Decomposition of a Multi-Peroxidic Compound: Triacetone Triperoxide (TATP)

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Summary

The thermal decomposition of triacetone triperoxide (TATP) was investigated over the temperature range 151 to 230 °C and found to be first order out to a high degree of conversion. Arrhenius parameters were calculated: activation energy, 151 kJ/mol and pre-exponential factor, 3.75×10^{13} s^{-1}. Under all conditions the principle decomposition products were acetone (about 2 mole per mole TATP in the gas-phase and 2.5–2.6 mole per mole in condensed-phase) and carbon dioxide. Minor products included some ascribed to reactions of methyl radical: ethane, methanol, 2-butanone, ethyl acetate; these increased at high temperature. Methyl acetate and acetic acid were also formed in the decomposition of neat TATP; the former was more evident in the gas-phase decompositions (151 °C and 230 °C) and the latter in the condensed-phase decompositions (151 °C). The decomposition of TATP in condensed-phase or in hydrogen-donating solvents enhanced acetone production, suppressed CO_2 production, and slightly increased the rate constant (a factor of 2–3). All observations were interpreted in terms of decomposition pathways initiated by O–O homolysis.

1 Introduction

Peroxides have a wide commercial use as bleaching agents and polymerization catalysts[1]. Due to the weak O–O bond peroxides undergo facile thermal decomposition to produce radicals. Many peroxides are shock sensitive and their overall decompositions are exothermic so that special handling precautions must be taken[2,3]. Depending on the molecular stoichiometry of the peroxide, its decomposition may be explosive. Most peroxides, such as the commonly used dibenzoyl peroxide or di-*t*-butyl peroxide, contain too much carbon to be true explosives; but they have been rated as having TNT equivalence of 25% and 30%, respectively[4]. On the other hand, the stoichiometry of hydrogen peroxide is perfect to allow it to act as an explosive; albeit, it does so only in concentrations exceeding those at which it is commonly available[5]. This study examines the decomposition behavior of multi-peroxidic triacetone triperoxide (TATP) and compares it with that of diacetone diperoxide (DADP), both of which exhibit explosive behavior. In recent years TATP has been used as an improvised explosive because its precursor chemicals are readily obtained and its synthesis is straightforward. However, it is frequently prepared in admixture with diacetone diperoxide (DADP), and this mixture readily undergoes accidental initiation[6].

The alkyl cyclic diperoxides have been the subject of mechanistic studies since the 1970's[7,8]. Concerted decomposition has been considered because luminescence at 435 nm was observed in the thermolysis of gaseous DADP which could indicate a concerted electrocyclic reaction yielding acetone in an excited singlet state[9], but stepwise decomposition is usually postulated. Recent AM1 molecular orbital calculations on DADP[10] indicated that C–O scission (Figure 1, route 3) is only slightly more energetic than that of O–O, but O–O homolysis (Figure 1, route 2) is the generally accepted mechanism. Following initial O–O homolysis, both C–O and C–C bond scission have been suggested as routes to products (Figure 1 route 2 a and b).

There have been several studies on series of diperoxides. McCullough et al. found that the yield of ketone from cyclic diperoxides $(R_2COO)_2$ decreased as the stability of the radical fragment R· increased, thus, making radical reactions more important. Diacetone diperoxide decomposed to acetone ($\sim 68\%$), acetic acid, carbon dioxide and ethane; and since the thermolysis was performed in benzene, toluene and biphenyl were also observed[8]. Cafferata et al. reported that the decompositions of various diperoxides in a variety of solvents were first-order to about 50% decomposition[11-13]. Since the rate constants were generally independent of initial concentration and solvent effects, they concluded the first decomposition step was O–O bond homolysis. Plotting ΔH versus ΔS showed that five diperoxides fit an isokinetic relationship, but DADP did not[11]. Furthermore, at elevated temperatures DADP decomposition exhibited linear dependence on the initial concentration of DADP suggesting induced decomposition[12]. In addition, the decomposition rate of DADP exhibited a degree of solvent dependence not observed with the other cyclic diperoxides[13]. This latter observation was interpreted as adduct formation between the peroxide and the solvent. This is important with DADP due to its relatively low steric hindrance. Decomposition products of DADP have been reported as acetone in the gas-phase decomposition[9] and acetone, methyl isopropyl ether, and oxygen in benzene solution[12].

The decomposition of few cyclic triperoxides have been studied: tricyclohexylidene triperoxide[14], diethyl ketone

