Reaction Kinetics of Acetone Peroxide Formation and Structure Investigations Using Raman Spectroscopy and X-ray Diffraction

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Triacetone triperoxide (TATP) has been prepared in order to study the effect of pH and temperature on the reaction kinetics. Raman spectra of liquid mixtures of acetone and hydrogen peroxide were recorded versus time throughout the experiments. The spectral data of the liquid phases indicate that at 25 °C the reaction between acetone and hydrogen peroxide proceeds to form intermediates within one day. Based on the assumption that a likely reaction path involves a sequence of reaction steps between acetone and hydrogen peroxide, calculations of Raman spectra were performed using a density functional theory (DFT)/Hartree–Fock approach. It was not possible from this to assess with certainty which intermediate products formed most extensively in an acetone/hydrogen peroxide mixture. However, it was concluded that the most likely reaction mixture is a mixture of the different intermediate products and that the rate determining step is the ring closure. The reaction rate of TATP formation was found to increase with temperature and with sulfuric acid additions to the acetone/hydrogen peroxide mixture. By correlation of the induction time of TATP crystallization against pH it was shown that the reaction rate is first order with respect to the H^+ concentration. Raman spectra of the precipitates from mixtures were in agreement with previous studies done for TATP, except in one case in which a crystal crystallized at 343 K had a distinctly different Raman spectrum. Comparison with calculated spectra revealed that the crystal produced could be diacetone diperoxide (DADP) or tetraacetone tetraperoxide (TrATrP). Single crystal X-ray diffraction analyses revealed that the crystal crystallized at 343 K was DADP.

Index Headings: **TATP; DADP; Cyclic peroxide explosives; Raman spectroscopy; X-ray diffraction.**

INTRODUCTION

Triacetone triperoxide (TATP; 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, $C_9H_{18}O_6$), tetraacetone tetraperoxide (TrATrP; 3,3,6,6,9,9,12,12-octamethyl-1,2,4,5,7,8,10,11-octaoxacyclododecane, $C_{12}H_{24}O_8$), and diacetone diperoxide (DADP; 3,3,6,6-tetramethyl-1,2,4,5-tetroxane, $C_6H_{12}O_4$) are a family of explosive organic cyclic peroxides that can be produced from acetone and hydrogen peroxide. TATP is well known to be obtainable through the following stoichiometric reaction:

$$3CH_3COCH_3 + 3H_2O_2 \rightarrow \text{TATP} + 3H_2O \qquad (1)$$

The TATP compound is simple to synthesize, the reactants are easy to obtain, and it is almost as powerful an explosive as TNT.[1,2] The potential danger of the compound should always be taken into consideration, because the explosive is known to be extremely sensitive to impact, friction, static electricity, and temperature changes.[1,2] Furthermore the explosive risk is significantly larger for dry crystals than in solution.

The synthesis of TATP was originally discovered in the 19th century by Wolffenstein,[3] who noted that a mixture of acetone and hydrogen peroxide over a period of 3 weeks would precipitate into an explosive white compound. Later Milas and Golubovic[4] discovered that the reaction rate as well as the yield would be significantly increased by adding acid to the reactants. However, even though the synthesis has been known for a long time, the exact course of the reaction is not known.

In this paper we report an investigation on TATP crystallization with focus on the effect of temperature and pH on the reaction kinetics. The induction time for TATP crystallization was measured for a number of sample mixtures with different pH values and at different temperatures. Throughout the experiments, the liquid and solid phases were analyzed using Raman spectroscopy. The crystal phases were characterized using X-ray diffraction. In addition to this, molecular simulations have been used to analyze the obtained spectral data.

EXPERIMENTAL

Chemicals and Procedures. TATP was synthesized by mixing acetone (min. 99% purity, Merck) with hydrogen peroxide (34.5–36.5% purity with max. 0.02% H_2SO_4, Riedel-de Haën).

The acetone and hydrogen peroxide were mixed in a weight ratio of 1 g acetone to 1.673 g aqueous hydrogen peroxide, which should give an equimolar solution (standard solution). The pH of the acetone and hydrogen peroxide solution was adjusted by addition of a dilute H_2SO_4 solution while measuring the pH using a PHM92 Lab pH-meter from Radiometer. The induction time of TATP crystallization was measured as a function of pH.

Different reaction temperatures were obtained by placing the samples at room temperature, in an oven, or in a refrigerator, respectively. In Table I an overview of the systems investigated in this study can be seen.

