EVALUATION OF ADIABATIC RUNAWAY REACTION AND VENT SIZING FOR EMERGENCY RELIEF FROM DSC

Y. W. Wang[1], Y. S. Duh[2]* and C. M. Shu[3]

[1]Doctoral Program of Engineering Science and Technology, National Yunlin University of Science and Technology, NYUST 123, University Rd., Sec. 3, Douliou, Yunlin, Taiwan 64002, ROC
[2]Department of Occupational Safety and Health, Jen-Teh Junior College of Medicine, Nursing and Management, 1, Jin-The Rd. Houlong, Miaoli, Taiwan 356, ROC
[3]Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, NYUST 123, University Rd., Sec. 3, Douliou, Yunlin, Taiwan 64002, ROC

Analytical equations related adiabatic runaway reactions to programmed scanning thermal curves from differential scanning calorimetry (DSC) were proposed. Thermal or pressure hazards can be assessed from the adiabatic trajectories expressed in the analytical equations. These industrially energetic materials include polymerizable monomers, unstable organic peroxides and nitro-compounds. Various emergency relief behaviors, such as tempered vapor, gassy, and hybrid were re-evaluated for calculating vent sizing or mass flow rates from DSC thermal curves and the related physical properties.

Keywords: analytical equations, DSC, emergency relief behaviors, mass flow rates, vent sizing

Introduction

Under the patronage of the American Institute of Chemical Engineers (AIChE) in 1976, an international consortium of 29 companies constituted the Design Institute for Emergency Relief System (DIERS) to evaluate existing methods and develop new technologies to design emergency relief system (ERS) for runaway reactions. Of utmost importance was the stress of when the two-phase flow would occur and the prediction of vapor-liquid swell which were neglected in the traditional methodologies. In case of the activation of the relief device, the discharge was well demonstrated to be two-phase flow, such as highly exothermic reaction, self-reactive system, high liquid level and highly viscous system. During the venting of the runaway reaction, the pressure in vessel will be tempered by volumetric rate of discharge and by the effect of temperature, composition and mass flow on the reaction system. If two-phase flow occurs, the vapor-liquid phase ratio in the venting system will strongly influence the rate of volumetric discharge, mass loss, and evaporative cooling. In general, vent area in a two-phase flow must be larger than the relief area at all vapor or subcooled liquid flow. In practice, the ratios of vent area for two-phase flow compared to single-phase flow may be from several times to hundredfold. The research efforts and overview of DIERS technology were presented in a project manual that discussed the details of the recommended methodologies [1]. Besides, OSHA (29 CFR 1910.119)

has also recognized the DIERS technology is a good engineering practice [2].

Center for Industrial Safety and Health (CISH) of ITRI in Taiwan followed and developed the DIERS technology in 1992. ITRI is also a member of the DIERS Users Group. In the past two decades, several incidents of fire, explosion or atmospheric released which were originally come from the runaway reactions occurred at reaction vessels or storage tanks. Thermal explosions of organic peroxides caused the most severe damages and losses [3]. To date in Taiwan, more than eight chemical or petrochemical companies had adopted DIERS technology for re-evaluating the ERS in existing plants. These evaluations included acrylonitrile-butadiene-styrene (ABS), acrylic polymer, purified terephthalic acid (PTA), styrene-acrylonitrile (SAN or AS), polystyrene (PS), high density polyethylene (HDPE), polypropylene (PP), styrene-butadiene rubber (SBR) and thermoplastic elastomer (TPE) plants. Vent sizing, construction of piping systems (inlet and outlet), mass flow rates, two-phase flow behaviors, vapor-liquid separation tanks, flares and scrubbers are individually or in whole re-verified by using DIERS methodology.

Application of design in ERS for two-phase flow using DIERS methodology is very complex and can be solved by a number of approaches. These different ways are grouped into two important categories, which are detailed computer simulations and simplified methods, respectively. Computer method can trace the dy-

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namic behaviors of the system during the pre-relief and relief stages that may occur in the vessel. Nevertheless, by using the computer code, a lot of chemical and physical properties are needed to be putting in to describe the hydrodynamic system during venting. In addition, the operation of the program should be easy or friendly to users and engineers. Most of the user or designer appear to prefer the using of simplified or ω methodology. These simplified approaches repudiated the complexity of computer code and demonstrated the excellent results, which were in good agreement to those acquired from computer codes. These facile and fluent modes are the Huff's method, the Fauske's nomographs and simplified equations, and the Leung's ω methods [4–6].

The simplified methodologies also require the data of the physical and chemical properties of the reactive systems including possible intermediates. These data must be known or determined experimentally. Especially, the calorimetric measurements corroborated the chemical kinetics, thermodynamic data and pressure history. For a reactive system, the definition of the credible or the worst case is very important for determining the design base of the ERS. In case of a two-phase flow occurred at a runaway reaction, Leung has developed a simplified methodology for calculating emergency relief area without knowing detailed kinetics. These critical data required for vent sizing are the self-heat rate, the specific heat of the reactant, the average heat generation rate, heat of vaporization and over-temperature and pressure behaviors. Practically speaking, self-heat rate, the average heat generation rate, over-temperature and pressure behaviors can be obtained from an adiabatic calorimeter of a bench-scale size, such as VSP2, Phi Tec II or adiabatic DEWAR calorimeter.
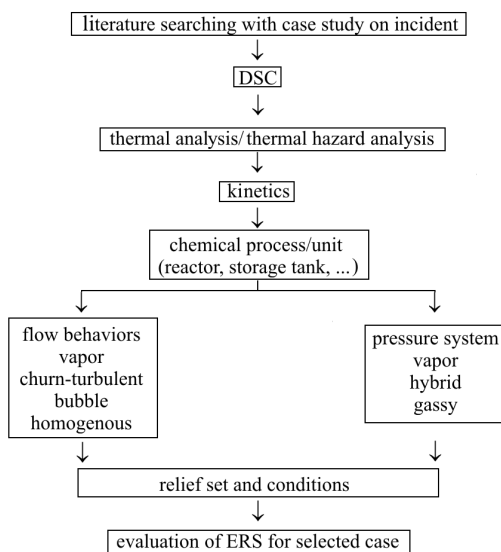
In this study, we suggested a mathematical model to reproduce the required data to match the Leung's ω method. For these reasons of simple, effective, less expensive, avoidance of danger, easy for operation, etc., the thermal curve determined from DSC associated with its intrinsic kinetics and physical data to build up this approach. Pressure behaviors of the tempered, gassy or hybrid were discussed by the data from experimental results or calorimetric measurements. Vent sizing by using the Leung's ω methodology was discussed with examples of reactive monomer and organic peroxide. Kinetic model of the nth order or auto-catalytic was adopted for verifying the effectiveness of this study. The information and procedure for designing of ERS are shown in Fig. 1.

