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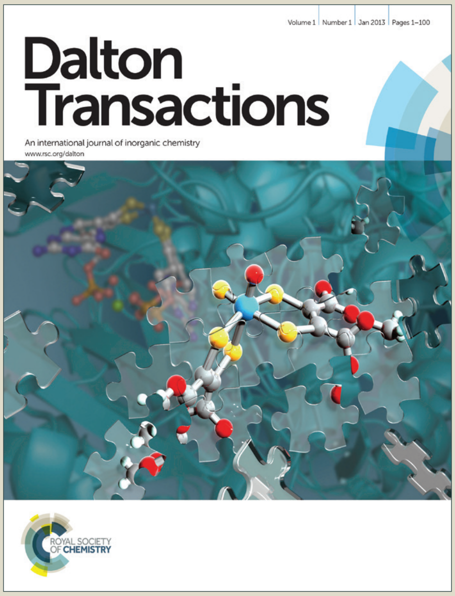

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PAPER

Rapid degradation of cyclic peroxides by titanium and antimony chlorides

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First responders face extraordinary risks when dealing with organic peroxides such as TATP due to the extreme sensitivity of this class of explosives, and to a lack of a robust chemical means of safe and rapid neutralisation. The Lewis acids $TiCl_4$ and $SbCl_3$ have been found to demonstrate a novel degradation mechanism, with $TiCl_4$ degrading a model cyclic peroxide in minutes when used in a two-fold excess, or ~3 hours at half equivalence. The products cannot re-form peroxide compounds as is the case with acid degradation, suggesting the two mechanisms are fundamentally different. The Lewis acids mediate a rearrangement reaction in the cyclic peroxide backbone leading to relatively innocuous products through deactivation of oxidising O. Sub-stoichiometric $TiCl_4$ reactions highlight a secondary reaction pathway that also leads to some oxidative chlorination products, possibly mediated by an unconfirmed titanium-oxychloride species. $SbCl_3$ was found to exhibit similar reactivity to $TiCl_4$, although at a slower rate. A mechanism is proposed, consistent with the observations for both stoichiometric and sub-stoichiometric quantities of $TiCl_4$.

Introduction

Triacetone triperoxide (TATP) is an organic peroxide explosive readily manufactured from easily sourced chemical reagents and with relatively simple equipment. As a consequence it has found widespread use in the terrorist community. Its friction sensitivity of < 0.1 N and impact sensitivity of 0.3 Nm make it dangerous to handle and unpredictable in an explosive device.[1] Consequently, it has been a stated aim of several research groups to find a rapid and safe chemical method of degrading TATP.[2-4] Much work on TATP degradation has centred on acid-catalysed degradation. As an example, hydrochloric acid will degrade TATP, forming mainly acetone,[2] in essentially a reversal of the equilibrium for the synthesis of TATP. Accordingly there is the potential for peroxides to re-form. Furthermore, it has been reported that treating solid TATP with concentrated sulfuric acid causes initiation of explosion in > mg quantities.[3] This observation makes the use of a protic acid problematic as a means of safely disposing of significant quantities of organic peroxide.

Alternative methods have been investigated, such as the use of tin chloride, which destroys TATP within 2 h but requires heating under reflux.[4] The heating of explosives samples is neither acceptable nor practical in a field environment. More recently, Oxley *et al* have investigated the use of zinc and copper salts and found that TATP solutions could be neutralised within 24 h at room temperature in the presence of a three-fold excess of either salt in combination with their respective pure metals.[3] While this represents a promising alternative to acid there are still disadvantages in the time and the quantities of deactivating agents required. Hexamethylene triperoxide diamine (HMTD), another common organic peroxide explosive is also reported to be degraded under these conditions.

Theoretical studies on the metal ions Ti^{4+}, Sb^{3+} and Sc^{3+} in the gas phase have indicated a significant binding affinity with TATP and were predicted to trigger its complete destruction.[5,6] This work encouraged us to examine reactivity of Ti^{4+} and Sb^{3+} compounds in solution with a cyclic peroxide model.

We report that both $TiCl_4$ and $SbCl_3$ react with cyclic peroxides via a rearrangement mechanism to give ester and ketone as primary products, with no peroxides formed. The reaction rate can be extremely fast or moderate depending upon the stoichiometric ratio of the catalyst. The identification of this reaction presents a substantial contribution to the chemistry of organic peroxide degradation, and may also provide insight into a potential catalytic approach to the problem.

Our investigations have largely utilized the model compound tripentanone triperoxide (TPTP), which we have previously demonstrated as an effective model for TATP in degradation reactions.[7] Detailed experiments were conducted using this compound as a safer and readily accessible cyclic peroxide.