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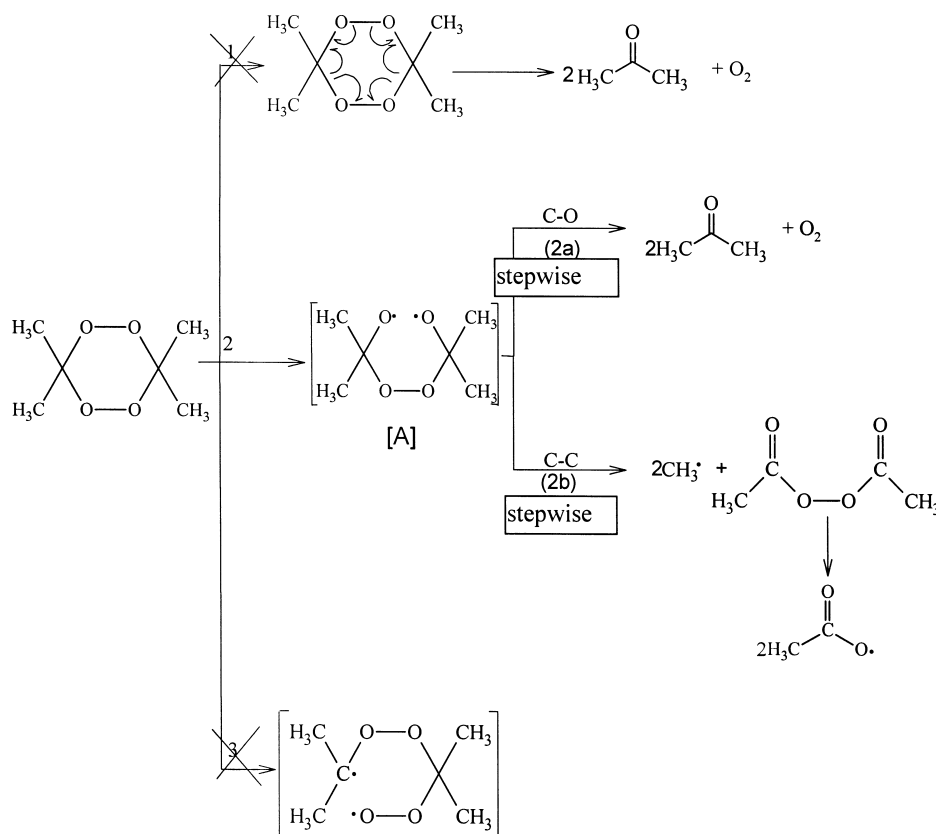* Corresponding author; e-mail: joxley@chm.uri.edu

Figure 1.   Proposed mechanisms for diacetone diperoxide (DADP) decomposition

cyclic triperoxide[15] and TATP in solution[16]. The decomposition of TATP in toluene was found to be first-order and independent of initial TATP concentration out to 78% conversion. The authors concluded the decomposition included no second-order processes which would induce decomposition; however, they did note that toluene would be a good trap for radicals[16]. This study examines the decomposition of neat TATP as the first step to assessing the hazards associated with explosive peroxides.

2 Experimental Section

2.1 Sample Preparation

Preparation of TATP followed the method of Milas with modifications as follows: a 100 mL round bottom flask was charged at room temperature with 5 mL of acetone and 5 mL of 35% hydrogen peroxide[17,18]. The flask was immersed in a dry ice bath; and when the mixture reached $-20\,°C$, 3 mL of sulfuric acid was added dropwise taking care to maintain the temperature below $-10\,°C$. Addition of acid typically took 30 minutes; to hurry the process was to invite a violent event which in one case cracked a shatterproof shield and the Corning stirrer/hot plate top. The reaction was considered complete when further addition of acid did not evoke violent bubbling. This usually required the entire 3 mL of acid. After the acid had been added, and

while the mixture was still cold, 20 mL of methylene chloride were added. The resulting solution was transferred to a separatory funnel and allowed to warm to room temperature. The remaining H_2SO_4 was removed by washing three times with distilled water. TATP was separated from the methylene chloride by allowing the solvent to evaporate as the solution sat in the hood overnight. The isolated TATP was re-crystallized in methanol, resulting in 0.649 g (13% yield) of white crystals with melting point of $95-96\,°C$. Poor yield may be a result of high volatility; we observed that TATP sublimes at the rate of about 0.9% per hour.

^{1}H-NMR (400 MHz, CDCl$_3$) δ 1.43 (s); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 21.4 (CH$_3$), 107.5 (ring C).

GC/MS using Finnigan TSQ 700 triple-stage: CI (methane): 223 (M+1). EI 222 (P); 117 {HOO[C(CH$_3$)$_2$]$_2$}; 101{HO[C(CH$_3$)$_2$]$_2$}; 75 [HOOC(CH$_3$)$_2$]; 59 [HOC(CH$_3$)$_2$]; 43 [CH(CH$_3$)$_2$].

2.2 Thermal Analysis

A TA Instruments Model 2910 Differential Scanning Calorimeter (DSC) was operated under nitrogen flow and calibrated against indium (m.p. $156.60\,°C$, ΔH_f 28.5 J/g). The TATP samples (0.1 to 0.4 mg) were sealed in capillary tubes (1.5 mm O.D., 0.28 mm wall thickness, and 8 mm length) which were held in aluminum cradles[19]. Thermo-

grams of the samples were recorded from 40 °C to 500 °C, generally at a ramp rate of 20 °C/min. The exothermic peak maximum temperature was used to indicate the relative stability of samples. For isothermal kinetics studies, samples (0.1–0.6 mg) were sealed in glass capillary tubes of various sizes. Primarily tubes of dimensions 2 mm I.D. × 50 mm (150 μL volume) were used, but in some experiments the surface area and volume of the tube were purposely varied – 5 mm × 50 mm (1 mL) and 1 mm × 50 mm (25 μL). In one set of experiments 3 mg TATP samples were sealed in 25 μL ampoules to ensure reaction occurred in the condensed phase. Generally samples were sealed under air, but we found no difference in the product distribution whether samples were sealed under vacuum rather than air. Thermolyses at 150 °C were conducted in an oven (+/−1 °C), while those at higher temperatures were performed in a molten metal bath.

