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Phosphorus Oxychloride and Acetone: An Incompatibility Investigation Using ARC

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Abstract:

This paper presents thermal analysis data for the investigation of an incident that occurred at our research facility. It was determined that the incident involved the combination of phosphorus oxychloride reaction distillates and rinse acetone used to clean a vacuum pump that resulted in the explosion of a sealed waste bottle. The purpose of this report is to highlight this potentially hazardous incompatibility.

Introduction

An explosion of a 2.5-L PVC-coated waste bottle containing reaction distillates of phosphorus oxychloride ($POCl_3$) and a mixture of solvents occurred recently in one of our laboratories. Phosphorus oxychloride was being vacuum distilled from a reaction mixture using a LABOPORT (KNF Neuberger GmbH) vacuum pump. Following the distillation of the reaction mixture, the residue in the secondary condenser of the vacuum pump, consisting of approximately 100 mL of $POCl_3$, was transferred to the 2.5-L bottle. The secondary condenser was then rinsed with acetone and ethyl acetate, and the contents were combined in the waste bottle and sealed. The contents of the waste bottle were estimated to be 100 mL of $POCl_3$, 500 mL of acetone, 200 mL of ethyl acetate, and a small amount of unknown residue from the vacuum pump trap. After 1−2 h, the waste bottle violently exploded, expelling contents throughout the hood and laboratory. The explosion was severe enough to shear off the top of an Erlenmeyer flask in the hood near the waste bottle without spilling the flask contents. Glass shards were projected across the laboratory, while the PVC coating of the bottle was found on the floor; fortunately, no injuries resulted.

The incompatibility was quickly narrowed down to $POCl_3$ and acetone by small-scale screening tests. Accelerating rate calorimetry (ARC) was used to simulate the explosion. The ARC's high sensitivity (0.02 °C/min) to detecting self-heating was essential for this investigation, and its ability to measure pressure was also important. The theory of ARC operation can be found in the literature.[1]

Results and Discussion

Prior to ARC testing, the incompatibility was narrowed down to acetone/$POCl_3$ by simply combining equal volumes of each solvent in a small vial and allowing them to be in contact for a few hours. Only the $POCl_3$/acetone combination was found to change appearance, from a clear solution to a burnt orange color, which was identical to that observed in the aftermath of the laboratory explosion.

Literature references[2] for phosphorus oxychloride contained no mention of an incompatibility with acetone or ketones in general.[3] We found from ARC experiments that a slow, self-accelerating exothermic reaction occurs instantaneously upon combination of these materials at 25 °C. By utilizing the ARC and the syringe injection method (see Experimental Section), we were able to detect a slow but accelerating exotherm 100 min (Figure 1) prior to reaching the maximum rate of temperature rise. In addition, the time to maximum rate (TMR) at 24 °C was 1.7 h. This was consistent with the facts from the incident investigation, namely, that the rupture occurred 1−2 h after the bottle was filled and sealed (Figure 2).

To establish that the incompatibility was not unique to the distillates, a second ARC run was performed using reagent-grade $POCl_3$ and reagent-grade acetone. This would eliminate any impurity effects from possible reaction mixture carryover and/or excess moisture. Data from this experimental run agreed well with data from the first, with the exception of total adiabatic temperature rise. This difference in adiabatic temperature rise was due to a shut-down condition in run 1 that did not allow the reaction to proceed to its final end point; i.e., the ARC forced cooling after a temperature of 250 °C was reached.

experiment	onset temp (°C)	ΔT_{ad} (°C)	permanent gas (mol/kg of total reaction material)
run 1 ($POCl_3$ distillates)	upon addition at 25 °C	305	2.5
run 2 (reagent grade $POCl_3$)	upon addition at 25 °C	395	2.1

The Φ factor for the 2.5-L bottle and solvent system in the incident was calculated to be 1.6, where the Φ is defined as unity plus the ratio of thermal mass of the sample and container relative to the sample. The ARC sample of run 1, using $POCl_3$ distillates, and the actual incident conditions had similar Φ factors; therefore, the ARC experiment closely modeled the actual thermal dilution of the incident (Figure 3).

(1) Townsend, D. I.; Tou, J. C. *Thermochim. Acta* **1980**, *37. Thermal Hazard Evaluation by an Accelerating Rate Calorimeter*; CSI-ARC Manuals; Columbia Scientific Industries: Austin, Texas, 1996.

(2) Urben, P. G. *Bretherick's Handbook of Reactive Chemical Hazards*, 5th ed.; Butterworth-Heinemann, Ltd.: Oxford, 1995.

(3) MSDS for Phosphorus oxychloride CAS#10025-87-3, Sigma-Aldrich Co., Inc., 1998.