Results and discussion

Titanium tetrachloride

Degradation of TPTP

The treatment of TPTP with excess $TiCl_4$ (>2:1) at room temperature in dry $CDCl_3$ resulted in the instantaneous generation of a pale yellow/green coloured solution. ^1H NMR spectra taken immediately after addition (< 2 min) showed no TPTP remaining (see ESI). The primary products were ethyl propanoate (EP) and 3-pentanone (3P), with the proton signals strongly shifted downfield from those of the free ligands, indicating they are bound to titanium (these shifts are further discussed below). The addition of pure 3P and EP (either individually or as a mixture) directly to a solution of $TiCl_4$ resulted in the same immediate colour change and downfield shifts, which appear to be indicative of the formation of a Ti-(O=C) complex. Thus the degradation of TPTP under these conditions is extremely fast.

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In experiments where $TiCl_4$ was in excess, the initial ratio of products was extremely consistent regardless of the ratio of $TiCl_4$ used. Each molecule of TPTP that reacted resulted in two molecules of EP and one of 3P:

$$\text{TPTP} + \text{TiCl}_4 \rightarrow \text{Ti}_A + 2(\text{EP}) + (3\text{P}) \quad \textbf{(R1)}$$

where Ti_A represents a new (unknown) titanium species.

With lower ratios of $TiCl_4$, the rate of degradation of TPTP decreased, but even when sub-stoichiometric amounts (0.5 equivalent) were used the degradation was still complete within ~3 h (Fig 1). However, these experiments also showed that with lower amounts of $TiCl_4$ the degradation seems to occur in two general phases: a fast initial stage (ie **R1**) followed by a slower phase (discussed later). While the same major products, EP and 3P, were formed in all cases, their relative proportions varied slightly as the ratio of $TiCl_4$ was lowered, and a number of other minor products were formed. The reactions were therefore examined in more detail.

Effect of reagent stoichiometry

Samples with sub-stoichiometric quantities of $TiCl_4$, were used to study the slower phase of the reaction which was most pronounced under these conditions. Although EP and 3P were the major products, as observed in **R1** above, the ^1H NMR spectra of the reaction mixture also showed the formation of various chlorinated products derived from both EP and 3P (Fig 1). However, under these conditions the ketone 3P (including its chloro-derivatives) was formed as the major solution product. In addition, sub-stoichiometric amounts of $TiCl_4$ led to a pale yellow precipitate that began to form after ~1 h, and accumulated over several days.

This two-stage reaction model is supported by observing the dependence of the degradation rate on the ratio of added $TiCl_4$. Figure 2 shows the progress of the reactions over 30 minutes. In these experiments, the rate of the slower step appeared to follow pseudo first-order kinetics. Where $TiCl_4$ was used in a two-fold excess (Fig 2d), the large difference between the known moles of TPTP at t_0 and the extrapolated t_0 intercept indicates that most degradation occurred by the much faster reaction **R1**. The extrapolated t_0 values for TPTP can therefore be used to approximate the proportion of the reaction that took place at faster kinetics (i.e. **R1**): 1TPTP:0.5$TiCl_4$ – 33%; 1:1 – 52%; 1:1.5 – 60%; and 1:2 – 81%.

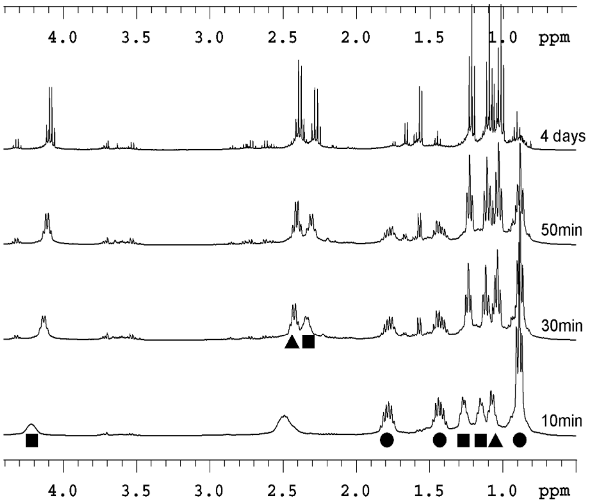

Fig 1. ^1H NMR spectra ($CDCl_3$) following the reaction of TPTP with 0.5 equiv $TiCl_4$ over time. ■- ethyl propanoate, ▲- 3-pentanone, ●- TPTP. The minor peaks are chlorinated organic products, due to side reactions.

These observations are consistent with a two-stage general reaction of $TiCl_4$ with TPTP:

$$\begin{aligned} &2(\text{TPTP}) + \text{TiCl}_4 \rightarrow \text{TPTP} + \text{Ti}_A + 2(\text{EP}) + (3\text{P}) && \textbf{(R1)} \\ &\text{Ti}_A + \text{TPTP} \rightarrow x(\text{EP}) + y(3\text{P}) + \text{Cl}^* + \text{Ti}_B && \textbf{(R2)} \end{aligned}$$

where Cl* represents an active chlorinating agent, and Ti_A and Ti_B refer to the first and second titanium products respectively. It is also possible that Ti_B is itself the active chlorinating agent (Cl*). Arbitrary product stoichiometry is shown in equation **R2** above, as the exact ratio of products was not as clear as that in **R1** (see later discussion). Overall, one mole of $TiCl_4$ can degrade two equivalents of TPTP within ~3 h under the conditions described.