2.3 Gas Chromatography/Electron Capture Detector (GC/ECD)

After thermolysis the sample tubes were rinsed with acetone and volumes were adjusted to 10 mL. To assess TATP remaining, a 1 μL aliquot of solution was injected via a Hewlett Packard (HP) 6890 auto-sampler into an HP 5890 series II GC with DB-5MS megabore column (6 m × 0.53 mm) and ECD detector. Helium was used as carrier gas, and nitrogen as anode purge gas for the detector. The injector temperature was 165 °C; the detector temperature, 300 °C; the oven was programmed to run at an initial temperature of 50 °C for two minutes, then ramped at 20 °C/min to a final temperature of 280 °C where it was held 3.5 minutes.

2.4 Analysis of Gaseous Decomposition Products

Complete thermolysis of TATP left no visible residue. Decomposition gases were analyzed by gas chromatography/mass spectrometry (GC/MS). An HP 5890 GC, equipped with model 5971 electron impact mass selective detector, was run in scan mode (mass range 12 to 200)

with a threshold of 150 and a sampling of 2 (3.5 scans/s). Helium was used as the carrier gas, and the GC column was a PoraPLOT Q (0.25 mm diameter × 25 mm length) purchased from Chrompack. The injector temperature was 100 °C; the detector temperature, 190 °C; the oven was programmed to sit for 5 minutes at −80 °C, then ramped at 15 °C/min to a final temperature of 190 °C where it was held 10 minutes[20]. The sealed samples were injected into the GC by placing them in a Nalgene (I.D. 1/8 inch and O.D. 3/16 inch) sample loop in line with the carrier gas to the injector. The sample loop was purged with helium. The decomposition gases were introduced to the system by bending the flexible Nalgene loop, thus, breaking the capillary tube. Decomposition gases were identified by comparing their GC retention times and mass spectra to authentic samples. When authentic samples were not available, sample spectra were compared with the NIST MS library for a tentative assignment.

3 Results

The thermolysis of neat TATP was generally performed in ∼160 μL ampoules over the temperature range 150 to 225 °C. These thermolyses were first-order out to about 90% conversion at least at temperatures above 160 °C. Generally first-order plots were constructed with seven to eight data points with a R^2 fit better than 0.99. Even at 150 °C TATP samples appeared to be gaseous. To ensure that condensed-phase kinetics were examined, the reaction tubes were reduced to 25 μL and the sample size increased to 3 mg. Thermolyses were also performed in the presence of agents which would

(a) produce methyl radicals (di-*t*-butyl peroxide);
(b) trap radical (di-*t*-butyl cresol); and
(c) donate hydrogen (isopropanol and 1,4-cyclohexadiene).

Table 1 shows the resulting rate constants. DSC was used for initial screening of the TATP samples. Although the melting point was relatively sharp, centered at 98 °C

Table 1. Kinetics of TATP decomposition

T (°C)	k	R^2	Fract. Remain. (%)	State, Container Size
225	5.69E-03	0.997	12	neat, 160 μL
210	1.19E-03	0.994	5	neat, 160 μL
200	4.70E-04	0.991	10	neat, 160 μL
180	1.10E-04	0.987	13	neat, 160 μL
160	1.60E-05	0.984	64	neat, 160 μL
150	7.37E-06	0.996	38	neat, 160 μL
150	1.01E-05	0.971	38	neat, 1 mL
150	9.01E-06	0.912	44	neat, 25 μL
150	2.32E-05	0.982	25	0.02 M TATP in isopropanol
150	6E-06		70	with 20% t-butyl peroxide
150	3.17E-05	0.987	24	neat liquid, 25 μL

	neat 150–225 °C
E_a kJ/mol	151
kcal/mol	36.3
A s^{-1}	3.75E+13
R^2	0.994

(109 J/g), the exotherm (215 °C, 3400 J/g, 800 cal/g) was extremely broad ranging about 80 °C at a scan rate of 20 °C/min. For this reason the variable heating rate ASTM DSC method could not be used to assess activation parameters for TATP[21]. In fact, at heating rates below 10 °C/min, the exotherm appeared to consist of several partially overlapping peaks, indicating the decomposition included multiple reaction steps.

TATP decomposition products were identified and quantified by GC/MS at two temperatures and two degrees of conversion. At 230 °C thermolysis was run in air and in vacuum; no significant difference in the products was noted. Acetone and carbon dioxide were the main products; these were identified and quantified by comparison to the authentic compounds. Other species were present as less than 6% of the total ion current (TIC). Most were identified by matching against a computer library (Table 2).

4 Discussion

Across a 75 °C temperature range the gas-phase decomposition of TATP was first-order out to a high degree of conversion, indicating induced decomposition was not

important. The Arrhenius plot was linear over the entire temperature range (Figure 2) suggesting the same rate-determining step was operative over the entire range. At 151 °C the decomposition of TATP was not accelerated by the presence of di-t-butyl peroxide, but thermolysis in the condensed phase or in 2-propanol slightly increased the rate of decomposition (Table 1). Figure 2 plots the rate constants determined in this study of neat TATP along with those obtained by another laboratory for the thermolysis of TATP in toluene and acetone[16]. That data fit reasonably well with ours indicating that the decomposition pathway is essentially the same regardless whether TATP is in toluene solution or in the gaseous state. This result differs from the decomposition of DADP where in solution the decomposition of DADP is significantly accelerated (Figure 3). Though the decomposition of gaseous DADP is much slower than that of TATP, the decomposition of DADP in solution is similar to that of TATP (Figure 3)[12,13]. The activation energies for the decomposition of gaseous DADP (163 kJ/mol)[9] and TATP (153 kJ/mol) are quite similar to each other and in line with O−O bond cleavage energy.