Experimental

Samples

80 mass% cumene hydroperoxide (CHP) in cumene was supplied from the local firm, pure styrene without adding inhibitor was provided from the Grand Pacific Petrochemical Company, high purity di-*tert*-butyl peroxide (DTBP) and 2-nitrotoluene were purchased directly from Merck Co., then were all stored in a refrigerator at 4°C. 4-Chloro-3-nitro benzoic acid with a 98 mass% purity was purchased from Sigma-Aldrich Co.

DSC (differential scanning calorimetry)

Temperature-programmed screening experiments were performed on a Mettler TA8000 system DSC821^e. The test cell (Mettler ME-26732) could withstand high pressure until about 100 bar [7]. STAR^e software was operated for acquisition of thermal curves and for analyzing chemical kinetics. Scanning rate chosen for the temperature-programmed ramp was at about 4°C min^{-1} to maintain better thermal equilibrium. About 1 to 10 mg of the testing sample was used for acquiring the experimental data. The test cell was sealed manually by the special tool equipped with Mettler's DSC, and conducted the dynamic scanning by starting the programmed setting.

VSP2 (vent sizing package 2)

Vent sizing package 2 (VSP2) manufactured by Fauske & Associates, Inc., which is a PC-controlled adiabatic calorimeter system, it can be used to acquire the temperature and pressure traces *vs*. time. An adiabatic calorimeter with the low heat capacity of the test cell ensures essentially all the reaction heat released remains within the tested sample. The thermal inertia factor of the test cells are about from 1.05 to 1.32 that

Fig. 1 A flow chart for designing of ERS

can assess the thermokinetics and thermal hazards, then directly extrapolate to the process conditions [8]. To protect the normal operation of this apparatus and avoid bursting the test cell and missing the exothermic data, CHP 35 mass% was deliberately chosen for the experiments of VSP2. The injected volume of CHP 35 mass% was controlled at about 16.4 mL into the spherical test cell. Then, standard heat-wait-search (HWS) procedure was operated to conduct the adiabatic runaway test. If there was any prominent temperature or pressure rises, then the program terminated the HWS step and switched off the main heater and turned on the guard heater for closely tracking runaway reaction.

Mathematical model

For a reactive system, overpressure in a vessel is normally due to heat of reaction that obeys the overall energy balance of the reactants and products. The worst-case scenario is the most severe up-set that may be encountered in process deviations, which can be determined by adiabatic calorimeter or the experience of process engineers. The severity of a runaway reaction is usually ranked by the self-heat rate or pressure-rising rate. For the empirical formula proposed by Fauske and Leung, the emergency relief area is directly proportional to the self-heat rate [9]. In general, the analytical equation proposed by Leung is one of the most commonly used models. The most critical parameter needed for vent sizing is the self-heat rate, which can be directly detected by the adiabatic test device that has a low ϕ. An ARC or an similar equipment with a high ϕ from 2 to 10 may be also used in the earlier development of adiabatic calorimetry. The self-heat rate obtained at the condition of a high ϕ should be corrected to a phi factor as low as $\phi=1.3$ [10].

Two methods for correcting ϕ were proposed by Fisher and Huff [1, 11], respectively. From the study of Wilcock and Rogers [10], the simulated data from Huff's method seemed to be more fitted than that of Fisher's one. Besides, among the data acquired from adiabatic calorimetry, self-heat rate can be expressed by kinetic data from DSC or by conventional data from chemical kinetics. Fisher suggested the following equation for correcting ϕ value.

$$T_A = T_{A_0} + \phi(T_M - T_{M_0}) \tag{1}$$

$$\frac{1}{T_{A_0}} = \frac{1}{T_{M_0}} + \frac{R}{E_a}\ln\phi \tag{2}$$

$$\left(\frac{dT}{dt}\right)_{A(\phi=1)} = \phi\left[\frac{E_a}{R}\left(\frac{1}{T_M} - \frac{1}{T_A}\right)\right]\left(\frac{dT}{dt}\right)_{M(\phi>1)} \tag{3}$$

These corrective methods may be unable to obtain the actual self-heat rate, because they do not take reaction order, auto-catalytic behaviors, gas evolution and heat transfer effect into account. For avoiding an incorrectly sized relief area, self-heat rate has better to be measured from an excellent adiabatic calorimeter or calculate from chemically kinetic parameters. In this study, we selected both n^{th} order reaction and auto-catalytic reaction for verification of our approaches. For an nth order reaction,

$$\frac{dT}{dt} = -\left(\frac{\Delta H_{tot}}{C_p}\right)\frac{d\alpha}{dt} = -\left(\frac{\Delta H_{tot}}{C_p}\right)k(1-\alpha)^n \tag{4}$$