Binding of reaction products to titanium species

Under anhydrous conditions, the products EP and 3P coordinate with the Ti_A species, as indicated by a strong de-shielding effect visible by ^1H NMR (see ESI). The Ti_A-bound ligands are immediately released upon moisture entering the solution, and a white precipitate forms, which is reasonably assumed to comprise titanium hydroxide and oxide products. Table 1 shows the chemical shift of the reaction products at various ratios of $TiCl_4$ to TPTP and thereby Ti_A to ligand (Ti_A:L, where L = EP or 3P).

Deshielding of a similar magnitude was found when EP and 3P were added to $TiCl_4$ under identical conditions (Table 1). The size of the shift is correlated with the amount of titanium species present, with $\Delta\delta$ increasing to a maximum at 1:1 $TiCl_4$ to L ratio, indicating fast intermolecular exchange between bound and free L and the formation of a strongly associated 1:1 $TiCl_4$:L complex. This behaviour is consistent with that observed for other reported $TiCl_4$-ketone adducts.[8] Variable temperature experiments showed that at higher temperatures the chemical

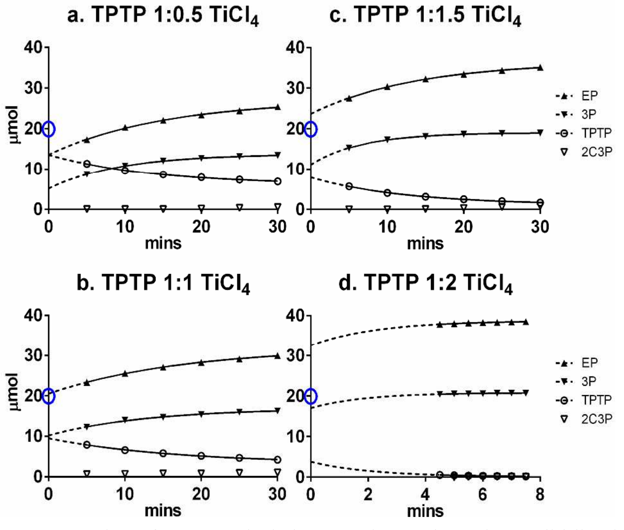

Fig. 2. Reaction of TPTP and $TiCl_4$ at varying molar ratios. Solid line is based on a single phase exponential decay fitted using GraphPad PRISM software, dashed line indicated extrapolation. Blue circle on y axis indicates actual n_{TPTP} at t_0.

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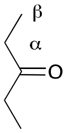
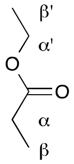
Table 1. Chemical Shift of ^{1}H NMR of EP and 3P at given titanium ratio

			Ti:TPTP ratio (calc'd. Ti:L ratio)			Ti:L ratio
		Free	0.5 (0.33^a)	1 (0.33)	3 (1)	1^b
	α	2.37	+0.10	+0.33	+0.60	+0.56
	β	0.99	+0.08	+0.18	+0.30	+0.31
	α'	4.08	+0.13	+0.29	+0.49	+0.48
	α	2.26	+0.14	+0.40	+0.63	+0.60
	β'	1.21	+0.06	+0.12	+0.22	+0.22
	β	1.09	+0.07	+0.14	+0.21	+0.21

Ti:L refers to titanium to ligand ratio, which in the case of TPTP reaction mixtures is calculated as Ti:(EP+3P). Shifts of bound ligands are given in ppm as a shift from free ligand (+ indicates downfield shift). ^{a} Value at close to t_0 when 3 ligands are formed per titanium centre. This ratio changes over time as the reacted titanium continues to slowly degrade TPTP. ^{b} Free ligand added directly to TiCl$_4$ in the absence of TPTP.

Table 2. IR Data for reaction participants and mixtures (CH$_2$Cl$_2$ solution).

	Reference samples (cm^{-1})
TPTP	595(w), **927(s),** 951(w), **973(s), 1133(s), 1158(s),** 1464(s), 2978(s)
DPDP*	669(m), 928(s), 957(s), 1144(s), 1157(s), 1464(s), 2980(s)
DPDHP*	570(s), 615(s), 921(s), 966(s), 1155(m), 1130(m), 1386(s), 1463(m), 2978(m), 3415(m)
EP	**806 (w), 860(w),** 1196(s), 1346(w), **1728(s)**
3P	812(w), 1122(w), 1460(w), **1713(s)**
TiCl$_4$-EP	**405(s),455(s),495(s) , 802(w), 858(w),** 1330(m),**1616(s)**
TiCl$_4$-3P	**397(m), 457(s), 496(s),), 813(w), 860 (w),** 1097(w), 1381(w), 1460(w), **1651(s)**
TiCl$_4$	496(s)
	Reaction mixtures (cm^{-1})
2:1 TiCl$_4$:TPTP rxn mix (Ti$_A$ /TiCl$_4$)	**374(s), 389(m), 452(w), 804(m), 860(m),** 1026(w), 1087(m), 1196(w), 1331(m), 1377(m), 1462(w), **1628(s)**
0.5:1 TiCl$_4$:TPTP at rxn mix, t=10min (Ti$_A$)	**366(m), 376(s), 397(w),** 418(w), 808 (w), 860(w), **924(m), 951 (w), 976(m)**, 1032(w), 1134(m), 1157(m), 1196(s), 1346(w), 1373(w), 1462(m), **1730(s)**

Peaks highlighted in bold are the main ones discussed.

