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Abstract. To date, diacetone diperoxide (DADP) has been significantly less studied than its well-known counterpart, triacetone triperoxide (TATP). Much of this disparity in the literature is due to the harsher conditions/multi-step syntheses required to obtain DADP leading to much lower evidence of frequency of use. Because of this, DADP is often misrepresented as being more dangerous (i.e. more sensitive and less stable) than TATP. This paper discusses the synthesis and characterization (sensitivity, thermal stability, etc.) of DADP with comparisons to other energetic organic peroxides (TATP, HMTD and MEKP) and differences in polymorphism, crystal habit and effects of aging and processing differences are discussed. Additionally, the deflagration-to-detonation transition (DDT) behavior of DADP is discussed with comparison to TATP.

INTRODUCTION

Diacetone diperoxide (DADP) is the thermodynamically-favored acetone peroxide, as opposed to the more commonly formed and kinetically-favored triacetone triperoxide (TATP). As a 6-membered ring, DADP has significantly more inherent bond strain than its larger, 9-membered counterpart. Research by Matyáš *et al.* has shown friction sensitivity differences between DADP, HMTD and TATP[1]; other research indicates conversion of TATP to DADP can occur spontaneously if conditions are correct.[2] Additionally, vapor pressures of both acetone peroxides are significant and thus are capable of being detected by the human olfactory sense.[3] It is still debated on which pathway(s) acetone and hydrogen peroxide follow to form TATP and whether DADP forms directly, or if TATP forms first followed by rearrangement to DADP in solution.[4] The synthesis of TATP occurs slowly over time when hydrogen peroxide (HP) and acetone are combined for a sufficiently long period, but addition of an acid catalyst significantly accelerates the process.[5,6] With low to moderate levels of acid catalyst, a mixture of TATP and DADP will form, but at high levels of added acid DADP is the sole product. Although these compounds are regarded more as an illicit threats, recent studies has indicated interesting behavior of DADP when co-crystallized with other explosive materials.[7]

EXPERIMENTAL

CAUTION: Molecular peroxides (such as TATP, DADP, HMTD, MEKP, etc.) are highly sensitive to impact, friction, spark and shock stimuli; they should be handled in small quantities in explosive facilities by individuals who have proper training and experience.

Synthesis

All reagents were purchased from Fisher Scientific. Preparation of diacetone diperoxide (DADP) was similar to the procedure used in Oxley et al.[6] Equimolar quantities of hydrogen peroxide (30 wt%) and acetone (0.027 moles) were mixed together and cooled in an ice bath. A 1.5:1 molar ratio of sulfuric acid (65 wt%) was added to the HP/acetone over the course of a few minutes, while maintaining the temperature below 30 °C. After acid addition, the solution was allowed to stir and warm to room temperature overnight. A 24 hr reaction period was followed by an aqueous rinse of the crude DADP. The crude melting point, 98-104 °C is consistent with Oxley et al.

Purification was achieved by recrystallization from hot methanol. Two different methods of cooling were chosen to determine the effects of particle size on sensitivity: rapid cooling by immersion in dry ice/acetone bath and slow cooling by allowing the solution to cool to room temperature over the course of ~ 1 hr. The melting point (131-133 °C) was consistent with literature values.

Preparation of hexamethylene triperoxide diamine (HMTD) was similar to literature wherein hexamethylene tetramine (hexamine) was dissolved in 30 wt% HP (1:8 mol ratio) and citric acid was added as a catalyst.[8]

Triacetone triperoxide (TATP) was prepared similar to literature as well.[6] A 1:1 molar ratio of HP and acetone were mixed together and concentrated hydrochloric acid (0.5 molar equivalent) was added dropwise to a cooled solution (0-5 °C).

Methyl ethyl ketone peroxide was prepared by mixing methyl ethyl ketone (0.01 moles) and 30 wt% hydrogen peroxide at a 2:1 mole ratio of ketone to hydrogen peroxide. To this, a catalytic amount of sulfuric acid (0.3 g) was added and the mixture was allowed to stir for 30 mins. After stirring was ceased, the organic layer was removed, washed with hexanes and all volatile components were evaporated away leaving behind the liquid mixture of peroxidic methyl ethyl ketone species (herein referred to as MEKP).

DDT Apparatus

The deflagration-to-detonation transition (DDT) cell consisted of three stainless steel parts (Fig. 1):
- Main body: 7.62 cm diameter, 10.16 cm long cylinder with a 7 mm diameter, 9.42 cm long central bore.
- Ignition flange: 7.62 cm diameter, 3 mm thick plate that had a 1 mm through hole.
- Top plate: 7.62 cm diameter, 25.4 thick cylinder with a stepped central bore.