For an auto-catalytic decomposition which possessed the simplified mechanism as following,

$$A \xrightarrow{k_1} B \tag{5}$$

$$A + B \xrightarrow{k_2} 2B \tag{6}$$
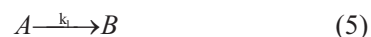
The rate law can be expressed as

$$r = -k_1[A] - k_2[A]^m[B]^n \tag{7}$$

or

$$\frac{d\alpha}{dt} = k_1(1-\alpha) + k_2\alpha^m(1-\alpha)^n \tag{8}$$

Then the self-heat rate can be deduced to be

$$\frac{dT}{dt} = -\left(\frac{\Delta H_{tot}}{C_p}\right)[k_1(1-\alpha) + k_2\alpha^m(1-\alpha)^n] \tag{9}$$

In these equations, α is evaluated from the thermal curve detected by DSC.

$$\alpha = \frac{\int_{T_0}^{T}\dot{Q}dt}{\int_{T_0}^{T_f}\dot{Q}dt} \tag{10}$$

Pressure system

Systems of pressure behaviors are characterized by the generation of pressure from reactants, intermediates, and products in case of runaway. Tempered, gassy and hybrid systems are discussed in DIERS methodology. For a tempered system, the vapor pressure obeys the Antoine's equation or follows the Clausius–Clapeyron equation. Most of the non-condensable gases came from decomposition of reactants contribute the pressure build-up of a gassy system. The pressure behaviors between vapor and gassy system are hybrid system. Vapor pressure of the volatile components and non-condensable gases result in the total pressure of gas phase.

The equation of state for the vapor component can be represented by Antoine equation as follows:

$$\ln P_V = a - \frac{b}{T} \qquad (11)$$

where b is equal to $\Delta\overline{H}_{vap}/R$ via the Clausius–Clapeyron equation.

For the pressure of non-condensable, ideal gas law is approximately obeyed.

$$P_g = \frac{m_g RT}{M_{wg} V_g} = \frac{m_g RT}{M_{wg}(V_0 - mV_1)} \qquad (12)$$

For the gassy or hybrid system, Dalton's law of partial pressure is followed. The total pressure is expressed as the sum of partial pressures.

$$P_{tot} = P_V + P_g \qquad (13)$$

Once the (dT/dt) and pressure equation are solved, these analytical equations give the time evaluation of temperature and pressure, the relation of pressure *vs.* temperature and pressure-rising rate (dP/dt).

Venting behaviors

Computer simulation performs the time evolution and dynamic behaviors before and after the relief situation. A delicate equation combined mass balance and energy balance for expressing the dynamic self-heat rate during relief was proposed by Rota *et al.* [12]. For a tempered system, the simplified energy equation for the reactor is presented in a general formula [5, 6].

$$mC_v \frac{dT}{dt} = Q - \frac{W_v h_{fv}}{mv_{fv}} \qquad (14)$$

The flow regimes in vessel hydrodynamic behaviors are pure vapor venting, bubbly flow, churn-turbulent flow and homogenous flow. These flow regimes were thoroughly described by the drift flux model. Phenomena of vapor-liquid disengagement were discussed in a DIERS report [3]. Overpressure and venting behaviors during emergency relief of these flow regimes were discussed by Leung [5, 6]. From these studies, the largest relief vent rate was generally the homogeneous-vessel venting. In addition, at the same overpressure the largest relief area needed was also the homogeneous-vessel flow. For a more conservative and straight-forward viewpoint for engineering purpose, the flow regime of homogeneous flow in vapor pressure system was proposed.

By making certain simplifications and assumptions, an analytical equation for the mass flow rate (W) was arrived.

$$W = GA = \frac{\overline{q}m_0}{\left(\sqrt{C_p \Delta T} + \sqrt{\dfrac{Vh_{fv}}{m_0 v_{fv}}}\right)^2} \qquad (15)$$

or

$$A = \frac{m_0 \overline{q}}{G\left(\sqrt{\dfrac{V}{m_0} T_s \dfrac{dP}{dT}} + \sqrt{C_p \Delta T}\right)^2} \qquad (16)$$

$$\overline{q} = \frac{1}{2} C_p \left[\left(\frac{dT}{dt}\right)_s + \left(\frac{dT}{dt}\right)_m\right] \qquad (17)$$

Vent sizing for gassy system

Decomposition of organic peroxides accompanies considerable quantity of releasing of non-condensable gases. Various simplified sizing equation for gassy system are widely discussed and used. These methods were suggested by Fauske *et al.* [13–15], respectively. For the gassy and non-tempered system, it is important to size the relief area and evaluate the mass flow rate. Evaporative cooling by latent heat of solvent, hence reaction temperature is not tempered. Based on steady-state assumption, the design method is based on volumetric rate balance. This simplified volumetric rate balance is assessed at the maximum allowable pressure, so that the evaluation is conservative one. Consequently, Leung's method is the most popular and discussed in this study. Vent area of a gassy system is calculated by the following equation.

$$A = \frac{\dot{Q}_{g,max}}{G\left(\dfrac{V}{m_0}\right)} = \frac{\rho_0 \dot{Q}_{g,max}}{G} \qquad (18)$$

where

$$G = \frac{\sqrt{\dfrac{2}{\alpha_0}\left[\left(\dfrac{1-\alpha_0}{\alpha_0}\right)(1-\eta) - \ln\eta\right]}\sqrt{P_m \rho_0}}{\dfrac{1}{\eta} + \dfrac{1-\alpha_0}{\alpha_0}} \qquad (19)$$

and

$$\eta_c = \left[2.016 + \left(\frac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714} \qquad (20)$$

Vent sizing for hybrid system with tempered behaviors

From the behaviors of pressure relief, three kinds of runaway reactions can be characterized as the vapor