Raman Spectra. Raman spectra were obtained by use of a DILOR-XY 800 mm focal length multichannel spectrometer with horizontal Nd:YVO_4 laser excitation (532.8 nm, ~300 mW, vertically polarized). Rayleigh scattered light was filtered off with a double pre-monochromator (slit widths 200, 2000, and 200 μm). The Raman light was collected after 90 degrees of scattering, dispersed by use of an 1800 lines/mm grating, and focused onto a charge-coupled device (CCD) detector, cooled to 140 K by liquid nitrogen. The spectral resolution was approximately 4 cm^{-1}. Measurement on crystals of TATP was done with low laser intensity over a longer period in order to avoid evaporation and explosion.

X-ray Diffraction. Data were collected at 140 K on a Siemens SMART diffractometer using monochromated Mo-K_α-radiation ($\lambda = 0.71073$ Å, $\mu = 4.898$ mm^{-1}). Unit cell dimensions were refined and intensity data were reduced

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TABLE I. Experiments (conditions for equimolar mixtures of hydrogen peroxide and acetone, also containing water and sulfuric acid).

Mixture name	Acidity (pH)	Temperature T (K)
T1	3.2	277
T2		298
T3		313
T4		343
P1	6.8	298
P2	2.5	
P3	2.2	
P4	2.0	
P5	1.75	
P6	1.3	
P7	0.54	
P8	0.26	

(corrected for Lorentz and polarization effects) by use of the Siemens SAINT program system. The structures were solved by direct methods and refined by full-matrix least squares fitting of positional and anisotropic thermal parameters. Details of the structure solutions have been deposited at Cambridge Crystallographic Data Centre (deposition numbers CCDC 692537 and 692538).

Harmonic Frequency Calculations. The optimized structure and vibrational spectra (Raman band wave numbers and intensities) were calculated using quantum mechanical density functional theory (DFT) methods, utilizing Becke's three-parameter exchange functional with the Lee–Yang–Parr non-local correlation functional (B3LYP) with 6-31G(d,p) basis sets. Full optimization calculations were performed to determine the structure corresponding to the global minimum; these calculations were made without obtaining imaginary frequencies. The calculated spectra were used for qualitative comparison; thus, no scale factor has been applied to correct band frequencies. All the calculations were carried out with the Gaussian 03W software,[5] including the calculations of Raman intensities.[6]

RESULTS AND DISCUSSION

Raman Spectroscopic Studies. At first Raman spectra of the starting components (hydrogen peroxide and acetone) were recorded. The spectra are shown in Fig. 1 along with a spectrum recorded immediately after mixing of the two components (experiment P1). Upon comparing the spectra it is clear that many new bands show up after the mixing. It clearly indicates that a very fast reaction between hydrogen peroxide and acetone is taking place. The reagents were also mixed at lower temperatures, in an attempt to avoid the initial reaction between acetone and hydrogen peroxide, but the spectra of the initial reaction mixture looked the same as shown in Fig. 1.

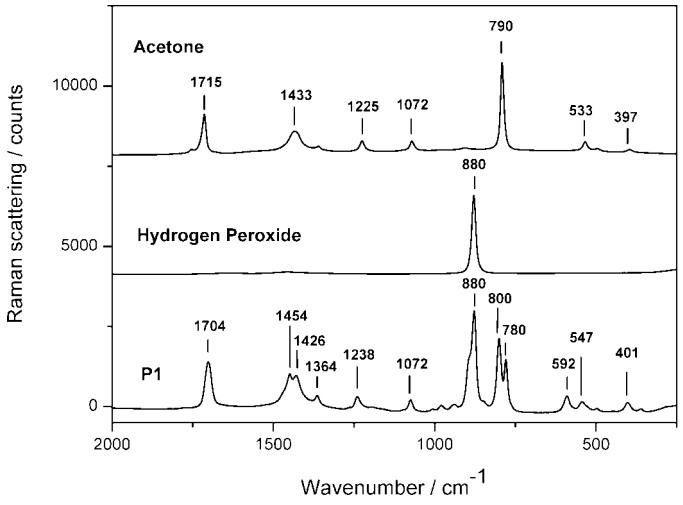


FIG. 1. Raman spectra of acetone, hydrogen peroxide, and the mixture P1.