*DPDHP (1,1'-[Dioxybis(1-ethylpropylidene)]-bis-hydroperoxide) and the dimer DPDP (dipentanone diperoxide), which are thought to bear a strong resemblance to the intermediates present in the acidic breakdown of TPTP,[7,9] were also included for comparison.

shifts returned closer to those of the free ligand in both TiCl$_4$:L and Ti$_A$:L samples, again indicating very fast intermolecular exchange (see ESI).

These observations were supported by FTIR studies of the reaction progress. Table 2 summarises the data for reaction mixtures together with comparative spectral data of key reaction participants (spectra are provided in ESI).

Upon 1:1 reaction of EP or 3P with TiCl$_4$ (analogous to the 3:1 degradation reaction), the carbonyl stretch was red-shifted by 112 or 62 cm^{-1} respectively, consistent with the bonding of the C=O moiety to the titanium centre. For EP the C-O stretch was also shifted, but in the opposite direction (135 cm^{-1}). Strong peaks appeared in the low frequency region where the Ti-Cl stretches would be expected (at ~400, 455, 495 cm^{-1}).

A similarly red-shifted carbonyl peak was seen for the products (EP and 3P) of TPTP reactions where excess TiCl$_4$ was used. At a 1:1 ratio of TPTP to TiCl$_4$, peaks for both free and bound carbonyl could be seen, consistent with the NMR experiments that showed resonances intermediate between free and bound ligands under the same conditions. However, no strong bands were evident in the low frequency region in this case, confirming Ti$_A$ as a different species to TiCl$_4$. The general broad absorption at ~350-500 cm^{-1} seen at a 1:2 ratio of TPTP to TiCl$_4$ could indicate that TiCl$_4$:L complexes still occur in the presence of Ti$_A$:L complexes, but loss of the clear TiCl$_4$:L pattern indicates that the complex geometry has been affected.

In reactions of TPTP with 0.5 equivalent of TiCl$_4$, carbonyl peaks were observed at frequencies corresponding to free EP and 3P. This observation, together with the significant broadening effect and very small downfield shifts seen by ^{1}H NMR for the equivalent reaction sample, suggests weaker binding of the ligands with Ti$_A$ compared to TiCl$_4$, and/or altered molecular geometry.

Interestingly, the ^{1}H NMR spectra of TiCl$_4$:L complexes were sharp at ambient temperatures whereas TPTP degradation mixtures exhibited broadening that was most evident at low initial ratios of TiCl$_4$ (see ESI). Dynamic behaviour is frequently observed for titanium complexes in solution,[10] and can arise from various phenomena including ligand exchange and aggregation of titanium species to form dimers and higher oligomers. Fluxional behaviour is common in pentacoordinate metal centres[11] and has also been reported for hexacoordinate titanium centres.[12] In the present case, the slight broadening of peaks observed in reactions of TPTP could be caused by a somewhat slower rate of ligand exchange with the Ti$_A$ centre than with the TiCl$_4$ centre, or by altered geometry, or both. The very broad peaks initially observed in the titanium-limited reactions seem to be related to the presence of excess TPTP, which showed reactivity towards the Ti$_A$ species after consumption of TiCl$_4$. The broadening effect could not be investigated by varying temperature, as increasing temperature expedited further reaction in titanium-limited samples where the broadening was most evident, and lower temperatures precipitated the analytes.

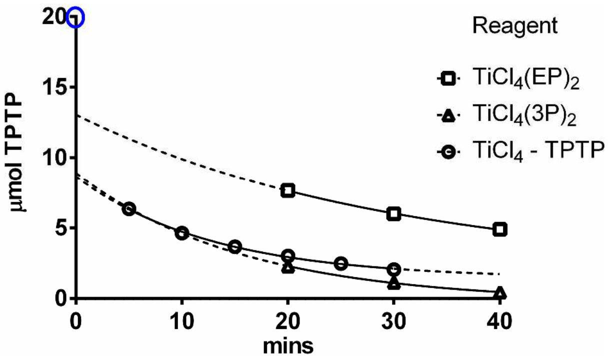


Fig. 3 The reaction of TPTP and TiCl$_4$L$_2$/TiCl$_4$. Solid line is based on a single phase exponential decay fitted using GraphPad PRISM software, dashed line indicates extrapolation. Blue circle on y axis indicates actual nTPTP at t_0.

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Since the products 3P and EP bond to titanium, it was anticipated that this may have an effect on the TPTP degradation reaction. To better understand this each of the potential ligands were pre-reacted with $TiCl_4$ before adding this reagent to the TPTP. Over a 40 min reaction period $TiCl_4(3P)_2$ showed little effect on the initial degradation (R1), in contrast to $TiCl_4(EP)_2$ which slowed the reaction (Fig 3) relative to that observed with $TiCl_4$ alone. A progressive slight increase in the degradation rate with $TiCl_4(3P)_2$ was observed, which is discussed later in the context of a side chlorination reaction. The slower reaction of $TiCl_4(EP)_2$ may be linked to the stronger carbonyl binding indicated in the IR results.

