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Communication to the Editor

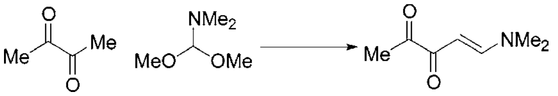
Polymerization Hazard

David J. am Ende,* David R. Bill, David B. Ripin, and Nancy A. Sage
Chemical R&D, Eastern Point Road, Pfizer, Inc., Groton, Connecticut 06344, U.S.A.

We call your attention to an unexpected and violent polymerization that occurred recently while attempting to prepare the condensation product of 2,3-butanedione with dimethylformamide dimethylacetal (DMF−DMA).

The desired chemistry, shown in Scheme 1, was attempted based on a literature precedent for the condensation of the analogous ethyl pyruvate (*J. Heterocycl. Chem.* **2003**, *40*, 487−498).

Scheme 1



Running the literature procedure with ethyl pyruvate revealed a dose-controlled exotherm which raised the temperature of the reaction to approximately 50 °C over the course of the addition.

The conditions used in our work included a 500-mL flask filled with 96 g of 2,3-butanedione, a stir bar, a temperature probe, a 125-mL addition funnel, and a short-path distillation head. Dropwise addition of (DMF DMA) was started via an addition funnel. The initial temperature was 10 °C. After the addition of 2−10 mL of DMF−DMA over 3−4 min, the temperature steadily rose to a temperature of 15 °C. The addition of DMF−DMA was stopped for an analytical check of reaction progress. At this point the addition funnel was violently ejected from the top of the flask, and the round-bottom flask ruptured spraying glass and orange reaction material toward the chemist. Fortunately, the chemist was wearing proper protective equipment, including nitrile gloves, a disposable lab coat, and safety glasses, and was not injured. It was also noted that the reaction material exuded a strong stench.

Follow-up investigation by thermal analysis and NMR confirmed that polymerization of butanedione had occurred, presumably initiated by DMF−DMA. A literature search had not identified prior evidence of this incompatibility.

Thermal analysis in an adiabatic calorimeter (PhiTec, Hazard Evaluation Laboratories) simulated the incident and is shown in Figure 1. In the calorimeter, approximately 25 mL of 2,3-butanedione was charged to a 110-mL test-can under vacuum; 1.23 g of DMF−DMA was charged to the can. The temperature rapidly increased to 150 °C upon the addition. The maximum self-heat rate exceeded 3000°C/min during which time the rate of pressure-rise briefly reached 1300 psi/min. Following the sharp temperature rise, the exotherm and pressure continue to rise, reaching 250 °C and 700 psia. The adiabatic temperature rise ($\phi = 1.2$) was approximately 230 °C. The heat of polymerization was calculated to be $\Delta H = 60.9$ kJ/mol of butanedione or 14.6 kcal/mol of butanedione. At the end of the experiment upon cooling, CO_2 gas and methanol vapors were detected by mass spectrometry.

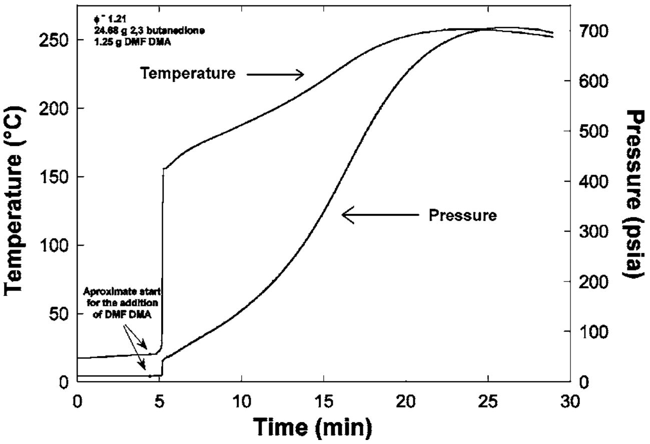


Figure 1. **Simulation in an adiabatic calorimeter of conditions that led to the suspected polymerization incident characterizing the severity of the thermal runaway reaction.**

Thermal analysis via accelerating rate calorimetry of the individual components revealed that DMF−DMA had no measured exotherm, while the butanedione had an onset near 145 °C.

On the basis of these results, it appears that small quantities of DMF−DMA act to initiate the rapid polymerization of 2,3 butanedione. Preliminary tests of reversing the addition by adding butanedione to DMF−DMA showed that partial conversion of the desired condensation product (in Scheme 1) were obtained. However, given the hazardous polymerization potential of the butanedione, the route was not explored further.

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