Sanderson and Story compared the decomposition of dicyclohexylidene diperoxide and tricyclohexylidene triper-

Table 2. TATP decomposition products under various conditions

Temperature °C		230	225	150	150	150	150	150	150	150
Time at temperature		40 min	1 min	64 h	5.25 h	70 h	94 h 35 min	93 h	71.6 h	70 h
TATP (mg)		0.32	0.59	0.36	0.23	3.13	0.27	0.29	0.26 in 1 μL	0.44 in 1 μL
% Decomposition		100%	38%	100%	20%	100%	100%	100%	100%	100%
Special condition		gas	gas	gas	gas	liquid	20% diBucresol	20% (t-BuO)₂	2-propanol	Cyclohexadiene

Principle Products mol/mol TATP										
Acetone		1.83	0.63	1.38	0.26	2.62			7.21	2.48
CO₂		1.43	0.60	0.85	0.39	0.85			0.46	0.38
Percent acetone/final acetone			34%		19%					
Percent CO₂/final CO₂			42%		45%					

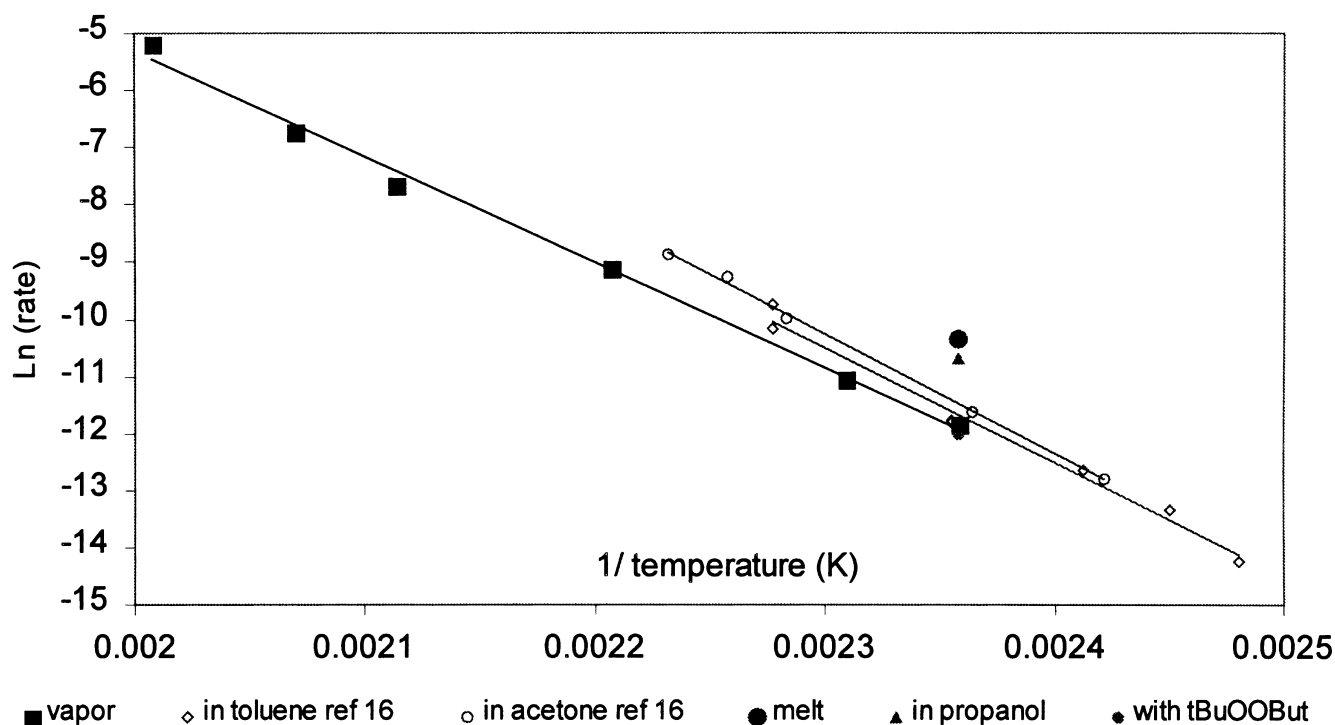| Product	Ret. time min	Ratio of Product to Tallest Peak								
CO	4.9	1	trace	trace	trace	trace	trace	trace	–	–
Methane	9.8	trace	–	trace	trace	trace	trace	trace	trace	trace
CO2	13.9	51	17	19	42	3	15	21	2	4
Ethane	16.6	13	2	1	2	0.2	trace	1	trace	trace
Water	19.5	some	some	some	some	trace	some	some	some	some
Propane	20.5	3	1	–	–	–	–	–	–	–
CH₃OH	22.0	12	2	trace	13	trace	trace	trace	trace	trace
CH₃CHO	22.8	trace	–	trace	trace	–	–	trace	–	–
Isobutene	23.2	trace	–	–	–	–	trace	–	–	–
2-methyl-1-propene	23.4	–	–	–	–	–	1	–	–	–
HC(O)OCH₃	23.7	1	trace	5	trace	0.6	3	5	–	trace
Ethanol	24.6	3	1	trace	2			trace	–	–
Acetone	25.8	100	100	100	100	100	100	100	74	86
2-propanol	25.8	–	–	–	–	–	–	–	100	–
CH₃CO(O)CH₃	26.9	14	17	20	21	5	15	23	–	4
CH₃C(O)OH	29.3	9	trace	28	24	22	14	31	trace	3
HC(O)OCH(CH₃)₂	30.0	–	–	–	–	–	–	–	trace	–
CH₃CH₂C(O)CH₃	30.4	14	13	trace	some	trace	trace	trace	–	–
CH3C(O)OCH₂CH₃	30.9	8	18	2	some	0.6	–	2	–	–
Benzene	32.0	–	–	–	–	–	–	–	–	100
1,4-Cyclohexadiene	34.8	–	–	–	–	–	–	–	–	28