Proposed Primary Degradation Mechanism

The experimental observations point toward a near instantaneous reaction between $TiCl_4$ and TPTP (**R1**), followed by a further (but slower) reaction (**R2**), which is also associated with oxidative chlorination. Since the chlorination reaction becomes significant only at low molar ratios of $TiCl_4$, where a precipitate is also formed, these side reactions are not included here but are discussed separately below.

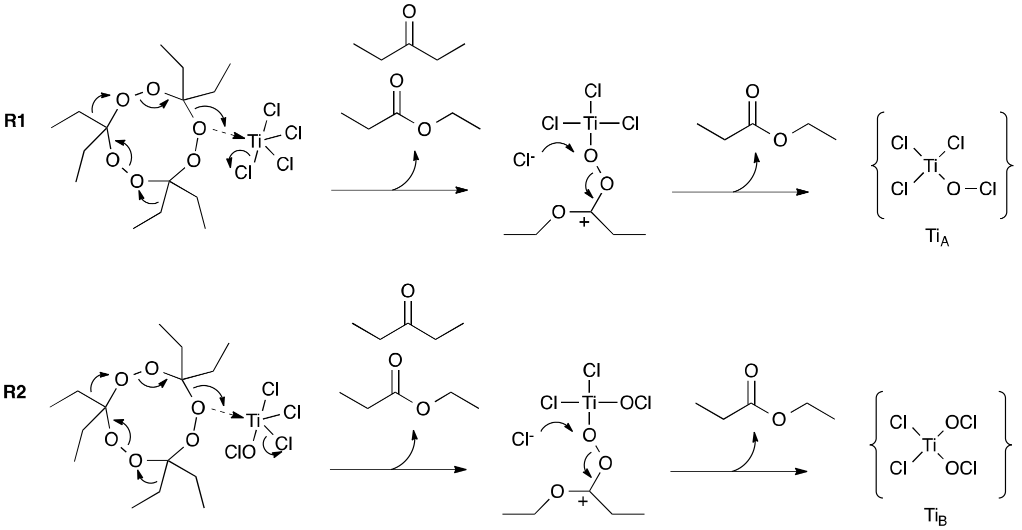
Scheme 1 provides an interpretation of the reaction progression that is consistent with the experimental results. Complexation of organic products to titanium species has been omitted in this scheme for clarity. A concerted mechanism is postulated, based on the very fast rate of **R1**; and an analogous mechanism is proposed for **R2**, which gives identical *initial* product ratios (EP : 3P 2:1 respectively). The slower rate of **R2** can be accounted for by a lower reactivity of TPTP toward Ti_A, produced during **R1**. Rapid stepwise reactions cannot be ruled out; however no intermediate peroxy compounds were observed by NMR or IR even in the slower **R2** reactions. Cyclic peroxide breakdown intermediates under *acidic* conditions have been proposed to be peroxy/hydroperoxy oligomers or dimers.[2,7,13] It seems therefore, that the present reaction is fundamentally different to the broadly accepted mechanism of acidic degradation.

The reaction products EP and 3P account for only 5 of the 6 oxygen atoms contained in 1 mole of TPTP. Given the well-established oxophilicity of titanium, it is assumed the remaining oxygen atom is bonded to titanium. The species represented as Ti_A and Ti_B have yet to be characterised conclusively; however we found no IR evidence for $TiOCl_2$ (as Ti_A), for which a strong absorption at ~820cm^{-1} could be expected.[14] We postulate that a Ti-OCl species is formed in **R1** (Ti_A), which is still reactive towards TPTP in **R2** where it might also act as a source of chlorination (discussed below).

Side reactions with limited $TiCl_4$: chlorination and precipitation

At low molar ratios of $TiCl_4$, **R2** is linked with oxidative chlorination (primarily forming 2-chloro-3-pentanone), and the slow formation of a precipitate.

The chlorination products were identified by comparison against NMR spectra from the literature of probable rational products, and further validated by structural information from COSY experiments conducted on the reaction mixtures (see ESI). All identifiable organic products were quantified after chlorination reactions had stabilised (9 days) using ^1H NMR integration (Table 3). The results showed that ketone (or ketone-derived chloro-species) form a greater proportion of the total solution product distribution in sub-stoichiometric reactions. The overall 51% mol equivalent of chlorine atoms (with respect to all soluble organic products) quantitatively accounts for ~3 chlorine atoms from $TiCl_4$, with ~2 of those being related to oxidative chlorination processes (2-chloro-3-pentanone, 2-chloropropanoyl chloride).



Scheme 1. A possible mechanism for the concerted decomposition of TPTP by $TiCl_4$ in anhydrous conditions. Coordinated ketone/ester products are omitted for clarity.

