

Nonclassical Thermal Runaway: The Bhopal Disaster and Liquid Hydroperoxide Explosives

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1 Introduction

More than 25 years after the Bhopal disaster its horrific legacy is now well-documented [1], but the causes are still being debated in the international media. Was the disaster caused by neglect, parsimony, or procrastination by Union Carbide on safety and maintenance? Ignorance, corruption, sabotage and cover-up? Inadequate regulation of urban and industrial development? Possibly all of the above, but they are putative, secondary or socioeconomic contributing factors not causes.

The primary *cause* of the thermal runaway that led to the venting of a deadly mist of methyl isocyanate over the city of Bhopal was physicochemical. In this belated work I present a stability analysis of methyl isocyanate (MIC) hydrolysis using a homogeneous flow reactor paradigm. Results indicate that the thermal runaway may have been due to a large amplitude, hard thermal oscillation initiated at a subcritical Hopf bifurcation. This type of thermal misbehavior cannot be predicted using Semenov theory and conventional thermal diagrams, and may be endemic to liquid thermoreactive systems.

A strong driver for better understanding of thermoreactive processes in liquids is the use of organic hydroperoxide liquid explosives by terrorists. The ingredients for making such bombs are cheap and widely available and they cannot be detected by metal and nitrogenous explosives detectors or distinguished from hand lotion by x-ray machines [2]. They were used in the suicide attacks on the London transit system in 2005, and the terrorists convicted of the foiled 2006 transatlantic aircraft conspiracy had planned to use them. (Many more accounts of peroxide misuse incidents are easily found on the web.) To this day there are restrictions on carrying liquids through security barriers at most airports. It seems grimly inevitable that the use of liquid peroxide explosives as mass murder weapons will increase. Knowledge of their fundamental mechanism of action may help to counter their use.

The open literature on thermal runaway criteria in batch reactors and storage tanks was summarized by Velo *et al* [3]. In defining critical conditions they, along with other authors cited therein, begin with the assumption that storage tanks can be modelled as well-stirred batch reactors with linear thermal coupling to the environment. However batch reactors have no non-trivial steady states, and there is no general theory for determining whether a thermal excursion will grow or decay. It is shown in this work that a simple model with nonequilibrium steady states that is also spatially homogeneous — the continuous-flow stirred tank reactor (CSTR) paradigm — can provide great insight into thermoreactive instabilities in liquid systems, and provide fundamental causative information that cannot easily be extracted from detailed numerical simulations that include convective motions.

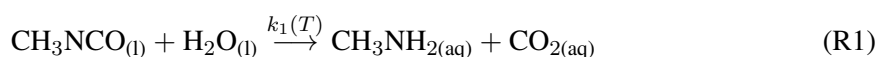
Table 1: Physical, kinetic, and thermochemical parameters for MIC hydrolysis and TATP thermal decomposition.

Specific heat capacity $C_p^\circ(298)$ MIC	1959 J/(kg K)	[7]
Specific heat capacity $C_p^\circ(298)$ H ₂ O	4181 J/(kg K)	
Boiling point MIC at 1 atm	38.3°C	[6]
R1 reaction enthalpy	80.4 kJ/mol	[6]
R1 activation energy	65.4 kJ/mol	[8]
R1 pseudo first order frequency factor	4.13e08/s	[8]
Molecular weight TATP	222.236 g/mol	
Specific heat capacity $C_p^\circ(298)$ toluene	1698.25 J/(kg K)	[7]
Boiling point toluene at 1 atm	110.8 °C	
R3 reaction enthalpy	330–420 kJ/mol	[9]
R3 activation energy	178.52 kJ/mol	[10]
R3 frequency factor	9.57e16/s	[10]
Feed concentration of TATP	2 mol/kg	

2 Chemistry and data

MIC hydrolysis

Isocyanates hydrolyse exothermically to the corresponding amine and carbon dioxide. In excess water isocyanates react exothermically with the hydrolysis product amine to form the disubstituted urea [4, 5]. With MIC the product is N,N-dimethyl urea and the reaction sequence is as follows:



For reaction R2 $\Delta H_2(298 \text{ K}) = -174.6 \text{ kJ/mol}$ and overall $\Delta H_{\text{tot}}(298 \text{ K}) = -255 \text{ kJ/mol}$ [6]. No kinetic data are available for reaction R2 so only reaction R1 is used in the model. It will be seen from the results that reaction R1 alone is sufficient to induce thermal runaway. Relevant physicochemical data are given in table 1.

Thermal decomposition of triacetone triperoxide (TATP)

Triacetone triperoxide, a cycle trimer, is an explosive made by mixing acetone and hydrogen peroxide, both of which substances are legal, cheap and readily available over the counter. Pure TATP looks like white sugar. The thermal decomposition of TATP does not involve combustion; the main reaction products are acetone, methyl acetate, carbon dioxide, and ozone [10, 11]. Its high explosive power is in part due to the large entropy increase of formation of four gas molecules from one condensed-phase molecule [9]. Relevant data for the thermal decomposition of TATP in toluene are given in table 1.