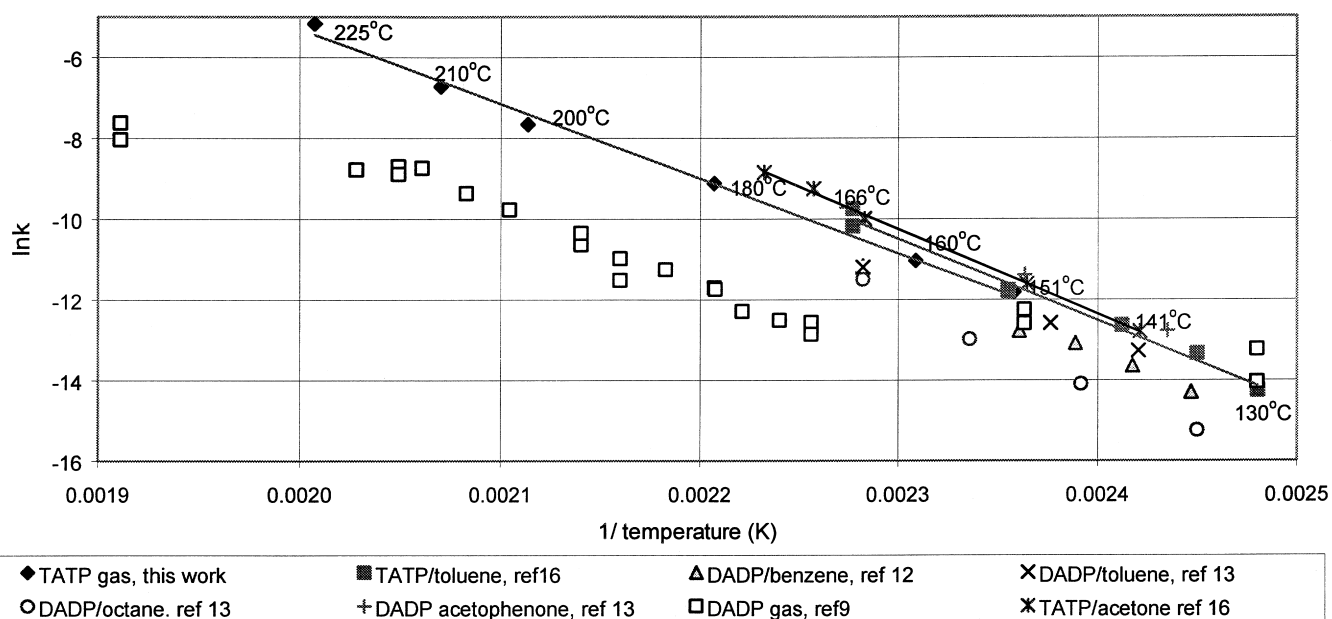**Figure 2.** Arrhenius plots for TATP decompositions, neat and in solution

Figure 3. Arrhenius plots for TATP and DADP decompositions

oxide and observed a difference in the way their decompositions were affected by the solvent[14]. The diperoxide decomposition showed a linear dependence on solvent polarity, while the triperoxide showed linear dependence with the cohesive energy density of the solvent (i.e. the energy necessary to form a solvent cavity as the reactant goes from initial to transition state). It was concluded that the transition state of the diperoxide was sensitive to the solvent, while in the triperoxide, the initial state was more