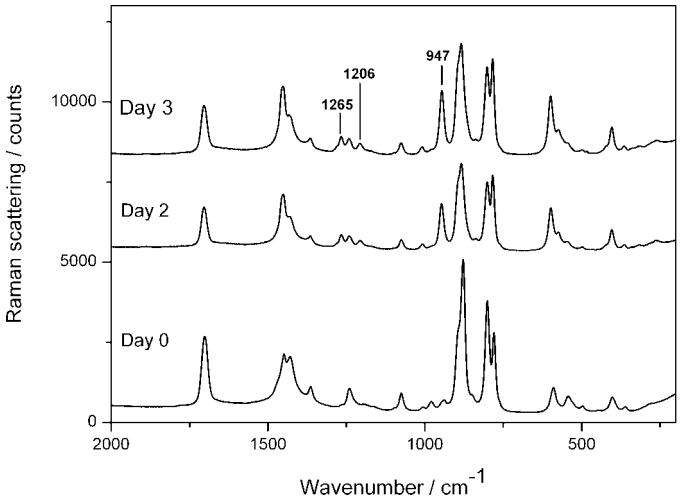


FIG. 2. Raman spectra of a liquid mixture of hydrogen peroxide, acetone, sulfuric acid, and water (P2). Spectra were recorded immediately after preparation of the mixture and after two and three days, as labeled.

An interesting observation was that the C=O stretching band was slightly displaced from 1715 cm^{-1} in acetone to 1704 cm^{-1} in the mixture. Such a shift may be taken to indicate a strong solvent interaction or may even be due to the phenomenon normally called the "Raman noncoincidence effect" (NCE). The effect causes a split between the isotropic and anisotropic Raman bands due to symmetrical vibrational intramolecular oscillations, as, e.g., in the case of the C=O stretch of acetone.[7] Solvent–solute interactions may cause a band to move towards higher frequencies; however, in this case the C=O stretching for the mixture has actually moved to a lower frequency. Such a negative shift has also been found for a mixture of acetone and $LiClO_4$.[8] An explanation could be that both systems are capable of cross associating.

Raman spectra of liquid mixtures of hydrogen peroxide, acetone, and sulfuric acid were taken with appropriate time intervals starting after mixing of the components and continuing until precipitation of TATP occurred. In Fig. 2 Raman spectra of the mixture P2 are shown for the first three days (spectra recorded later than this were all very similar to the spectrum of day 3). A comparison of the spectrum recorded immediately after mixing with the one obtained after just two days reveals that several new peaks have appeared. The new peaks are indicated in the figure by their wavenumbers. The band that appeared at 947 cm^{-1} is quite strong, indicating that a new compound was formed in the liquid phase and a further reaction was taking place in the liquid. The 947 cm^{-1} band is possibly caused by O–O stretching because such vibrations are known to be Raman active around this region. Another reason for this assumption is that intermediate reaction components are likely to contain O–O bonds. The two bands observed at