For all explosives, a 6.35 mm outside diameter, 0.14 mm wall thickness brass tube was hand loaded behind a protective shield.
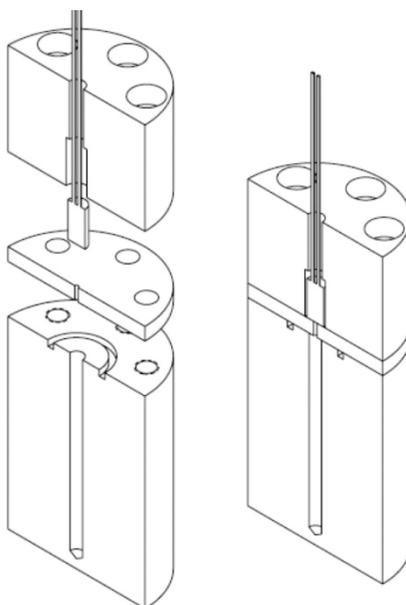

FIGURE 1. Schematic of DDT Cell

For HMTD and TATP, the brass tube was internally coated with 3M FC-2175 fluoroelastomer to inhibit reaction with the brass, and loaded wet with methanol behind a protective shield. The methanol was allowed to evaporate over several days before the test was carried out. The resultant material was estimated to be at 30-50 % theoretical maximum density (TMD) when tested. For DADP, the brass tube was not coated and the material was thoroughly dry before being hand-packed; due to the volatility of DADP, solvent packing was not employed. Likely because the DADP was loaded dry, only 25 % TMD was achieved.

The explosive/brass tube assembly was carefully slid into the central bore of the main body. A small Teflon gasket was placed between the main body and the ignition flange and an electric match was potted with epoxy, with the pyrotechnic exposed, into the stepped region of the top plate, and all three pieces were bolted together. After initiation, the resultant cell cut in half using wire-cut electrical discharge machining (EDM) for determination of the run length needed for transition of deflagration to detonation.

Standard Sensitivity Testing

A standard suite of sensitivity testing was performed on DADP; these included impact, friction and spark sensitivity and thermal stability via DSC. The sensitivity equipment used has been described elsewhere.[9] For DSC analysis, a pressure pan with a gold liner was used to prevent loss of DADP from evaporation at elevated temperatures prior to thermal decomposition.

Acid Drop

Determination of the speed of reaction between molecular peroxides and strong acid was carried out. This test was performed on small amounts (5-20 mg) of material. To the material, a single drop of 65 wt% and $\geq$ 96 wt% sulfuric acid was added to the loose, unconfined material.

Crystallographic Details

Multiple different recrystallization solvents were used to recrystallize DADP. These included: methanol, methanol with acetic acid (approx. 5%), dimethylsulfoxide and dichloromethane. Of these, suitable crystals for X-ray diffraction were obtained from methanol with acetic acid, dichloromethane; additionally, DADP crystals that sublimated above methanol with acetic acid were investigated.

The crystal was mounted in a nylon cryoloop using paratone-n oil (140 K). The data were collected on a Bruker SMART APEX II charge-coupled-device (CCD) diffractometer, with KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with graphite monochromatized MoKα X-ray source (λ = 0.71073 Å), with MonoCap X-ray source optics.

RESULTS

Detonation-to-Deflagration Transition (DDT)