Table 1 Kinetic constants of the Arrhenius equation from DSC thermal curves

Parameter	DTBP		2-Nitrotoluene	Styrene		CHP		3-Nitro-4-chlorobenzoic acid[a]
Mass/mg	3.93		1.0	6.49		9.07		2.58
ΔH/J g^{-1}	this work 1250	Leung 1212.2	2406.64	this work 641.1	Leung 724.8	80 mass% 1425.3	35 mass% 623.6	1369.7
E_a/kJ mol^{-1}	163.03	158	278.12	84	80.56	124.2		E_{a1}=157 E_{a2}=113
ln$A$/s^{-1}	37.76	36.73	46.23	15.48	14.0	27.85		A_1=24.2 A_2=15.48
n	1		1	2.5		0.5		m=0.5 n=1.8
C_p/J g^{-1} °C^{-1}	2.1		2.1	2.1		2.1		2.1
[b]T_{onset}/°C	160		340	140		150		320
[c]T_0/°C	110		290	90		100		270
ΔT_{ad} ($\Delta H C_p^{-1}$)	595	577	1146	305	345	848	297	652
T_f ($T_0+\Delta T_{ad}$)	705	687	1436	395	435	948	397	922

[a]Auto-catalytic model: $r=-k_1[A]-k_2[A]^m[B]^n$ [16]; [b]T_{onset} is typically defined as the intercept of the baseline and maximum heat-releasing line of a DSC curve; [c]T_0 is assumed to be at ($T_{onset}-50$°C).

system, the gassy system and the hybrid system. The gaseous components of hybrid system composed of vapor and non-condensable gases. Hence, the relief behavior of hybrid system possessed the characteristics fell in the region between pure gassy and pure vapor system. For matching with the need and importance of industry, an analytical treatment was proposed by Leung [15]. By considering the unsteady conservations, a set of governing equations for venting a hybrid system was obtained and suggested. The evaluation of discharge flow of a hybrid mixture through nozzle under homogeneous equilibrium assumption was described by the typical mass flux equation. For application in relief design or vent sizing, a set of analytical solution fitted to the discharge rate equation and have to be obtained. For practical design viewpoint, it merits of reducing the relief of hybrid system to either pure gassy system or pure vapor system. It is also for safety reason to choose one of the larger vent area calculated by pure gassy or pure vapor case.

Results and discussion

Thermal hazard analysis

Figure 1 shows the approaches and procedures for evaluating ERS from a single DSC thermal curve. It is a more convenient method than the earlier published studies and without sacrificing the accuracy. Especially, in the investigation of exothermic runaway reaction from adiabatic calorimeter, the experimental methods cost much and spend more time to perform the runaway reaction. For a highly exothermic reaction, we might have to endure the higher ϕ value. For some tests, the ϕ was as higher as 10. Variation in ϕ

will influence not only the measured kinetics of the reaction, but also the thermodynamics and pressure behaviors. Therefore, the development of a runaway reaction and thermal hazard data were changed inevitably. Correction of adiabatic runaway reaction data for the effect of ϕ spend more efforts, and may lead to larger deviation from real data with ϕ equals unity. For example, nitro-compounds and organic peroxides of high concentration have been operated with a small quantity in adiabatic calorimeter under a ϕ value quite larger than unity. Hence, adiabatic runaway hazard could be distorted and vent sizing or mass flow rate might be underestimated. From simulation of this model from Table 1, Figs 2 and 3, the runaway reactions of nitro-compounds and organic peroxides of high concentration were hardly to be reduced or dictated by emergency relief. By the trends of these characteristic data, there will result in the thermal explosions. These runaway reactions should be avoided only by process control associated with careful designs in advance. Protection by the emergency relief has to be excluded in these cases due to the severity of consequence in case of runaway reaction being occurred.

Vent sizing calculation

It is worthwhile in this study to emphasize the application of DIERS methodology in runaway system of styrene polymerization and decomposition of CHP within the concentration from 20 to 35 mass%.