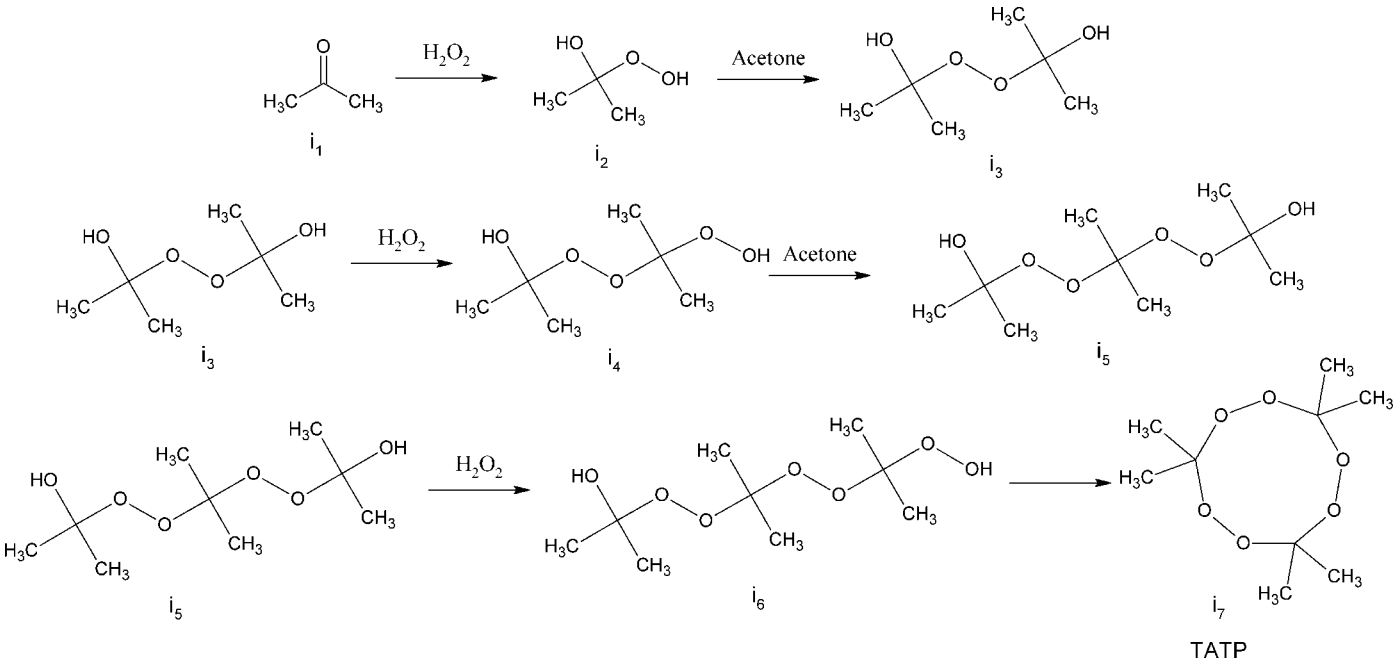


FIG. 3. Intermediate products of the reaction between acetone and hydrogen peroxide.

1206 cm^{-1} and 1265 cm^{-1} could be caused by O–C–O bending. This kind of bonding type is also very likely to be formed in intermediate components. The doublet band at 1440 cm^{-1} was seen to disappear during a couple of days, turning itself into a peak with a shoulder.

Based on the above considerations on the existence of intermediate components between acetone and hydrogen peroxide, the reaction mechanism in Fig. 3 for the formation of TATP is proposed.

To further test this hypothesis, Raman spectra (Fig. 4) of the proposed compounds have been calculated using the DFT calculation procedure as implemented in the Gaussian 03W software.[5]

From Fig. 4 it can be seen that the measured spectrum of experiment P1 resembles the calculated intermediates. This can be seen, e.g., for the peak at 592 cm^{-1}, which has an equivalent peak in all three of the calculated spectra. Also the group of peaks from 750–1000 cm^{-1} can be seen to have some degree of accordance to the calculations. However, in general it can be seen that the measured spectrum does not resemble any of the individual intermediates but could resemble a mixture of them.

When comparing the calculated spectra, it should be taken into account that the models are based on isolated molecules of the different intermediates. If the liquid P1 in reality is a mixture of reaction products, a favorable single component comparison must be difficult to make, because the calculations do not take intermolecular interactions into account. Therefore, the comparison of the obtained spectrum of P1 on day 2 to the average of the three calculated intermediates should only be an indication and not a sufficient proof of what happens. Our data do not allow us to discuss details of the kinetics for the formation of TATP, but they show that we have a complex mixture of compounds. To conclude whether or not the formation of TATP takes place through the reaction mechanism presented in Fig. 3, further investigation is needed.

Crystals were formed in the case of experiments T2–T4 and P2–P8. The Raman spectra of the TATP crystals were recorded and images were acquired through a microscope. In Fig. 5 two

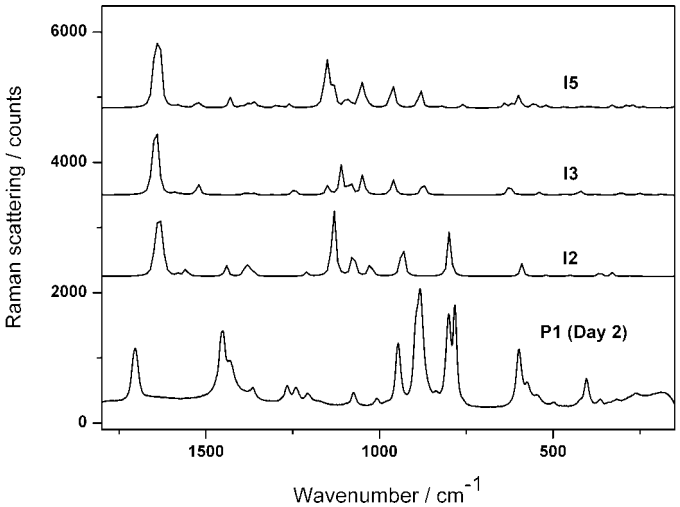


FIG. 4. Spectra calculated of intermediate molecular structures, i_2, i_3, and i_5 according to Fig. 3.