sensitive. DADP has been shown to be somewhat unique among the diperoxides because its low steric hinderance makes interaction with solvent possible. TATP is much less sensitive to the presence of toluene than is DADP. Such solvent interactions may not be possible for the larger TATP. However, TATP is sensitive to hydrogen-donating solvents. Hydrogen donation was indicated in the thermolysis of TATP in 1,4-cyclohexadiene because large amounts of benzene were formed. This cannot be explained by methyl
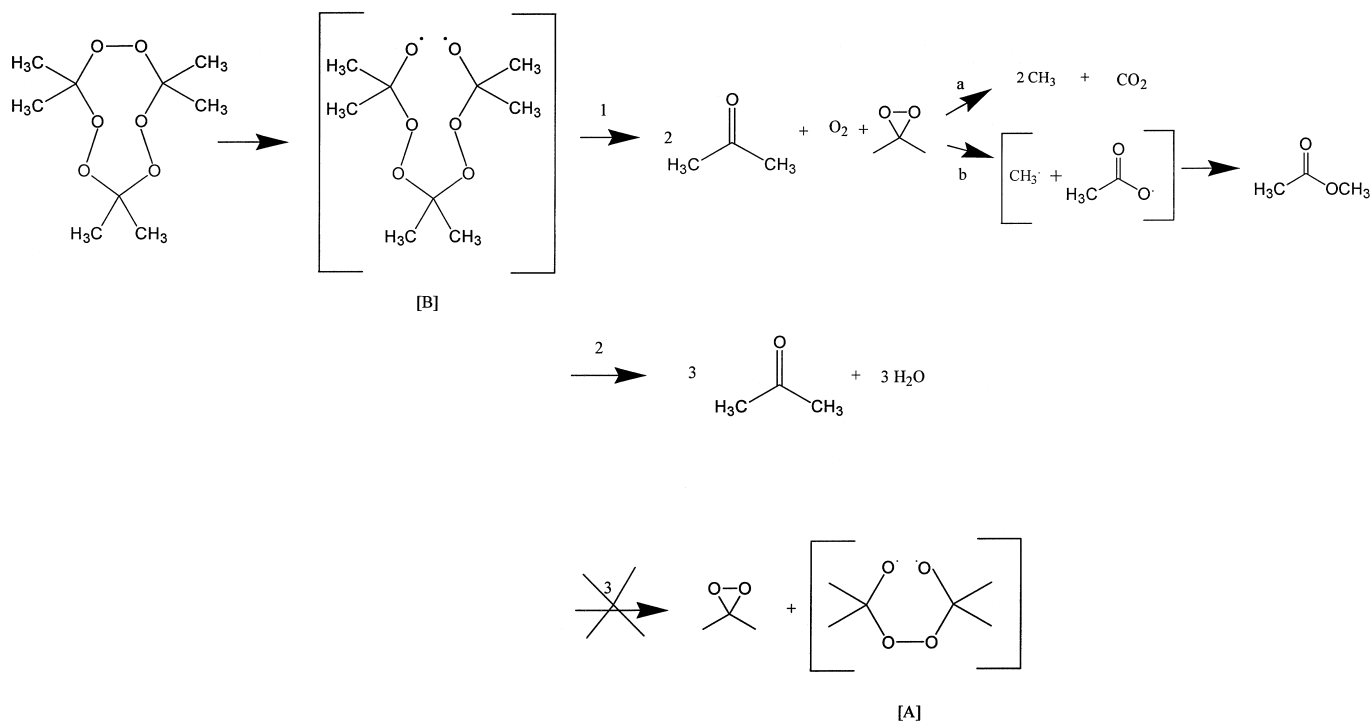
Figure 4. Proposed mechanism for triacetone triperoxide (TATP) decomposition:
(1) favored in gas-phase (a high temperature; b lower temperature)
(2) favored in condensed-phase or hydrogen-donating solvents

radical scavenging since no increase in methyl radical derived products was observed.

TATP product distributions were dependent on experimental conditions (Table 2). Thermolysis of TATP gave principally acetone and CO_2. These products were quantified against standard calibration curves (Table 2). Complete decomposition of TATP could theoretically give three moles of acetone, and oxygen:

$$C_9H_{18}O_6 \rightarrow 3\ OC(CH_3)_2 + 1.5\ O_2$$

Although oxygen was not observed under the thermolysis conditions, at 151 °C in the melt phase and in hydrogen-donating solvents (2-propanol and 1,4-cyclohexadiene) up to 2.6 moles of acetone formed per mole TATP. Under these conditions, CO_2 production was suppressed, and decomposition rate constants were enhanced by factors of 2 to 3.

The decomposition of TATP over the temperature range 230 °C – 151 °C yielded a single Arrhenius plot with decompositions first-order to a high degree of conversion. These observations suggest a single rate-determining step over the entire temperature range. Homolysis of an O–O bond is in line with the observed activation energy. Following O–O homolysis, both C–O and C–C bond cleavage have been considered for cyclic diperoxides. For TATP a second O–O bond homolysis might also be postulated. This would produce dioxirane and the diradical [A] (Figure 4 route 3). The diradical [A] would then decompose as shown in Figure 1, explaining the similarity of the decomposition

products of DADP and TATP. The problem with this pathway is that the diradical [A] should also form some DADP; and even though DADP decomposes much more slowly than TATP, no DADP was observed in any of the TATP thermolyses.

Under the experimental conditions, C–C scission producing methyl radical was a minor decomposition path for the [B] diradical. We identified certain products as arising from methyl radical reactions [ethane (methyl coupling); methanol (methyl + OH), 2-butanone (methyl + acetone), ethyl acetate (methyl + methyl acetate)] under most reaction conditions, more abundant at 230 °C than 151 °C, more abundant in gas phase than condensed (151 °C), and extremely minor in hydrogen-donating solvents (Table 2). At 230 °C CO_2, which can be thought of as a byproduct of methyl radical formation, was at the highest value found in this study. To determine whether carbon dioxide was a late breakdown product in the gas-phase reaction, its distribution was determined during the decomposition cycle. At 151 °C the acetone/TATP ratio matched that of the fraction decomposed (20%), but carbon dioxide was slightly high (Table 2). At 230 °C the fraction of CO_2/TATP and acetone/TATP ratios matched the fraction of TATP decomposed (38%) to within experimental error. Thus, carbon dioxide is mainly formed in the primary decomposition rather than in the breakdown of some other product.

Postulating C–O bond homolysis in diradical [B] would account for the major decomposition product acetone, at least two moles/mole TATP. However, the mechanism should also account for the formation of minor products

methyl acetate and acetic acid. Both species were almost non-existent in the thermolysis of TATP in hydrogen-donating solvents, but in each case their gas-phase formation was greater at 151 °C than at 230 °C. These two observations might suggest these minor products arise from a common source, such as the $CH_3COO^{\bullet}$ radical. However, not all aspects of their formation were parallel. Furthermore, acetic acid formation was not enhanced in hydrogen-donating solvents. Because CH_3COOR formation is uniformly enhanced at low temperature we postulate that its formation involves an internal re-arrangement or in-cage radical reaction. McCullough et al. did not observe methyl acetate in the thermolysis of DADP but did detect the corresponding ester in the decomposition of dibenzyl diperoxide[8]. They considered four routes to the ester:

a) in-cage radical recombination of $RCOO^{\bullet}$ with $R^{\bullet}$
b) induced decomposition of the diperoxide by $R^{\bullet}$
c) in-cage induced decomposition of the peroxide intermediate [A] by $R^{\bullet}$
d) alkyl migration in the intermediate biradical followed by a second O—O bond fission.