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Table 3. Organic products from 0.5:1 $TiCl_4$-TPTP reaction (9 days)

	Product	mol %	Sum
1	**ethyl propanoate**	**44**	57
2	1-chloroethanol	5	
3	chloroethane	2	
4	2-chloropropanoyl chloride	6	
5	**3-pentanone**	**11**	43
6	3-chloro-3-pentanol	6	
7	2-chloro-3-pentanone	26	
	Total mol % of chlorine	51[a]	

[a] 2-chloropropanoyl chloride contains 2 mole equivalents of chlorine

The yellow precipitate from **R2** after 9 days was isolated under N_2, dried and examined by FTIR (KBr disk). A strong broad peak at 3250-3400 cm^{-1} and broad absorption from 400-900 cm^{-1} were strongly indicative of a propanoate salt with the overall spectrum being very similar to that of potassium propanoate.[15] The precipitate was moisture-sensitive, and hydrolysis with D_2O caused the release of organic ligands. ^1H NMR analysis confirmed that the bulk of this organic component was propanoic acid (>80 mol %), along with a complex mix of chlorinated and non-chlorinated alcohols, acids and acid chlorides in minor quantities (these products were not exhaustively elucidated). We can thus reasonably conclude that precipitate from **R2** is largely compromised of titanium-propanoate species derived from the breakdown of EP. Thus the higher proportion of ketone (and ketone-derived chlorinated species) observed in solution in **R2**, compared to **R1**, is due to loss of the primary EP product within the precipitate.

Table 4. R2 precipitate elemental analysis.

Measured	C	H	Ti	Cl	O
R2 Precipitate	12.00	2.76	25.9	20.2	*39.11*[a]
Calculated	C	H	Ti	Cl	O
$(C_3H_5O_2)_2\ Ti_3H_5O_8Cl_3$	13.62	2.86	27.14	20.12	36.28

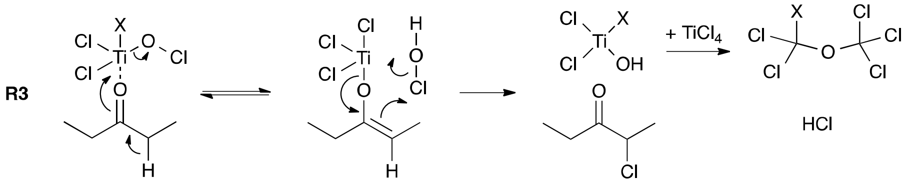
[a]The balance required to make 100% was used to estimate O content, a reasonable assumption as no other elements were present in the sample. N was not detected in the analysis.

The freshly prepared precipitate was analysed for C, H, N, Ti and Cl. Table 4 shows the results compared against a possible titanium propanoate species indicated by the stoichiometry of the reaction. Since the NMR spectrum indicates the precipitate is not a pure substance, this elemental analysis is not intended to provide a definitive proof of characterisation. Instead the results confirm an oxygen- and chlorine-rich content with a clear 1:1:4.5 Ti-Cl-O ratio in the precipitate. The 1:1 Ti:Cl ratio agrees well with the earlier chlorinated organics analysis, as it infers that the remaining chlorine of $TiCl_4$ remains bound to the Ti-centre. The inferred oxygen ratio of 4.5 per titanium accounts for the two oxygen atoms in propanoate, as well as the two oxygen atoms "missing" from the two units of degraded TPTP by each titanium centre (i.e. not accounted for in the 2(EP):1(3P) product distribution). The "excess" 0.5 oxygen might indicate further hydrolysis or formation of oxo-bridged species, which may be explained by the chlorination mechanism proposed in the next section. The precipitate produced in this reaction may resemble sol-gel products derived from the reaction of Ti-alkoxides and acetic acid, esters and water. These reactions have been shown to form highly ordered products such as hexameric ring structures,[16,17] which would account for the consistent microanalysis results between reaction samples in the present case.

Implication of chlorination reactions

Broadly speaking, where a half equivalent of $TiCl_4$ is used, two chlorines from $TiCl_4$ are accounted for in oxidative chlorination products. Oxidative chlorination of a degradation product (mainly 3P) may occur via its reaction with a Ti-OCl species. Thus the presence of chloro- adducts in the reaction mixtures may support the proposed mechanisms for **R1** and **R2** (Scheme 1) where the postulated Ti-OCl species as Ti_A and Ti_B, respectively, effects chlorination as outlined in the reaction **R3** (Scheme 2).

R3 relies on 3P forming a titanium enolate, which is known to be a highly favourable process due to the oxophilicity of titanium.[18] A similar mechanism has been used to explain an analogous α-chlorination of ketones using urea-hydrogen peroxide with $SiCl_4$, where a silyl-OCl species was postulated to be the active chlorinating agent.[18] Hypochlorous acid could then readily chlorinate 3P at the *α*-carbon position, breaking down the now-unstable titanium-adduct to leave a hydroxo ligand.



Scheme 2. Proposed mechanism **R3** - the α-chlorination of 3P by $TiCl_2X(OCl)$, where X = Cl or OCl.