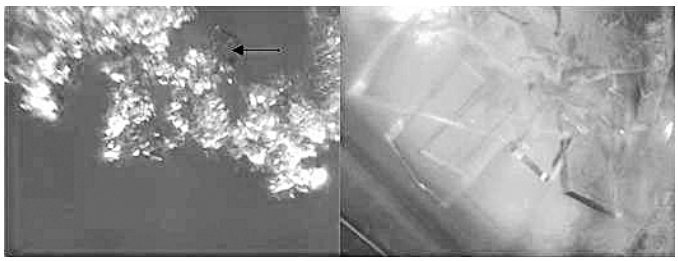


FIG. 5. Images taken through a microscope of the TATP crystals in (**left**) mixture T4 and (**right**) mixture P5. A single flat crystal is indicated with the arrow.

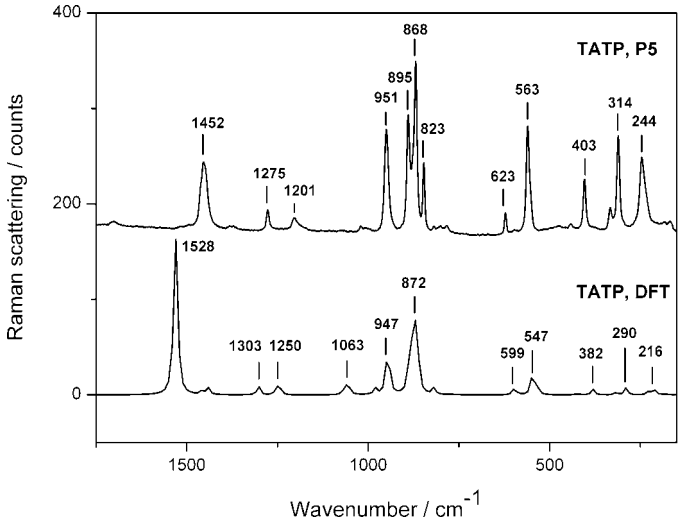


FIG. 6. Experimental Raman spectrum of TATP (P5) compared to the spectrum predicted using the Gaussian 03W DFT/B3LYP calculation.

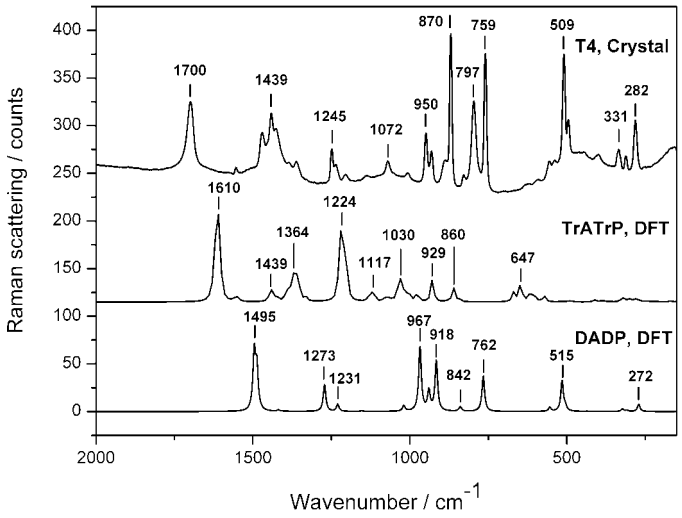


FIG. 7. Raman spectrum of the unknown crystal structure from mixture T4 and the calculated spectra of DADP and TrATrP using the DFT/B3LYP Gaussian 03W calculation.

crystal images are shown. The picture to the left is of T4 and the one on the right refers to P5. Quite some difference in the appearance of the crystals can be seen. In general, flat triangular or squared crystals were found in P5. However, in T4 only a single flat crystal, indicated with the arrow, was observed, whereas the other solid substances have more peculiar and not particular crystal-like appearances.

A typical spectrum of the obtained precipitates (P5) is shown in Fig. 6, along with the calculated spectrum of TATP. An overview of the calculated and experimentally obtained Raman bands is provided in Table II, including approximate descriptions of the types of group vibrations.