3 Dynamical model and stability analyses

For the CSTR paradigm the dynamical mass and enthalpy equations may be written as

$$M \frac{dc}{dt} = Mze^{-E/RT}c + F(c_f - c) \quad (1)$$

$$MC_r \frac{dT}{dt} = (-\Delta H)Mze^{-E/RT}c + F(C_f T_a - C_r T) - L(T - T_a). \quad (2)$$

The symbols and quantities are defined in table 2. For numerical and comparative reasons it is more convenient to work with the following dimensionless system corresponding to equations (1–2):

$$\frac{dx}{d\tau} = -xe^{-1/u} + f(1-x) \quad (3)$$

$$\varepsilon \frac{du}{d\tau} = xe^{-1/u} + \varepsilon f(\gamma u_a - u) - \ell(u - u_a), \quad (4)$$

where the dimensionless groups are defined in table 2. Numerical analysis of equations (3–4) was carried out using values of the dimensionless groups calculated from the data in table 1 and assigned values of the inverse residence time f , heat loss coefficient ℓ , and inflow concentration c_f .

Table 2: Quantities, definitions, and units.

A	reaction frequency	s^{-1}	ΔH	reaction enthalpy	J/mol
c	$c(t)$, concentration of reactant	mol/kg	M	mass of reaction mixture	kg
c	inflow reactant concentration	mol/kg	R	gas constant	J/mol K
C_r	specific heat capacity of reaction mixture	J/kg K	t	time	s
C_f	specific heat capacity of the inflow stream	J/kg K	T	$T(t)$ reaction temperature	K
E	activation energy	J/mol	T_a	ambient temperature	K
F	flow through rate	kg/s	L	heat loss coefficient	W/K
ε	$C_r E / c_f (-\Delta H) R$		τ	tA	
f	F/MA		u	RT/E	
γ	C_f/C_r		u_a	RT_a/E	
ℓ	$LE/c_f MA(-\Delta H)R$		x	c/c_f	

According to classical ignition theory [12] the reacting mixture self-heats if the rate of reactive heat generation r_g exceeds the linear cooling rate r_l . Thermal runaway occurs if r_g exceeds r_l beyond a system-specific threshold; for the hydrolysis of MIC this is taken as the normal boiling point of MIC. The steady-state rates r_g and r_l from (3) and (4), are plotted versus temperature in Fig. 1. The reaction

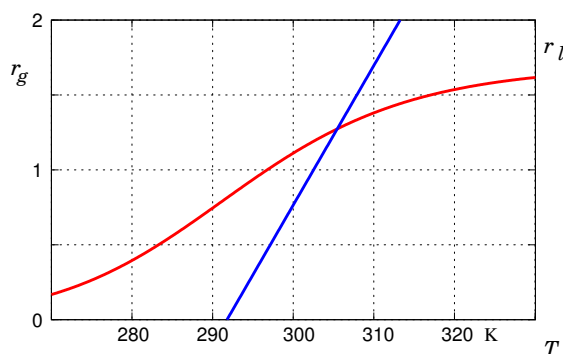


Figure 1: Rates of reactive heat generation r_g (red curved line) and heat loss r_l (blue straight line) versus T from (3) and (4). $u_a = 0.0379$ (corresponding to $T_a = 292$ K), $f = 1.7$, $\ell = 700$, $\varepsilon = 10$.

self-heats until the reactor temperature T reaches the steady state temperature of ~ 305 K at which the heating and cooling rates are balanced. Since the boiling point of MIC is 312 K, on the basis of this diagram we would not expect a thermal runaway to develop, even when the ambient temperature is allowed to drift slowly up to 292 K.

However thermal balance diagrams such as that in Fig. 1 can be dangerously misleading because they infer stability rather than assess stability rigorously, although such diagrams are often used in chemical reactor engineering. The steady states, eigenvalues, and periodic solutions of (3) and (4) were computed numerically and yielded a dramatically different picture of the thermal stability of MIC hydrolysis.