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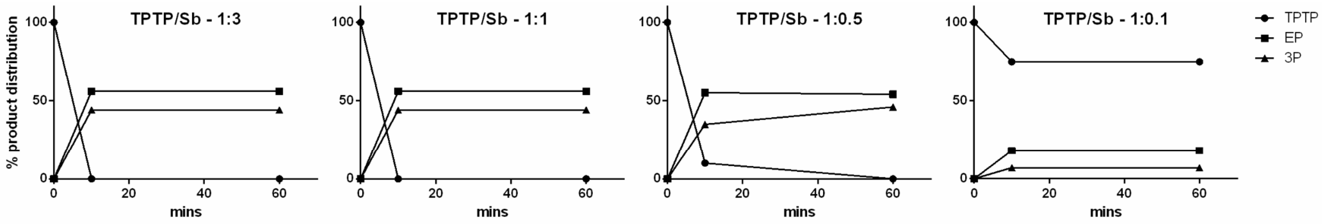

Fig 4. Reaction products of dry samples of SbCl$_3$ and TPTP injected directly into GC/MS inlet liner. The reaction was found to be occurring at the elevated temperature of the inlet liner.

The latter species could immediately form Ti-O-Ti bridges (a significant driving force in similar sol-gel reactions)[16] and may explain the precipitation that occurs with **R2**.

The suggestion of an OCl ligand in Ti$_A$ is unusual, though this moiety has been proposed previously, in the SiCl$_4$ chlorination reaction referred to above,[19] and in a theoretical study of the mechanism of manganese catalysts.[20] Direct spectroscopic evidence for the OCl ligand is troublesome, with the only potential reference source being the O-Cl stretch of hypochlorous acid[21] at 739 cm^{-1} in the IR spectrum, which is within the absorption band of the solvent CH$_2$Cl$_2$. However, the stringent anhydrous conditions make it difficult to suggest alternative explanations that account for the fate of the missing organic oxygen and the observed chlorination processes. The much smaller amounts of non-oxidative chlorination products seen in the late stages of reaction suggest the presence of trace levels of free Cl$^-$ such as HCl.

Antimony trichloride

The theoretical work by Dubnikova *et al.* suggested that the Sb^{3+} ion would be similarly active in facilitating the ring-opening of TATP, but less so than Ti^{4+}.[6] In initial experiments, aliquots taken directly from anhydrous reactions of SbCl$_3$ and TPTP were analysed by GCMS without workup. While this gave near-complete degradation within 10 minutes, even at 0.5 mol equivalent of SbCl$_3$ (Fig. 4), it was soon identified that this reaction was largely taking place at the GCMS injection liner at 130°C. Considering the absence of broad or tailing peaks in the chromatogram, it also appeared that the reaction was complete before the sample entered the column for separation (i.e., within seconds). These initial experiments still provided some useful information, with the 1:0.1 reaction suggesting that SbCl$_3$ can degrade at least two equivalents of TPTP. Modification of the sampling to quench and extract SbCl$_3$ before analysis showed that the reaction was sluggish at room temperature.

At 50°C under anhydrous conditions using 1 mol equivalent of SbCl$_3$, TPTP degradation was complete within 20 minutes (Fig 5). As with the direct injection results, EP was formed in only slight excess, relative to 3P, rather than the 2:1 ratio seen with the TiCl$_4$ reaction. Colorimetric speciation indicated that some Sb^{3+} was being consumed in the reaction, presumably by oxidation to Sb^{5+}. This loss of Sb^{3+} however, neither corresponds with the number of moles of EP/3P produced, nor the moles of TPTP consumed, suggesting that this oxidation process is not directly linked to the central degradation mechanism.

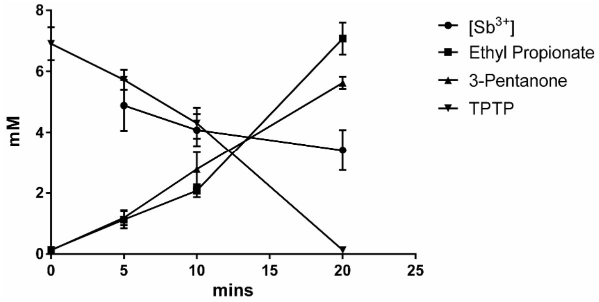

Fig 5. Reaction progress of sealed ampoules of 1:1 SbCl$_3$ and TPTP reacting in CH$_2$Cl$_2$ at 50 °C. Error bars reflect standard deviation from mean result.

The significant levels of ester production in the SbCl$_3$ reaction, and the ability to degrade ~2 equivalents of TPTP per unit of SbCl$_3$, suggest a similar mechanism to the TiCl$_4$ reaction, albeit with the requirement for heat to drive the reaction at comparable rates. The lower reactivity corresponds with the predicted relative rates of reaction of TATP with Sb^{3+} and Ti^{4+} ions in the gas-phase.[6] Potential oxidation of Sb^{3+} adds significant complexity to the reaction system, which is not a factor with TiCl$_4$. As a result, this reaction was not explored to the same extent as TiCl$_4$, where further oxidation of the metal is not possible.