Case study 1: Runaway on thermal polymerization of styrene

A typical runaway reaction from styrene monomer tank (5 bar MAWP) was verified for evaluation of the
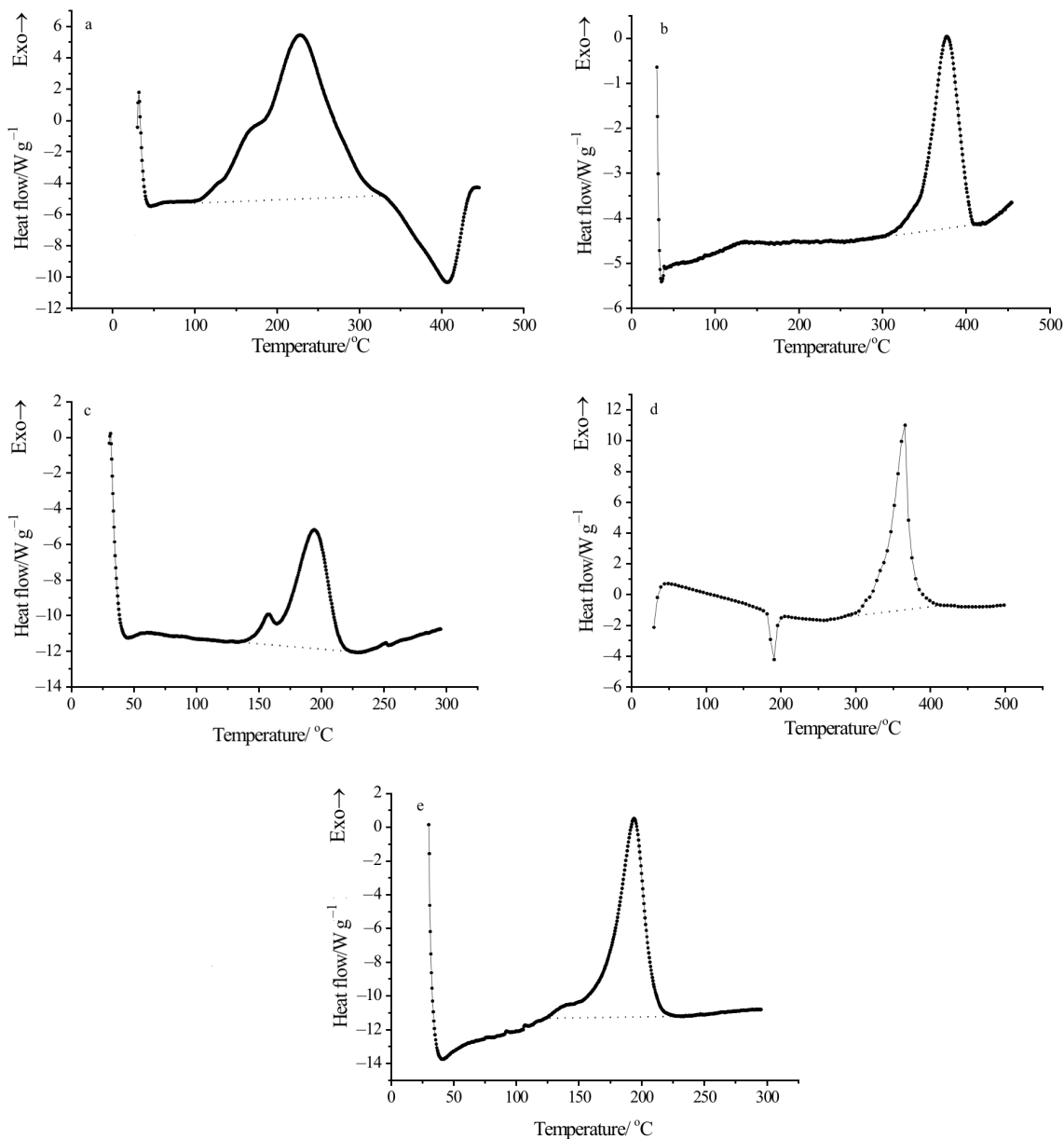
Fig. 2 Data of DSC thermal curves; a – styrene, b – 2-nitro-toluene, c – DTBP, d – 4-chloro-3-nitro benzoic acid and e – CHP 35 mass%

emergency relief system. Table 2 has its relief conditions. Adiabatic runaway data were determined by calorimeter and physical properties were from published studies [11, 17]. Figure 4 shows the temperature derivative with respect to time comparison this study to that of Leung.

The pressure behaviors of runaway reaction of styrene have been treated as a vapor system [17]. We adopted the Leung's ω-method to evaluate vent area, mass flux, and mass flow rate. At the set point:

$$\omega = \alpha_0 + \rho_0 C_p T_0 P_0 \left(\frac{v_{fg}}{h_{fg}} \right)^2$$

Table 2 Runaway and emergency relief conditions of a styrene monomer tank

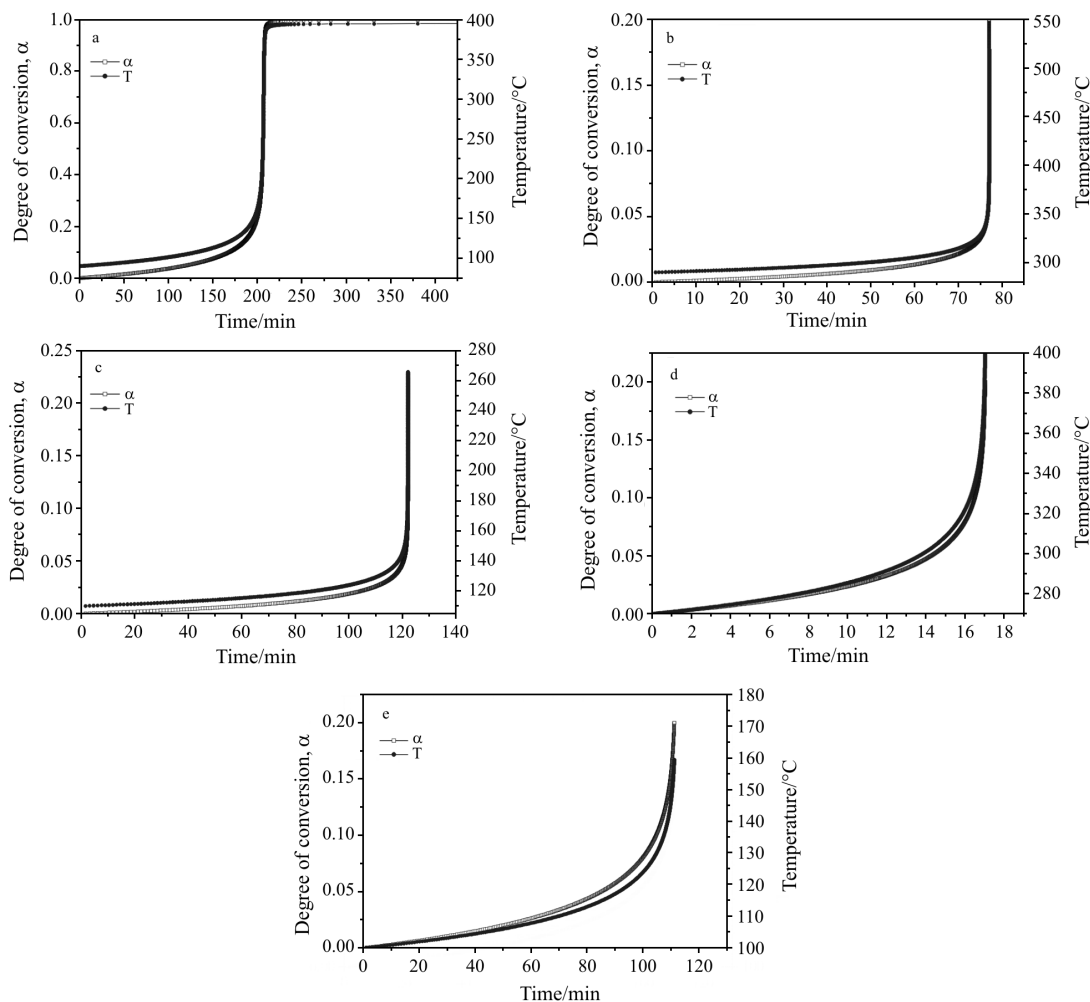|	4.5 bar set	5.4 bar peak
$v_f/m^3\ kg^{-1}$	0.001388	0.001414
$*v_g/m^3\ kg^{-1}$	0.08553	0.07278
$C_p/kJ\ kg^{-1}\ K^{-1}$	2.470	2.514
$h_{fg}/kJ\ kg^{-1}$	310.6	302.3
V	13.16 m^3 (3500 gal)	
m_0	9500 kg	
P_s	4.5 bar abs.	
T_s	209.4°C (482.4 K)	
$(dT/dt)_s$	22.5°C min^{-1}=0.375 K s^{-1}	
P_m	5.4 bar abs. (assuming 10% above MAWP)	
T_m	219.5°C (492.5 K)	
$(dT/dt)_m$	30.1°C min^{-1}=0.502 K s^{-1}	