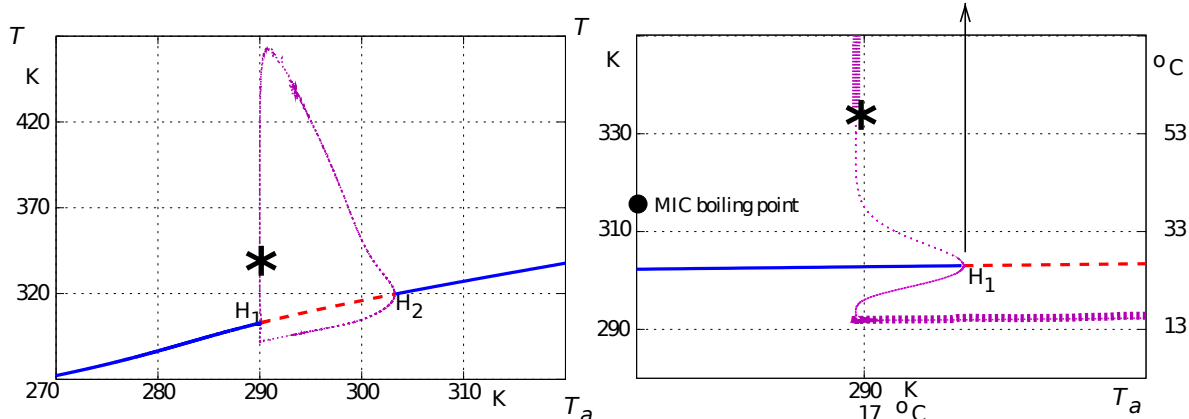


Figure 2: Bifurcation diagram. Stable steady states are plotted with solid blue line, unstable steady states with dashed red line, and the amplitude envelope of periodic solutions is marked with dotted magenta line. H_1 and H_2 label the Hopf bifurcations and the large * marks the change in stability of the limit cycles. $f = 1.7$, $\ell = 700$, $\varepsilon = 10$. On the right is a close-up of the region around the Hopf bifurcation H_1

In the bifurcation diagram of Fig. 2 the steady state is stable at $T_a \approx 286\text{ K}$, the temperature at which the tank of MIC had been held, but at $T_a = 290.15\text{ K}$ the steady state solutions become unstable at a subcritical Hopf bifurcation H_1 and the hard onset of a high amplitude thermal oscillation ensues. Clearly at $T_a = 292\text{ K}$ we have catastrophic thermal runaway, contrary to the prediction of Fig. 1.

This is quite different from classical (Semenov) ignition of a thermoreactive system, which occurs at a steady-state turning point [12]. In classical ignition theory no reference is made to the stability of steady states or the existence of oscillatory solutions, because reactant depletion is ignored and periodic solutions are forbidden in a system evolving in just one dynamical variable—the temperature.

The dynamics of non-classical, oscillatory thermal runaway can be understood by studying the close-up of the region around the Hopf bifurcation H_1 in Fig. 2. H_1 is subcritical and the emergent limit cycle is **unstable**. At the turning point * the limit cycles become stable. Thermal runaway *may* occur if there are significant perturbations while T_a is within the range * to H_1 and it *must* occur when T_a drifts above H_1 . The arrow indicates the rapid thermal excursion, in principle to the stable limit cycle but in reality the reactant has vaporized, the pressure has soared beyond the safety limits of the tank relief valve, and the system must vent since the peak temperature is far above the boiling point of MIC.

The behaviour of the system under a slow upwards drift of the ambient temperature can be simulated easily; a time series with $dT_a/dt = 0.02^\circ\text{C/s}$ is shown in figure 3, which confirms the abrupt onset of the instability. The decay in amplitude of the oscillations as the thermostat temperature *increases* occurs because the reactant is consumed faster than it is supplied as the temperature increases.

Qualitatively similar results were obtained for thermal decomposition of TATP. The time series in figure 4 shows that the system exhibits violent relaxation oscillations, suggesting that explosive thermal decomposition of TATP is initiated at the onset of oscillatory behaviour rather than by classical ignition.

4 Discussion

The presence of oscillatory instability is all-pervasive and dominant in these systems. This can be appreciated by inspection of Fig. 5. Within the regions circumscribed by the Hopf bifurcation loci thermal runaway will always be oscillatory. The bistable regime, indicated by the dashed line, occurs at very short residence times. However, classical thermal runaway at a steady state turning point does not

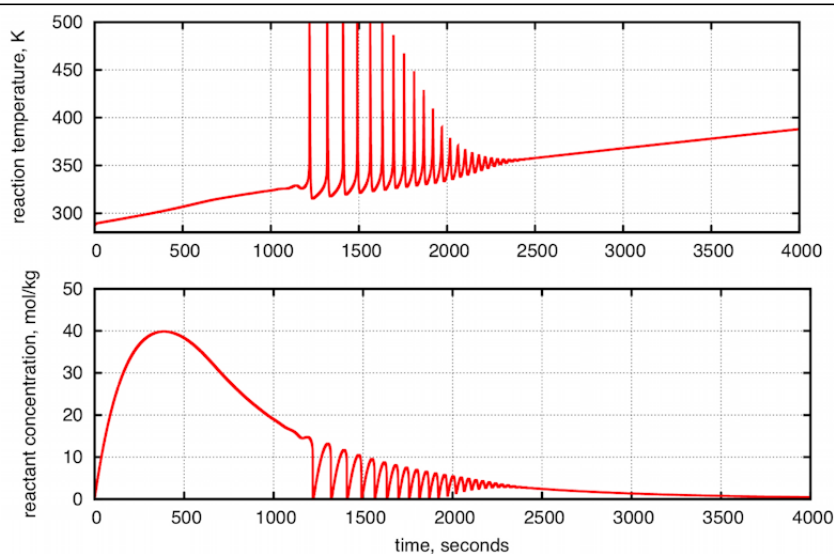


Figure 3: Computed time series for MIC hydrolysis with drift in thermostat temperature of 0.02°C/s . $F = 0.0016 \text{ kg/s}$, $L = 560 \text{ W/K}$.