Hence, the band at 868 cm^{-1} is due to the peroxide O–O stretching, while the band at 1201 cm^{-1} is identified as C–C–C bend and C–O stretching. The bands observed at 1275 cm^{-1}, 1021 cm^{-1}, 951 cm^{-1}, and 823 cm^{-1} are identified as being due to mixed CH_3 deformation and ring stretching and bending vibrations. These findings are in good agreement with previous Raman observations on TATP (work by Buttigieg et al.[9]). From these considerations it seems fair to conclude that the crystal formed was indeed TATP.

The calculated spectrum is seen to be in reasonably good agreement with the one obtained experimentally (Fig. 6). Although slight differences between the wavenumbers of the different bands in the calculated and experimental spectra exist, it should be noted that the bands in most cases are in the same region of the spectrum. The minor differences in wavenumbers can be assigned to the fact that the calculations are only conducted upon a single isolated molecule and with a model that has some limitations.

In one case, experiment T4, the obtained crystal gave a quite different Raman spectrum (Fig. 7). Visually the crystals looked smaller and not as square as the crystal from P5 (Fig. 5). In Fig. 7 the spectrum of the crystal from T4 and the calculated spectra of DADP and TrATrP are provided. This figure was made because we noted that the spectra of the T4 crystal did not compare well with the spectra of TATP even though there was a band at 870 cm^{-1} indicating the presence of a peroxide bond. In Table III the calculated Raman bands for DADP and TrATrP are compared with the Raman bands of the unknown crystal of T4. Approximate descriptions of the group vibration types have been based upon comparing vibration types for both DADP and TrATrP in the ranges where experimental Raman bands of T4 were found.

The comparison of the calculated bands of DADP and TrATrP with the experimentally obtained Raman bands of T4

TABLE II. Calculated and experimentally obtained Raman bands for TATP and the approximate description of the group vibration type.

Calculated frequency (cm^{-1})	Experimental frequency (cm^{-1})	Approximate description
216	244	C–CH_3 torsion
290	314	C–C–C bend
382	403	Ring breathing
547	563	O–C–O bend
599	623	O–C–O bend
819	823	Ring stretch
872	868, 895	O–O stretch
947	951	C–C and C–O stretch
1063	1021	CH_3 deformation
1250	1201	C–C–C bend and C–O stretch
1303	1275	C–C and ring C–O Stretch
1528	1452	H–C–H bend

TABLE III. Calculated Raman bands for DADP and TrATrP compared with Raman bands of the unknown crystal from mixture T4 and approximate descriptions of the group vibration types.

Calculated frequency (cm^{-1})		Experimental frequency (cm^{-1})	Approximate description
DADP	TrATrP		
272	–	282	CH_3 rocking
515	–	509	C–C–C bend
762	647	759	C–O and C–C stretch
842	860	797	C–O stretch and C–H bend
918	929	870	O–O stretch and C–H bend
967	–	950	O–O stretch and C–H bend
–	1030, 1117	1072	CH_3 deformation
1231	1224	–	O–O stretch and C–H bend
1273	–	1245	C–O stretch and C–H bend
1495	1439	1439	CH_3 deformation
–	1610	1700	H–C–H bend

TABLE IV. X-ray diffraction data of the crystals from the P5 and T4 mixtures.

	P5 (TATP)	T4 (DADP)
Z	2	1
a (Å)	13.7617 (7)	5.8881 (8)
b (Å)	10.6514 (6)	5.8935 (8)
c (Å)	7.8800 (4)	10.5238 (14)
β (°)	91.8240 (10)	94.380 (2)
V (Å^3)	1154.48 (11)	364.13 (9)
ρ (g cm^{-3})	1.670	1.351

show a better agreement between DADP and T4 bands at lower frequencies. However, at around 800–900 cm^{-1} where the peroxide vibrations are expected, both DADP and TrATrP are in reasonably good agreement with bands of T4, and at higher frequencies the calculated bands of TrATrP are in better agreement with the experimental Raman bands of T4. From this we conclude that T4 most likely contains a cyclic peroxide, but it is not possible to conclude whether it is DADP, TrATrP, or maybe a third substance.