*ideal gas assumed

Fig. 3 Simulation on adiabatic runaway; a – styrene, b – 2-nitro-toluene, c – DTBP, d – 4-chloro-3-nitro benzoic acid and e – CHP 35 mass%

$$\alpha_0 = 1 - \frac{m_0 v_f}{V_0} = 1 - \frac{9500 \cdot 0.001388}{13.16} = 0$$

$$\rho_0 = \frac{m_0}{V} = \frac{9500}{13.16} = 722 \text{ kg m}^{-3}$$

$$\omega = 0 + 722 \cdot 2470 \cdot 482.4(4.5 \cdot 10^5)\left(\frac{0.08414}{310600}\right)^2 = 28.4$$

Mass flux was corrected by using empirical curve-fitted equation.

$$\frac{G}{\sqrt{P_0 \rho_0}} =$$

$$[0.6055 + 0.1356 \ln \omega - 0.0131(\ln \omega)^2]/\sqrt{\omega} = 0.171$$

that is

$$G = 0.171\sqrt{P_0 \rho_0} = 0.171\sqrt{4.5 \cdot 10^5 \cdot 722} =$$
$$3082.3 \text{ kg m}^{-2} \text{ s}^{-1}$$

over-temperature:

$$\Delta T = T_{max} - T_{set} = 219.5 - 209.4 = 10.1 \text{ K}$$

average self-heat rate:

$$\bar{q} = \frac{1}{2} C_p \left[\left(\frac{dT}{dt}\right)_s + \left(\frac{dT}{dt}\right)_m \right] = \frac{2470}{2}[0.375 + 0.502]$$
$$= 1201.5 \text{ J kg}^{-1} \text{ s}^{-1}$$

mass flow rate:

$$W = \frac{m_0 \bar{q}}{\left(\sqrt{\dfrac{V}{m_0} \dfrac{h_{fg}}{v_{fg}}} + \sqrt{C_p \Delta T}\right)^2} =$$

$$\frac{9500 \cdot 1201.5}{\left(\sqrt{\dfrac{13.16}{9500} \dfrac{310600}{0.08414}} + \sqrt{2470 \cdot 10.1}\right)^2} = 216.8 \text{ kg s}^{-1}$$

Relief vent area:
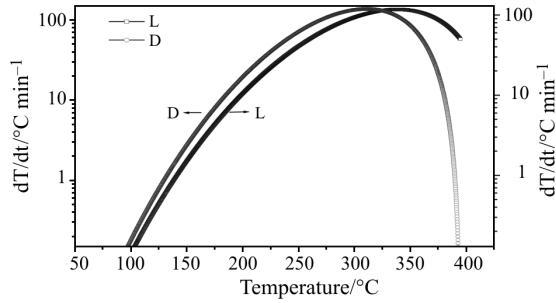
$$A = \frac{W}{G} = \frac{216.8}{3082.3} = 0.07 \ m^2$$

Fig. 4 Adiabatic self-heat rate (L – from Leung [17], D – this study) data for styrene polymerization

Case study 2: Decomposition of CHP 35 mass% in cumene

Table 3 displays the emergency relief conditions of a CHP 35 mass% tank. CHP is widely used in Taiwan as an initiator in polymerization, especially for the co-polymerization of acrylonitrile-butadiene-styrene (ABS). CHP is also used for producing phenol and acetone by acidic cleavage. It was produced by the oxidation reaction of cumene and oxygen in air. CHP was controlled at first stage from 20 to 35 mass% then for continuing concentration process. It may be further concentrated to 80 mass% or reacted with inorganic acid to make phenol or dimerized to be a dicumyl peroxide (DCPO).

Decomposition of organic peroxide can release non-condensable gases and major component of CHP 35 mass% is cumene, the pressure behavior of CHP is a hybrid system. We first treated it as the limit of vapor system, then treated it as another limit case of gassy system.