Deflagration-to-detonation transition (DDT) is the process in which an explosive material will transition from a subsonic burning process to a supersonic detonation. The organic peroxides in this study are relatively mild primary explosives in terms of DDT, with a clearly observable transition to detonation in multiple millimeters. Some primaries, namely the inorganic transition metal azides will transition in an almost unperceivable distance within a single crystal, whereas sensitive secondary explosives, such as PETN, RDX and HMX transition to detonation require longer distances, with factors such as particle size and density affecting this distance greatly.[10-12] Comparison between materials is achieved by determining the distance between ignition and transition to detonation.
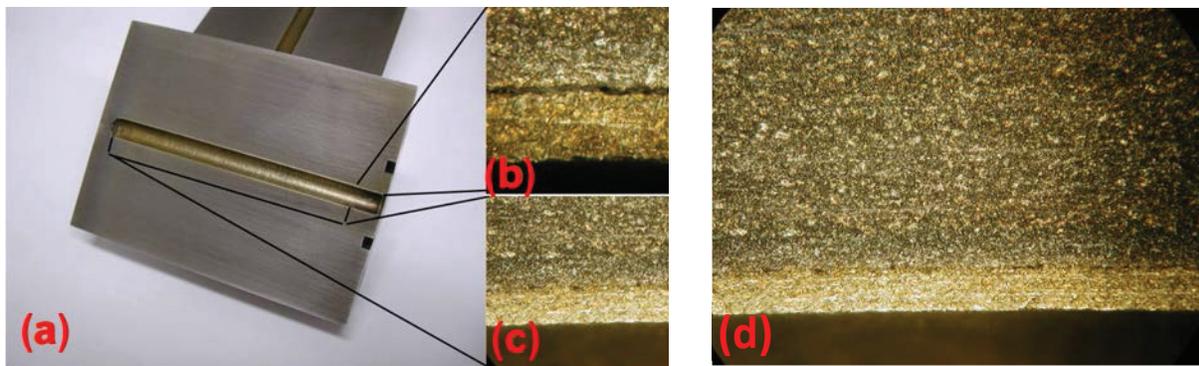
FIGURE 2(a),(b),(c) & (d): (a) TATP DDT cut-away, full scale. (b) non-welded deflagration section. (c) welded detonation section. (d) transition from deflagration (right side) to detonation (left side).
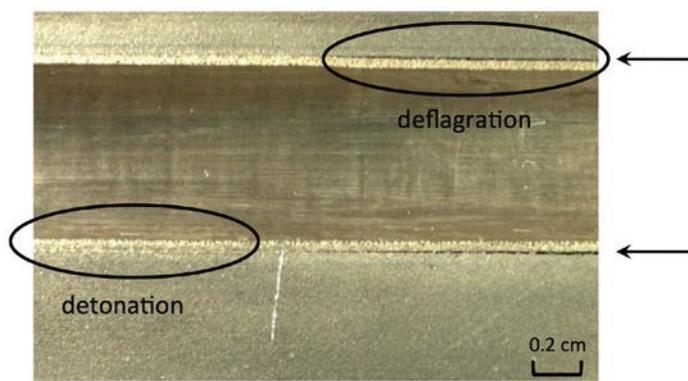

FIGURE 3. DADP DDT cell cut-away illustrating deflagration (right side), transition (middle) and detonation (left side)

For this series of molecular peroxides, the transition to detonation is visualized by welding of the brass tube to the stainless steel central bore, as observed in Fig. 2 and 3. Initially after ignition, the pressure associated with deflagration is too weak to cause welding and thus there is a visible gap between the brass tube and the central bore of the main body. Once the transition to detonation occurs, pressures are significantly increased and welding is observed. Measurements, under a microscope, of the DDT distances are tabulated in Table I. As shown, HMTD and TATP at 30-50 % TMD, had identical distances measured whereas DADP at 25 % TMD required three time the distance before detonation was observed. Even though DADP was at a lower % TMD than the other molecular peroxides, a significantly longer distance before transitioning to detonation was found.

TABLE 1. Sensitivity, thermal stability and deflagration-to-detonation (DDT) data for several molecular peroxides with comparison to PETN.[13]

Peroxide	Impact (cm)	Friction (N)	Spark (J)	% TMD	DDT Transition Distance (mm)
DADP (crude)	13.4 ± 1.8	49 ± 13	0.003		
DADP (fast rec.)	18.4 ± 2.9	19.5 ± 12.3	0.025		
DADP (slow rec.)	21.0 ± 6.9	18.4 ± 5.8	0.063	25	4.7
TATP	6.5	39	0.006	30-50	1.7
HMTD	4.2	5	0.006	30-50	1.7
MEKP	2.8	10	0.025		
PETN (standard)	15.0 ± 5	90 ± 15	0.062	50	1.0

Results from standardized sensitivity tests for multiple molecular peroxides and different processing methods of DADP are tabulated in Table I. Although DADP has impact sensitivity within the range of PETN, the friction sensitivity is significantly lower than PETN; increased friction sensitivity is similar to other molecular peroxides.

Drastic differences were also observed between crude and recrystallized DADP. Impact and spark sensitivities and thermal stability were observed to improve with purification. However, recrystallized material showed significantly higher friction sensitivity than crude DADP. Although particle sizes of fast and slow recrystallizations were not quantified, they were noticeably different. Because of this, the difference in friction sensitivity between crude and purified material is not obvious and is an area of ongoing investigation.