X-ray Diffraction. To further investigate the differences between the crystal of P5 (representing TATP) and the crystal of T4, X-ray diffraction was used to reveal the size, symmetry, and structure of the crystal unit cell. A colorless crystal of P5 was selected for investigation. The crystal was found to be monoclinic and the cell dimensions and calculated density are provided in Table IV and are in agreement with values found in the literature for TATP.[2]

Analogously for T4 a crystal was selected. The unit cell was found to be monoclinic and the dimensions and the calculated density can be seen in Table IV. These measurements show that the T4 crystal is DADP, as the values are similar to results from Dubnikova et al.[2] The reason that the Raman spectrum did not show the peaks that are representative for DADP is most probably due to the presence of the unknown substance that precipitated along with the DADP. This substance had a non-crystalline nature and was not appropriate for X-ray diffraction measurements. The experimental Raman spectrum in Fig. 7 is most likely dominated by the spectrum of this solid.

In Fig. 8 we show the molecular structures of TATP and DADP as obtained from our X-ray diffraction measurements.

One important conclusion from these observations is that the formation of DADP, though not always of very high purity, can be achieved under relatively simple conditions. In comparison with other studies where complex synthesis methods were used,[2] we have found that DADP can be simply synthesized analogously to TATP. More exactly, we used an aqueous equimolar mixture of acetone and hydrogen peroxide and let it react at 343 K for two days and then let it precipitate at room temperature.

The Reaction Rate. The reaction temperature for the synthesis of TATP is important, because a low temperature will increase the time needed before crystallization of TATP starts. We found that increasing the temperature up to 313 K will lead to faster precipitation. At temperatures above 333 K TATP will not precipitate. Here instead we observed precipitation of DADP.

An earlier study has shown that the formation of TATP is catalyzed by acid.[4] However, details on the dependency have, to our knowledge, not been reported. Such a dependency should have influence on the time needed to induce TATP

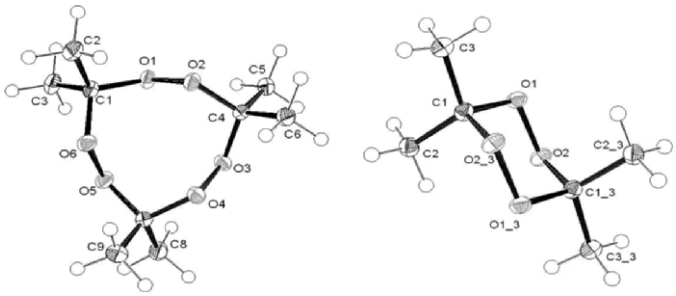


FIG. 8. Structures obtained from X-ray diffraction measurements. (**Left**) TATP; (**right**) DADP.

crystallization, if related to the pH value of the acetone/hydrogen peroxide mixture. This implies that the presence of acid promotes the reaction.

The rate expression for the formation of TATP is assumed to have the following appearance:

$$\frac{d[\mathrm{TATP}]}{dt} = k \cdot [\mathrm{Ace}]^a [\mathrm{H_2O_2}]^b [\mathrm{H^+}]^c \qquad (2)$$

Here k is a rate constant, [TATP], [Ace], [H_2O_2], and [H^+] are respectively the TATP, acetone, H_2O_2, and proton concentrations at a given time, and a, b, and c are the respective reaction orders. By rearrangement and integration of Eq. 2, we obtain:

$$t = \frac{[\mathrm{TATP}]}{k \cdot [\mathrm{Ace}]^a [\mathrm{H_2O_2}]^b [\mathrm{H^+}]^c} \qquad (3)$$

At the precipitation time, it is assumed that the concentration of TATP is saturated (in all of the solutions), which makes the value equivalent across all of the solutions, at a particular temperature. The pH of all mixtures was regulated on the basis of one equimolar standard solution. At the precipitation time it is therefore presumable that the concentrations in the different mixtures are the same. Because the mixtures were kept at the same temperature, we can therefore rewrite Eq. 3 to:

$$t_p = K \cdot [\mathrm{H^+}]^{-c} \qquad (4)$$

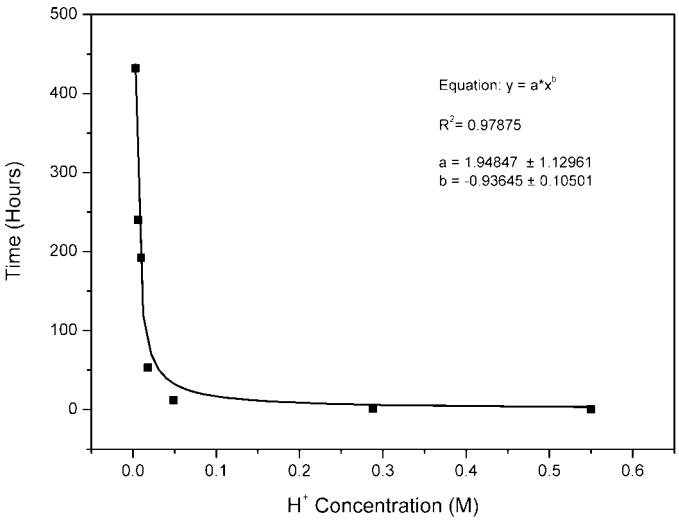


FIG. 9. Induction time as a function of H^+ concentration.