Limiting condition 1: Decomposition of CHP 35 mass% as a vapor system

Here, the Leung's ω-method was applied. At the set point:

$$\omega = \alpha_0 + \rho_0 C_p T_0 P_0 \left(\frac{v_{fg}}{h_{fg}} \right)^2$$

$$\alpha_0 = 1 - \frac{m_0 v_f}{V_0} = 1 - \frac{4162.05 \cdot 0.00108}{6} = 0.25$$

$$\rho_0 = \frac{m_0}{V} = \frac{4162.05}{6} = 693.7 \text{ kg m}^{-3}$$

$$\omega = 0.25 + 693.7 \cdot 1790 \cdot 387 \cdot (1.8 \cdot 10^5) \left(\frac{0.14992}{348400} \right)^2 = 16.27$$

Mass flux was corrected by using empirical curve-fitted equation.

$$\frac{G}{\sqrt{P_0 \rho_0}} =$$

$$[0.6055 + 0.1356 \ln \omega - 0.0131 (\ln \omega)^2] / \sqrt{\omega} = 0.219$$

that is

$$G = 0.219 \sqrt{P_0 \rho_0} =$$

$$0.219 \sqrt{1.8 \cdot 10^5 \cdot 693.7} = 2447.2 \text{ kg m}^{-2} \text{ s}^{-1}$$

over-temperature:

$$\Delta T = T_m - T_s = 150 - 114 = 36 \text{ K}$$

average self-heat rate:

$$\bar{q} = \frac{1}{2} C_p \left[\left(\frac{dT}{dt} \right)_s + \left(\frac{dT}{dt} \right)_m \right] =$$

$$\frac{1790}{2} (0.002 + 0.033) = 31.325 \text{ J kg}^{-1} \text{ s}^{-1}$$

mass flow rate:

$$W = \frac{m_0 \bar{q}}{\left[\sqrt{\frac{V}{m_0} \frac{h_{fg}}{v_{fg}}} + \sqrt{C_p \Delta T} \right]^2} =$$

$$\frac{4162.05 \cdot 31.325}{\left(\sqrt{\frac{6}{4162.05} \frac{348400}{0.14992}} + \sqrt{1790 \cdot 36} \right)^2} = 1.342 \text{ kg s}^{-1}$$

Table 3 Runaway and emergency relief conditions of a CHP 35 mass% tank

	1.8 bar set	5.5 bar peak
v_f/m^3 kg^{-1}	0.00108	0.00108
*v_g/m^3 kg^{-1}	0.151	0.151
C_p/kJ kg^{-1} K^{-1}	1.79	1.79
h_{fg}/kJ kg^{-1}	348.4	348.4
V	6 m^3	
m_0	4500 L·d=4500 L·$\dfrac{0.35 \cdot 1.038 + 0.65 \cdot 0.864}{0.35 + 0.65}$ kg L^{-1}=4162.05 kg	
P_s	1.8 bar abs.=1.8·14.7 psi=26.46	
T_s	114°C (387 K)	
$(dT/dt)_s$	0.1°C min^{-1}=0.002 K s^{-1}	
P_m	1.1·5 bar (10% above MAWP)=5.5·14.7 psi=80.85 psi	
T_m	150°C (423 K)	
$(dT/dt)_m$	2°C min^{-1}=0.033 K s^{-1}	

*Ideal gas assumed.

Table 4 Runaway and emergency relief conditions of CHP 35 mass% system

VSP 2 apparatus	Process vessel
m_t=15.12 g(CHP 35 mass% in cumene)	V=6 m^3
V_c (in VSP 2)=3.8 L	MAWP=5 bar
$(dT/dt)_{max,\phi=1.45}$=108°C min^{-1}	MAP=1.1 MWAP=5.5 bar
$(dP/dt)_{max}$=0.1544 atm min^{-1}=260.74 N m^{-2} s^{-1}	P_{max}=MAP=5.5 bar
	P_b=1 bar=14.7 psi
	m_0=4500d=4162.05 kg
	ρ_f=d=0.35·1.038+0.65·0.864=0.9249 g cm^{-3}

relief vent area:

$$A=\frac{W}{G}=\frac{1342}{2447.2}=0.00055 \text{ m}^2$$

Limiting condition 2: decomposition of CHP 35 mass% as a gassy system [18, 19]

The stoichiometry is proposed by Kharasch *et al*. [20]. Table 4 shows the thermal decomposition of CHP released only methane gas. The mole faction of methane to CHP was measured to be 0.256.

volumetric rate:

$$\dot{Q}_{g,max}=\frac{m_0}{m_t}\frac{V_c}{P_m}\left(\frac{dP}{dt}\right)_{max}$$

$$=\frac{4162.05}{0.001512}\cdot\frac{3.8\cdot10^{-3}}{5.5\cdot10^5}\cdot260.74=$$

$$0.5 \text{ m}^3 \text{ s}^{-1} (V_g=V_c \text{ in VSP})$$

mass flux:

$$\alpha_0=\frac{V-m_0/\rho_f}{V}=\frac{6-4162.05/0.9249\cdot1000}{6}=0.25$$

$$\rho_0=\frac{m_0}{V}=\frac{4162.05/1000}{6}=693.7 \text{ kg m}^{-3}$$

non-flashing flow model:

$$G=\frac{\sqrt{\frac{2}{\alpha_0}\left[\left(\frac{1-\alpha_0}{\alpha_0}\right)(1-\eta)-\ln\eta\right]}\sqrt{P_m\rho_0}}{\frac{1}{\eta}+\frac{1-\alpha_0}{\alpha_0}}=$$

$$\frac{\sqrt{\frac{2}{0.25}\left[\left(\frac{1-0.25}{0.25}\right)(1-0.25)-\ln0.25\right]}\sqrt{5.5\cdot10^5\cdot693.7}}{\frac{1}{0.25}+\frac{1-0.25}{0.25}}=15050$$

$$\eta_c=\left[2.016+\left(\frac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714}=\left[2.016+\left(\frac{1-0.25}{2\cdot0.25}\right)^{0.7}\right]^{-0.714}=0.42$$

$$P_c=\eta_c P_0=0.42\cdot5.5 \text{ bar}=2.31>P_b$$

If $P_b/P_0<\eta_c$, P_b=1 atm, then $\eta=\eta_c$. Otherwise, $\eta=P_b/P_0$.