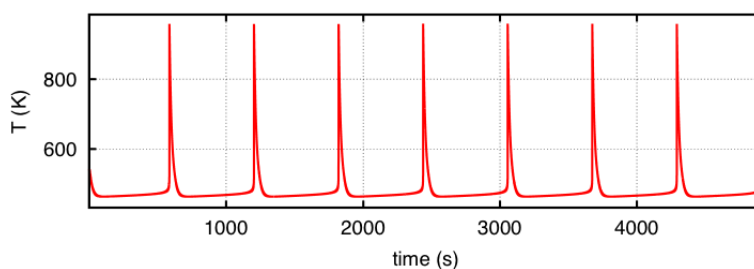


Figure 4: Strong relaxation oscillations in the TATP thermal decomposition.

occur because the oscillatory instability is still present and dominant.

The tendency for oscillatory thermal runaway may be typical of exothermically reactive liquids. In [13] the hydration of 2,3-epoxy-1-propanol was found to exhibit non-classical thermal misbehavior.

Is the CSTR paradigm appropriate for a reacting volume inside a storage tank or, for that matter, a peroxide bomb? Yes, on a timescale over which the reacting volume is approximately constant and gradientless relative to the much faster rate of reaction. Since the focus here is on the dynamics we can circumscribe a reacting volume in which spatial gradients are insignificant in comparison to the time evolution and can be neglected. Much of the heat transfer would be convective rather than conductive, and on convective timescales the approximation does not hold — but that is for a separate study.

5 Conclusions

The CSTR paradigm was applied to investigate the thermal stability of MIC hydrolysis and the thermal decomposition of TATP in solution. Stability analyses found that in both cases thermal runaway occurs due to the hard onset of a thermal oscillation at a subcritical Hopf bifurcation. Classical thermal ignition at a steady state turning point does not occur.

This oscillatory thermal misbehaviour may be generic in liquid thermoreactive systems where the specific heat capacity and activation energy are high. These results provide new information about the cause of thermal runaway that may inform improved designs of storage systems for thermally unstable

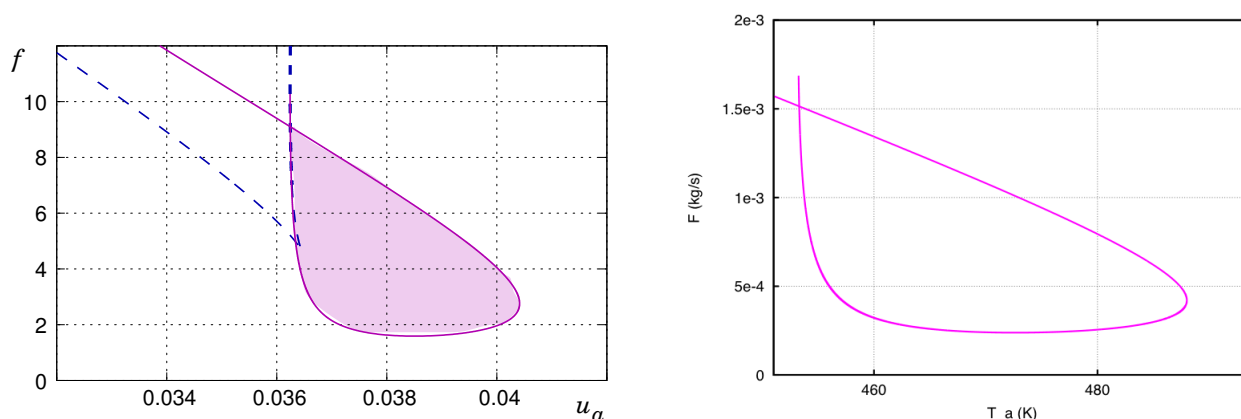


Figure 5: Loci of Hopf bifurcations are marked with a solid line, loci of steady-state turning points are marked with dashed line. Left: MIC hydrolysis. Right: TATP thermal decomposition.

liquids and better management of organic peroxide based explosives. Improvised explosive devices that employ such liquids may undergo explosive thermal decomposition under conditions where classical ignition theory predicts the liquids are stable.

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