They selected route c based on two observations. A mixture of two diperoxides failed to produce significant $RCOOR'$ (ruling out route a). The thermolysis of the cyclic diperoxide of benzyl phenyl ketone produced mainly benzyl benzoate, small amounts of phenyl benzoate (should be sole product if route a) and no phenyl phenyl acetate (should be formed to some extent if route d) nor benzyl phenyl acetate[8].

We cannot postulate that methyl acetate was formed by any of the pathways proposed by McCullough[8] because we do not believe the diradical [A] forms under our experimental conditions. If any of the four proposed reactions occurred starting with diradical [B], diradical [A] would form in addition to methyl acetate. Therefore, we must look for an alternative route to methyl acetate. We envision diradical [B] to decompose such that the end carbon groups form acetone while the remaining atoms $[(CH_3)_2CO_4]$ produce dimethyl dioxirane and oxygen. Dioxiranes undergo unimolecular conversion to the corresponding ester[22], and this would account for the formation of methyl acetate. Dimethyl dioxirane is a reasonable intermediate; in fact, under some conditions it even forms diacetone diperoxide[23]. Although dioxirane has not been proposed as an intermediate in the decomposition of DADP, the energetics may make it more likely when considering cyclic triperoxides.

In contrast with methyl acetate, acetic acid formation was significantly greater in the condensed-phase (151 °C) thermolysis compared to the gas-phase reaction. McCullough et al. observed acetic acid in the thermolysis of DADP but were unable to explain its formation[8]. It is somewhat puzzling that acetic acid production was enhanced in the condensed-phase decomposition of TATP and depressed when hydrogen-donating solvents were present. In most other respects, the two types of reaction conditions yielded similar results: increased acetone formation (2.5–2.6 mol/mol); lack of methyl-radical-produced

products; low quantities of methyl acetate; slightly elevated decomposition rates (2 to 3 fold). We speculate that when diradical [B] loses the two end groups forming acetone, under conditions where the intermediate can be stabilized, dioxirane is not formed. In the presence of stabilizing species, such as a hydrogen-donating solvent or another molecule of TATP, oxygen is captured as water, and the third $(CH_3)_2C$ group is often transformed to acetone. (It should be noted that unlike with the reported DADP thermolyses[12], oxygen was not observed in our experiments. Any oxygen produced was apparently consumed in oxidative processes. Attempts to show that singlet oxygen was involved in the decomposition of diperoxides were not successful[24].) The large amount of acetone produced when TATP was heated in 2-propanol (over 7 moles per mole TATP) undoubtedly arises from the oxidation of 2-propanol. McCullough reported a similar result for DADP[8].

5 Conclusions

The products and activation energies for TATP decomposition are similar to those of DADP. Over a large temperature range (230–150 °C), TATP decomposition is initiated by O—O bond homolysis. Acetone was the major decomposition product; carbon dioxide, methyl acetate, and acetic acid were also observed as well as minor species thought to result from methyl radical reaction. However, we do not believe the decomposition of TATP proceeds through the same intermediate diradical as DADP because no DADP was observed in partially decomposed TATP. Furthermore, neat TATP decomposed significantly faster than DADP. Had DADP formed, it should have been sufficiently long-lived for observation. Following O—O bond homolysis rapid C—O scission yields two molecules of acetone. The fate of the remaining atoms depends on the reaction conditions. Gas phase favors the formation of dimethyl dioxirane; high temperature favors its decomposition to carbon dioxide; lower temperature favors production of methyl acetate. Condensed-phase or reaction in a hydrogen donating solvent favors the formation of a third molecule of acetone rather than dioxirane.

6 References

(1) J. Kroschwitz (ed.), "Kirk-Othmer Concise Encyclopedia of Chemical Technology", 4th ed., 'Organic Peroxides' Wiley, New York, Chichester, 1999, pp. 1472–1483.
(2) S. M. Kaye (ed.), "Encyclopedia of Explosives and Related Items", PATR 2700 Vol. 8, U.S. Army Armament Research & Development Command, Dover, NJ 1978, p. 203.
(3) D. N-S Hon, "Take care when using organic peroxides in the laboratory", Pulp & Paper Canada 86(6), 129–131 (1985).
(4) T. Yoshida, K. Muraaga, T. Matsunaga, and M. Tamura, "Evaluation of Explosive Properties of Organic Peroxides with a Modified Mk IIII Ballistic Mortar", J. Hazardous Materials 12, 27–41 (1985).
(5) T. Urbanski, "Chemistry and Technology of Explosives" Vol. 3, Pergamon Press, Oxford, 1967, pp. 299–305.

