study it using the techniques of reaction calorimetry, adiabatic calorimetry, and in situ FTIR analysis. The experimental data generated would have allowed us to differentiate between the two proposed mechanisms. However, this did not prove possible.

Reaction calorimetry is used to study a desired synthetic reaction. It gives data not only on the overall heat liberated, or absorbed, by a reaction but also on the rate of heat production or uptake. In this case the overall heat released would have been the same if the reaction had proceeded by either separate dehydrogenation/hydrogenation or combined hydrogen-transfer, but the profile of the heat flow would have differed markedly. The separate dehydrogenation/hydrogenation reaction would have had distinct endothermic and exothermic portions, whilst the combined hydrogen-transfer reaction would have been exothermic throughout.

Adiabatic calorimetry is applied to the study of runaway reactions under heat-loss conditions similar to those on plant, that is essentially adiabatic. It yields data on the rates of temperature and pressure increase and also the final temperature and pressure attained by a runaway. Such data would have helped differentiate between the two proposed mechanisms.

In situ FTIR can be used to monitor the progress of a reaction. In this instance it would have been used to determine whether any unsaturated ketone was present in the reaction mixture. The presence of such material would suggest that the dehydrogenation and hydrogenation reactions had proceeded separately.

Theoretical Considerations

The fact that we could not recreate the incident practically led us to consider a theoretical approach. Various methods were used to derive an estimate of the heats of reaction of the dehydrogenation and hydrogenation steps. These included the use of heats of formation of structurally related compounds published in the literature[2] and also the computer-based predictive package, CHETAH[3] (this package takes the approach of using Benson groups[4,5] to estimate the thermodynamic properties of a molecule). The heats of reaction derived were considered, and values of $+60$ kJ mol^{-1} for the dehydrogenation and -120 kJ mol^{-1} for the hydrogenation were taken as being representative. This means that a value of -60 kJ mol^{-1} was used for the heat of reaction of the combined hydrogen-transfer reaction.

These estimated heats of reaction can be used to predict the maximum temperature the reaction mass will achieve in a thermal runaway, assuming that no further reactions occur at elevated temperatures. If a further reaction does occur, for example the exothermic decomposition of a product, the maximum temperature and pressure reached may be greater than that predicted from the heat of reaction alone.

Table 2. **Estimated parameters used for vapour pressure prediction**

parameter	estimated value[a]
critical temperature	386 °C
critical pressure	30.8 bar
acentric factor	0.39937

[a] All parameters were estimated in Predict.

Prediction of the maximum temperature reached can be simplified by treating the reaction mass as an adiabatic system. This is a valid assumption for large production scale reactors. In this case the extremely rapid temperature rise also supports this assumption, as the reactor heating/cooling system would not have had the capacity to remove sufficient heat in the time scale required.

A value of 2000 J/kg/K has been used for the specific heat capacity of the reaction mixture (estimated value). The predicted adiabatic temperature rises for the two hypotheses can then be compared. In the first hypothesis the dehydrogenation reaction occurs during the heating phase so that the runaway is caused purely by hydrogenation of the double bond. In this case the predicted adiabatic temperature rise is approximately 400 K. This figure can be amended to 360 K because the reaction went to 90% completion. Similarly, the predicted adiabatic temperature rise for the combined hydrogen-transfer scenario is approximately 164 K (at 90% conversion).

The maximum temperature of the reaction mass after the runaway is thus approximately 505 °C for the separate dehydrogenation/hydrogenation case or approximately 309 °C for the combined hydrogen-transfer case.

The vapour pressure of the system (effectively TCD Ketone A at this point in time) can then be estimated using a prediction package such as PREDICT.[6] This package offers a variety of methods for estimating vapour pressure, including the Pitzer, Riedel, and GomezThdos methods. These methods were evaluated for TCD Ketone A, and the Pitzer method was chosen as the most representative, although it is interesting to note that there was relatively little variation between the data generated by each model. It should be stated here that these figures are only approximations and that their derivation required the estimation of other parameters such as the critical temperature and pressure (Table 2). Therefore they should be treated with caution.

The data generated by the Pitzer model is presented in Table 1 for selected temperatures. It can be seen that in the region of 310 °C, the maximum temperature attainable for the combined hydrogen-transfer hypothesis, the vapour pressure of the system is approximately 11.6 bar. It was only possible to predict the vapour pressure at temperatures up

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(3) CHETAH, ver 4.4, *The ASTM Chemical Thermodynamic and Energy Release Evaluation Program*; American Society for Testing and Materials: West Conshohocken, PA, 1990.

(4) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546.

(5) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(6) PREDICT, *Prediction of Thermodynamics and Transport Properties*; Dragon Technology Inc., P.O. Box 16012, Golden, CO 80402, U.S.A.

to 380 °C, but at this temperature the predicted vapour pressure of the system is already in excess of 28 bar.

These data lead us to favour the combined hydrogen-transfer hypothesis, although it is not proved conclusively.

Conclusions

Whilst we have been unable to unequivocally explain this incident, we feel that there are important learning points which should be shared. This specific process was modified and carried out in a manner that precluded internal hydrogen transfer**. Whilst hydrogenations are generally run in a semi-batch manner, controlled to a large degree by the addition rate of hydrogen, this cannot be guaranteed where the possibility exists for hydrogen transfer within the molecule, thus rendering a batch reaction possible (with the dangers inherent to this mode of operation). Unsaturated alcohols are good examples of molecules where such a possibility exists. Our pre-scale-up reaction hazard assessment protocol now considers this point specifically (from a theoretical viewpoint, by looking for the presence of a group within a molecule that may dehydrogenate, supplying hydrogen to hydrogenate a second group).**

This incident also serves to reiterate the importance of considering reaction hazards whenever changes to a process (or the scales at which a process is operated) are made. Nowadays, one would assess the safety of a reaction such as this using various techniques, including differential scanning calorimetry, reaction calorimetry, and adiabatic calorimetry. However, it would not be plausible to study the effect of each possible contaminant on the reaction; therefore, a theoretical consideration of internal hydrogen transfer remains important.

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