Flow is choked

$$G_c=0.82\sqrt{P_0\rho_0}=0.82\sqrt{5.5\cdot10^5\cdot693.7}=16017 \text{ kg m}^{-2} \text{ s}^{-1}$$

vent area:

$$A=\frac{\dot{Q}_{g,max}}{Gv_0}=\frac{\dot{Q}_{g,max}}{G(V/m_0)}=\frac{\rho_0\dot{Q}_{g,max}}{G_c}=\frac{693.7\cdot0.5}{16017}=0.02 \text{ m}^2$$

Conclusions

A simple approach for both evaluating runaway reaction and emergency relief condition was suggested. Thermal curves detected by DSC combined with physical properties, pressure behaviors and mathematical methods offered an alternative course to assessment of runaway hazard and to basic data for emergency relief system. In this work, we examined highly exothermic compounds such as nitro-compounds, organic peroxides, and reactive monomers to verify the effectiveness of this method. As a rule of thumb, any material with self-heat rate exceeded 100°C min^{-1} was excluded for energy relief system design because of its very large relief area, mass flow rate, and potential risk which is unacceptable. This is a promising way to avoid the correction of thermal inertia to perfect adiabatic behavior, where phi value much larger than unity may lead to under-estimate of vent sizing or mass flow rate.

Nomenclature

A	vent area/m^2
C_p	liquid specific heat at constant pressure/kJ kg^{-1} °C^{-1}
C_v	liquid specific heat at constant volume/kJ kg^{-1} °C^{-1}
E_a	activation energy/kJ mol^{-1}
G	mass flux in vent leaving vessel/kg m^{-2} min^{-1}
ΔH_{tot}	heat of reaction/J kg^{-1}
h_{fv}	latent heat of vaporization
k_i	rate constant/s^{-1} M^{1-n}
m, n	order of reaction
m_0	mass of reactant/kg
M_g	molecular mass of gas/g mol^{-1}
m_g	mass of gas/kg
P_g	gas pressure/bar

P_{tot}	total pressure/bar
P_V	vapor pressure/bar
$\dot{Q}$	energy flux/W g^{-1}
$\bar{q}$	heat-releasing rate/J kg^{-1} s^{-1}
R	ideal gas constant/8.314 J g^{-1} K^{-1}
T_A	final adjusted temperature/K
T_{A0}	initial adjusted temperature/K
T_M	final measured temperature/K
T_{M0}	initial measured temperature/K
$(dT/dt)_m$	maximum self-heat rate/°C min^{-1}
$(dT/dt)_s$	self-heat rate/°C min^{-1}
dT/dt	temperature derivative with respect to time/°C min^{-1}
ΔT	temperature rise/°C
V	volume of vessel/m^3
V_0	volume of sample/m^3
v_{fv}	net volume change in vaporization
V_g	volume of gas/m^3
V_l	volume of liquid/m^3
W	relief mass flow rate/kg min^{-1}
W_v	vapor venting relief vent rate/kg min^{-1}
ϕ	thermal inertia
x	partial fraction
α	degree of conversion
η	pressure ratio relative to inlet pressure
ρ_0	density/kg m^{-3}

Subscript

c	chock condition
f	liquid phase
f_g	difference between gas (vapor) phase and liquid phase
g	gas phase
l	liquid phase
max	maximum
r	rate of reaction/M s^{-1}
s	set point
t	VSP 2 test cell
v	specific volume/m^3 kg^{-1}

References

1 H. G. Fisher, H. S. Forrest, S. S. Grossel, J. E. Huff, A. R. Muller, J. A. Noronha, D. A. Shaw and B. J. Tilley, AIChE (1992), New York, NY 10017.
2 G. W. Boicourt, Proc. Saf. Prog., 14 (1995) 93.
3 T. C. Ho, Y. S. Duh and J. R. Chen, Proc. Saf. Prog., 17 (1998) 259.
4 H. K. Fauske, Plant/Opera. Prog., 3 (1984) 145.
5 J. C. Leung, AIChE J., 33 (1987) 952.
6 J. C. Leung, AIChE J., 32 (1987) 1622.
7 STAR^e Software with Solaris Operating System, Operating Instructions, Mettler Toledo, Switzerland 2004.
8 VSP2 Manual and Methodology; Fauske & Associates, Inc., IL, USA 2002.
9 H. K. Fauske and J. C. Leung, Chem. Eng. Prog., 81 (1985) 39.
10 E. Wilcock and R. L. Rogers, J. Loss Preve. Proc. Ind., 10 (1997) 289.
11 J. E. Huff, Plant/Opera. Prog., 1 (1982) 211.
12 R. Rota, G. Ruggeri, M. Morbidelli and S. Ditali, J. Loss Preve. Proc. Ind., 15 (2002) 49.
13 J. C. Leung and H. K. Fauske, Plant/Opera. Prog., 6 (1987) 77.
14 J. E. Huff, Plant/Opera. Prog., 3 (1984) 50.
15 J. C. Leung, AIChE J., 38 (1992) 723.
16 S. Chervin and G. T. Bodman, Thermochim. Acta, 392 (2002) 371.
17 J. C. Jeung, 'Pressure Relief System Design Using DIERS Technology', 3 Day Seminar given at ITRI, Hesichu, Taiwan, May 10–12, 1995.
18 Y. W. Wang, C. M. Shu, Y. S. Duh and C. S. Kao, Ind. Eng. Chem. Res., 40 (2001) 1125.
19 H. Y. Hou, T. S. Liao, Y. S. Duh and C. M. Shu, J. Therm. Anal. Cal., 83 (2006) 167.
20 M. S. Kharasch, A. Fono and W. Nudenberg, J. Org. Chem., 15 (1951) 113.