From this expression it is expected that a plot of the induction time of TATP crystallization against the H^+ concentration should exhibit a markedly decreasing behavior. In Fig. 9 a plot of the measured data is shown and indeed such a behavior is observed. By fitting these points (using OriginPro 7.5 software[10]) to a power function of the form $y = a \cdot x^b$, in accordance with Eq. 4, we find that the best fit is obtained with $a = 1.9 \pm 1.1$ and $b = -0.93 \pm 0.11$. The value of a is seen to have a relatively high standard deviation, which can be explained through the many assumptions we made on the K parameter in Eq. 4, which is equivalent to a. The value of b, equivalent to $-c$ in Eq. 4, can be seen to lie in an interval containing -1. Thus, it follows that the formation of TATP most probably is first order with respect to the H^+ concentration.

CONCLUSION

Using Raman spectroscopy it was shown that the reaction between hydrogen peroxide and acetone quickly forms intermediates when reactants are mixed. With time the intermediates will form cyclic peroxide structures and in most cases TATP, which can easily be identified by Raman spectroscopy. In this study on the kinetics of the TATP formation, it was found that the reaction rate most probably is first order with respect to the H^+ concentration. This finding substantiates the early work of Milas and Golubovic[4] on the catalytic effect of acid in the synthesis. Furthermore, it was found that the reaction rate increased with temperature up to 333 K. If the temperature is higher than that, TATP will not be formed.

Our mechanistic study didn't provide sufficient proof for an exact reaction mechanism but indicated a probable agreement with the reaction sequence presented in Fig. 3. Our conclusion is, in agreement with prior literature, that the formation of TATP is probably a step growth reaction.

It was further found that formation of DADP can be achieved analogously to the TATP synthesis. We observed that an effective DADP synthesis can be achieved by letting an equimolar mixture of acetone and hydrogen peroxide react at 343 K through two days and then cooling it to room temperature.

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1. R. Schulte-Ladbeck, A. Edelmann, G. Quintas, B. Lendl, and U. Karst, Anal. Chem. **78,** 8150 (2006).
2. F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, and E. Keinan, J. Am. Chem. Soc. **127,** 1146 (2005).
3. L. Pacheco-Londono, Á. Pena, O. Primera, S. Hernández-Rivera, R. Garciá, R. Camberlain, and R. Lareau, Proc. SPIE-Int. Soc. Opt. Eng. **5403,** 279 (2004).
4. N. Milas and A. Golubovic, J. Am. Chem. Soc. **81,** 6461 (1959).
5. M. Frisch, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery, T. Vreven, K. Kudin, J. Burant, J. Millam, S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. Knox, H. Hratchian, J. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Ayala, K. Morokuma, G. Voth, P. Salvador, J. Dannenberg, V. Zakrzewski, S. Dapprich, A. Daniels, M. Strain, O. Farkas, D. Malick, A. Rabuck, K. Raghavachari, J. Foresman, J. Ortiz, Q. Cui, A. Baboul, S. Clifford, J. Cioslowski, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Martin, D. Fox, T. Keith, M. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez, and J. Pople, *Gaussian 03W*, Revision B.04 (Gaussian, Inc., Pittsburgh, PA, 2003).
6. M. J. Frisch, Y. Yamaguchi, J. F. Gaw, and H. F. Schaefer III, J. Chem. Phys. **84,** 531 (1986).
7. M. Giorgini, Pure Appl. Chem. **76,** 157 (2004).
8. Z. Kecki and A. Sokolowska, J. Raman Spectrosc. **25,** 7 (1994).
9. G. Buttigieg, A. Knight, S. Denson, C. Pommier, and M. Denton, Forensic Sci. Int. **135,** 53 (2003).
10. OriginPro 7.5 SR6 (OriginLab Corporation, Northampton MA, 2006).