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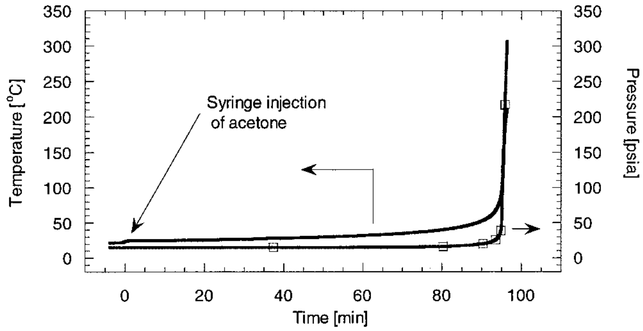

Figure 1. **ARC real-time plot: temperature and pressure vs time after the combination of $POCl_3$ distillates and acetone at 25 °C. The data show a thermal runaway commencing upon addition of acetone and reaching a maximum rate in about 96 min.**

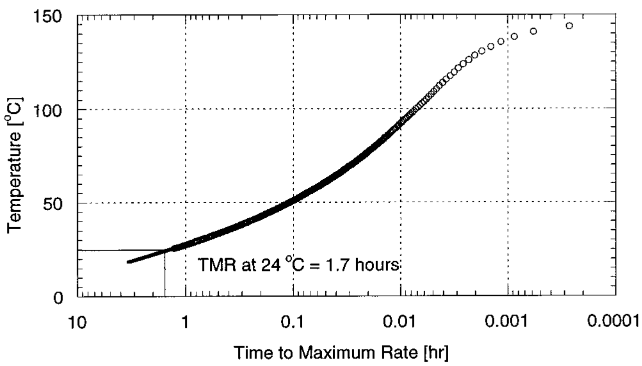

Figure 2. **ARC time to maximum rate plot. This plot shows the correlation between start temperature and time to reach maximum rate after the syringe injection of acetone. For example, at 25 °C this mixture will take 1.6 h to reach its maximum rate of heat generation. This figure has not been corrected for Φ because the bottle in the incident had a thermal inertia similar to that of the ARC bomb.**

Experimental Section

ARC experiments were performed using the estimated ratios in the waste bottle. The first ARC experiment consisted of phosphorus oxychloride reaction distillates combined with acetone from the same acetone bottle that was being used in the laboratory. The ARC bomb was loaded with $POCl_3$, connected to the calorimeter, and allowed to reach thermal equilibrium at 25 °C. Through a $^1/_8$-in. Swagelok ball valve, a syringe addition of acetone was introduced to the bomb. The bomb was quickly sealed and the run continued using normal heat−wait−search analysis.

A second run was completed using different materials, reagent grade phosphorus oxychloride and acetone, and the same experimental procedure.

Phosphorus oxychloride was purchased from Aldrich. Reagent grade acetone was purchased from J.T. Baker.

ARC Experiments. A Columbia Scientific Industries (now available through Arthur D. Little, Inc.) accelerating rate calorimeter using a $^1/_4$-in. stem titanium bomb with a thermocouple clip located on the bottom of the bomb was used.

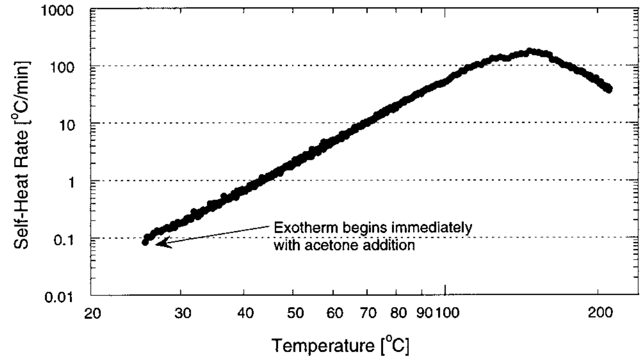

Figure 3. **ARC self-heat rate versus temperature data, showing that a thermal runaway occurs immediately after the syringe injection of acetone into phosphorus oxychloride. This self-heat rate reaches a maximum value of 200 °C/min that exceeds the adiabatic capability of the instrument.**

experiment	sample mass (g) total	sample mass (g) $POCl_3$	thermal inertia factor, Φ	end temp (°C)	heat step (°C)
run 1 ($POCl_3$ distillates)	3.01	0.50	1.643	250	1
run 2 (reagent grade $POCl_3$)	2.44	0.52	2.287	350	2

Conditions: initial temperature, 25 °C; slope sensitivity, 0.02 °C/min; calibration step temperature, 0.2 °C; wait time, 15 min.

Calculations. $\Delta T_{ad} = \Delta T_r \Phi$, where ΔT_{ad} is the adiabatic temperature rise, ΔT_r = reaction final temperature − reaction onset temperature, $\Phi = 1 + [(mC_p)_{sample}/(mC_p)_{container}]$ where m and C_p refer to mass and heat capacity, respectively.

Conclusions

An incompatibility exists between phosphorus oxychloride and acetone that results in heat generation and significant gas evolution when they are combined. Initially, the combination appears uneventful, but a slow self-heating occurs, causing a continuous rise in temperature until thermal runaway occurs. In this case, it was sealed in a glass bottle which resulted in an explosion. ARC proved a useful tool to investigate this incompatibility because of its ability to simulate adiabatic conditions and its high sensitivity.

The communication of this incident is intended to alert others using phosphorus oxychloride that careful attention should be given to the manner in which $POCl_3$ is handled and ultimately disposed.

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