(6) D. J. Reutter, E. D. Bender, and R. L. Rudolph, "Analysis of an Unusual Explosive: Methods Used and Conclusions Drawn from Two Cases", *International Symposium Analysis & Detection of Explosives*, U.S. Dept. Justice, FBI, Quantico (VA), March 1983, pp. 149–158.
S. Zitrin, S. Kraus, and B. Glattstein, "Identification of Two Rare Explosives", *International Symposium Analysis & Detection of Explosives*, U.S. Dept. Justice, FBI, Quantico (VA), March 1983, pp. 137–141. H. K. Evans, A. J. Tulleners, B. L. Sanches, and C. A. Rasmussen, "An Unusual Explosive, Triacetone Triperoxide", *J. Forensic Sci. 31(3)*, 1119–1125 (1986).
G. M. White, "An Explosive Drug Case", *J. Forensic Science*, 37(2), 652–656 (1992).
A. J. Bellamy, "Triacetone Triperoxide: Its Chemical Destruction", *J. Forensic Sci. 44(3)*, 603–608 (1999).
E. Shannon, "The Explosives: Who Built Reid's Shoes?", *Time*, Feb. 25, 50 (2002).

(7) H. A. Brune, K. Wulz, and W. Hetz, "Über den Substituenten-Einfluss auf die konformative Beweglichkeit zyklischer Peroxide", *Tetrahedron 27*, 3629–3644 (1971).

(8) K. J. McCullough, A. R. Morgan, D. C. Nonhebel, and P. L. Pauson, "Ketone-derived Peroxides. Part II. Synthetic Methods", *J. Chem. Res. Synopses* (*M*), 629–650 (1980).
K. J. McCullough, A. R. Morgan, D. C. Nonhebel, and P. L. Pauson, "Ketone-Derived Peroxides. Part III. Decomposition of Cyclic Diperoxydes Derived from Dialkyl Ketones", *J. Chem. Res. Synopses* (*M*), 651–676 (1980).

(9) L. F. R. Cafferata, J. D. Lombardo, "Kinetics and Mechanism of the Thermal Decomposition Reaction of Acetone Cyclic Diperoxide in the Gas Phase", *Int. J. Chem. Kinet. 26*, 503–509 (1994).

(10) S. G. Hong, Y. H. Li, "AM1 Study of Thermolysis of Acetone Cyclic Diperoxide", *J. Mol. Struct.* (*Theochem*) *363*, 339–342 (1996).

(11) L. F. R. Cafferata, G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. J. Borkowski, "Mechanism of the Thermal Decomposition of the Activation Parameters of the Unimolecular Reactions", *J. Org. Chem. 55*, 1058–1061 (1990).

(12) L. F. R. Cafferata, G. N. Eyler, and M. V. Mirífico "Kinetics and Mechanism of Acetone Cyclic Diperoxide (3,3,6,6-Tetramethyl-1,2,4,5-tetroxane) Thermal Decomposition in Benzene Solution", *J. Org. Chem. 49*, 2107–2111 (1984).

(13) L. F. R. Cafferata, G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. Alvarez, "Solvent Effect in the Thermal Decomposition Reactions of Cyclic Ketone Diperoxides", *J. Org. Chem. 56*, 411–414 (1991).

(14) J. R. Sanderson, P. R. Story, "Macrocyclic Synthesis. The Thermal Decomposition of Dicyclohexylidene Diperoxide and Tricyclohexylidene Triperoxide", *J. Org. Chem. 39*, 3463 (1974).

(15) G. N. Eyler, A. I. Cañizo, E. E. Alvarez, and F. R. Cafferata, "Solvent Effects on the Thermal Decomposition of Diethyl Ketone Cyclic Triperoxide", *An. Assoc. Quím. Argent. 82(3)*, 175–181 (1994).

(16) G. N. Eyler, C. M. Mateo, E. E. Alvarez, A. I. Cañizo, "Thermal Decomposition Reactions of Acetone Triperoxide in Toluene Solution", *J. Org. Chem. 65*, 2319–2321 (2000).

(17) N. Milas, A. Golubovic, "Studies in Organic Peroxides. XXIV. Preparation, Separation and Identification of Peroxides Derived from Diethyl Ketone and Hydrogen Peroxide", *J. Am. Chem. Soc. 81*, 3361–3364 (1959).

(18) G. N. Eyler, A. I. Cañizo, E. E. Alvarez, L. F. R. Cafferata, "Improved Procedure for the Preparation of Diethyl Ketone Triperoxide and Kinetics of its Thermal Decomposition Reaction in Solution", *Tetrahedron Lett. 34(11)*, 1745–1746 (1993).

(19) L. F. Whiting, M. S. Labean, S. S. Eadie, "Evaluation of a Capillary Tube Sample Container for Differential Scanning Calorimetry", *Thermochem. Acta 136*, 231–245 (1988).

(20) W. Zheng, X. X. Dong, E. Rogers, J. C. Oxley, and J. L. Smith, "Improvements in Determination of Decomposition Gases from 1,3,3-Trinitroazetidine (TNAZ) and 5-Nitro-2,4,-dihydro-3H-1,2,4-triazol-3-one (NTO) using Capillary Gas Chromatography/Mass Spectrometry", *J. Chromat. Sci. 35*, 478–482 (1997).

(21) *Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*, The American Society for Testing and Materials (ASTM) Committee E-27, Designation: E 698–79, reapproved 1993.

(22) R. W. Murray, "Dioxiranes", *Chem. Rev. 89*, 1187–1201 (1989).

(23) L. Cassidei, M. Fiorentino, R. Mello, O. Sciacovelli, and R. Curci, *J. Org. Chem. 52(4)*, 699–700 (1987).

(24) J. R. Sanderson, P. R. Story, "Singlet Oxygen Scavenger Method for the Determination of Ketone Peroxide Kinetics", *J. Org. Chem. 39(21)*, 31–3185 (1974).