DSC of the purified material was consistent with previously reported values obtained from sealed capillary DSC; melting occurred at 131 °C and an exothermic onset of 206 °C.[6]

Acid Reactivity

Reaction violence between molecular peroxides and strong acids was investigated on a milligram-scale. Approximately 10-20 mg of TATP, HMTD, MEKP and DADP were placed in a small pile on a glass plate with a divet in the center of the pile. A small amount (1-2 drops) of sulfuric acid was added to the center of the pile. All three ketone peroxides reacted violently, and HMTD reacted slowest and non-violently. In order of reaction speed, MEKP was observed to react instantaneously while TATP and DADP took a perceptibly longer amount of time before violent reaction occurred. For a violent reaction to occur with ≤ 20 mg of DADP, the material had to be mounded up like a volcano to allow decomposition to heat the sample rapidly enough to trigger vaporization and ignition (Fig. 4). If the DADP was laid out in a pile and the acid drop was slightly off center, non-violent rapid decomposition was observed – i.e. the material was absorbed into the liquid drop without substantial heat release and condensation products were not observed. Lower concentrations of sulfuric acid (65 wt%) were tried on TATP and DADP without any violent reaction over the course of many hours. These milligram-scale tests do not reflect what may occur if more time, quantity and/or confinement are given to these peroxides. Large-scale gentle destruction of TATP has been performed, but only with the use of a solvent to act as a heat sink.[14]

FIGURE 4. Time elapsed images (240 fps) of a drop of ≥ 96 wt% sulfuric acid placed into the center of a slightly mounded ~10-20 mg sample of DADP. Decomposition occurs quickly leading to condensation products (black spot), followed by vaporization and ignition of vapors. Note: the condensation products do not participate and are visible beneath the flames in the final frame.

Single Crystal X-Ray Diffraction

DADP is known to crystallize into the *P2/c*, monoclinic space group with two molecules per unit cell and twinned along the c-axis. Previous reports of single crystal X-ray diffraction (XRD) have all found the same polymorph independent on crystal forming methodology.[15-17] Crystals studied previously were formed from recrystallization from acetone, sublimation or a slightly more convoluted system involving heating acetone and hydrogen peroxide to 70 °C with an adjusted pH. Although polymorphism was not observed previously for DADP, TATP has been shown to exhibit several room temperature metastable polymorphs.[18] With this in mind, crystals of DADP were grown under various conditions to determine if DADP may also show polymorphism.

Crystals were successfully harvested from slow evaporation of saturated solutions of dichloromethane and methanol with acetic acid (< 5%) added to adjust the pH; additionally, crystals that sublimated over the methanol/acetic acid solution were also collected and analyzed. All crystals analyzed were twinned and belonged to the *P2/c* space group (Table II), indicating that polymorphism in DADP is either non-existent, or significantly

harder to access than TATP. This outcome is unsurprising since DADP is a highly constrained six-membered ring, whereas TATP is a nine-membered ring that can more easily vary its conformation.

TABLE 2. Single Crystal XRD information for DADP crystals obtained through various methods.

Author	Gelalcha[15]	Jensen et al.[16]	Dubnikova et al.[17]	This Study	
Method	Rec. from Acetone	Heated Acetone/HP mixture to 70 °C with adjusted pH to 70 C	Sublimation	DCM Recrystallization	Methanol / Acetic Acid
Crystal Habit	Prisms		Extremely fine	Striated blocks	Small blocks
Temp (K)	208	140	203	100	100
a (Ang)	5.9194	5.8881	5.9152	5.86(4)	5.86(4)
b (Ang)	5.9245	5.8935	5.9221	5.87(3)	5.88(4)
c (Ang)	10.5821	10.5238	10.585	10.43(5)	10.55(7)
Beta (°)	94.326	94.38	94.355	93.83(15)	93.03(19)
Volume (Ang^3)	370.05	364.13	369.7	358.(6)	358.(6)
Z	2	2	2	2	2
Crystal Density (g/cm^3)	1.330	1.351	1.331	1.372	1.372

CONCLUSION

Diacetone diperoxide (DADP) has been shown to be the "safest" molecular peroxide. Even with that moniker, it still has attributes that firmly place it into the category of primary explosives as a crude and pure material. It has been shown to be the least sensitive to impact and friction of materials tested and was found to have a significantly longer DDT distance than others tested. Acid sensitivity of DADP was shown to be similar to TATP and MEKP, whereas HMTD was found to be the least sensitivity to concentrated sulfuric acid.

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