Experimental

CAUTION! The organic peroxides detailed in this study have the characteristics of primary explosive with extreme levels of friction, heat and impact sensitiveness. All procedures must be carried out by properly qualified and equipped personnel taking all relevant precautions.

Materials

All chemicals and solvents were of analytical grade unless otherwise noted. CDCl$_3$ (99.9% D) was dried over freshly activated 4Å molecular sieves. TPTP, DPDP and DPDHP were synthesised and purified as published previously.[7] GC standards were made with ethyl acetate and 3-pentanone using capillary grade CH_2Cl_2. TPTP was purified by sublimation *in vacuo*. $TiCl_4$ (AR) was double distilled from copper turnings under dry N_2 gas, before being weighed and dissolved in a measured volume of CH_2Cl_2 (AR, freshly distilled from CaH_2 under N_2). $TiCl_4$ solutions were used and stored under a strict N_2 atmosphere, and discarded after 2 weeks.

Instruments

A Shimadzu QP 2010 Ultra fitted with a SGE SolGel Wax column (1.0 µm film, I.D. 0.25 mm, 30 m) was used for GCMS analyses. The method utilised an initial column temperature of 40°C for 1 min, 20°C/min ramp to 100°C, held for 3 min, followed by 30°C/min finishing at 190°C and held for 2 min. Injector temperature was 130°C, interface 200°C, and linear column flow at 2 mL/min of He gas. Split ratio was set at 40. Concentrations were quantified using external standards.

NMR spectra were recorded on a Varian Unityplus-400 spectrometer. All NMR experiments were conducted at 25°C unless otherwise stated. ^1H NMR spectra were referenced to TMS (0 ppm) at 25°C using the residual ^1H signal of the respective deuterated solvent. 1D spectra were recorded with between 16 and 1024 transients with a 6 s relaxation delay. COSY experiments were conducted with 1 scan per increment, 512 t_1 increments and 2 s relaxation delay. Integration data was processed and graphed using Graphpad Prism.

IR Spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. Samples were typically analysed between 350 and 3500 cm^{-1} with 16 scans. CH_2Cl_2 solutions were analysed in a 0.25 mm pathlength demountable liquid cell with KBr windows, which was oven dried and stored over phosphorous pentoxide. The cell filled with dry CH_2Cl_2 was used for the background measurement. The cell was rinsed with dry CH_2Cl_2 and purged with dry argon between samples. The liquid film spectrum of DPDP was collected with a drop of sample between two KBr discs.

UV/Vis spectra were recorded on a Cary 50 spectrometer. Sb^{3+} standard solutions for calibration curves were analysed within 2 h of preparation.

Methods

All weighing and handling was conducted in a dry N_2 atmosphere using a glovebox or standard Schlenk techniques with oven dried glassware and syringes. Any trace of moisture in the presence of $TiCl_4$ results in immediate cloudiness – any experiments where this was observed were discontinued and the samples re-prepared.

$TiCl_4$ experiments

The estimated $TiCl_4$ concentration from weight/volume calculations was confirmed by a modification of published titration methods.[22, 23] 0.1 M $EDTA_{(aq)}$ was standardised against 0.01 M $CaCO_{3(aq)}$ primary standard, and 0.1 M $ZnSO_{4(aq)}$ was standardised against the EDTA solution. A sample of the $TiCl_4$ solution was added to 5 mL of 3 M $H_2SO_{4(aq)}$ and heated to drive off CH_2Cl_2. After cooling, 3 drops of 30% $H_2O_{2(aq)}$ were added to stabilise titanium in solution followed by 10 mL aliquot of EDTA solution and 3.5 g solid hexamine as buffer. The mixture was adjusted to pH 5.5 with concentrated aqueous ammonia and diluted to 80 mL. 4 drops of xylenol orange indicator were added and the remaining free EDTA was back-titrated with $ZnSO_4$ solution to a lasting red-orange endpoint. The concentration derived from this titration ([Ti]) was used for all further calculations.

Analyte (TPTP, EP or 3P) was measured into a dry, sealed 5 mL volumetric flask and diluted with dry $CDCl_3$ to make a 0.05 M solution. $TiCl_4/CH_2Cl_2$ stock solution was diluted in dry $CDCl_3$ such that a 100 µL volume would provide the desired mole ratio when added to 500 µL of the analyte stock solution. 500 µL of analyte solution was placed in a dry 5 mm NMR tube and vacuum degassed. 100 µL $TiCl_4/CDCl_3$ was added (forming an immediate yellow/green clear solution) and the mixture immediately frozen in liquid N_2. The tube was flame sealed under high vacuum. The sample was thawed and well shaken immediately prior to inserting into the NMR spectrometer for measurement.

The sub-stoichiometric titanium reaction was conducted on a larger scale in order to isolate the precipitate for further analysis. TPTP (135 mg, 0.44 mmol) was weighed into a dry 10 mm NMR tube. 3 mL of dry $CDCl_3$ was added and the contents vacuum degassed. 0.87 M $TiCl_4$ CH_2Cl_2 solution (0.25 mL, 0.22 mmol) was added and the mixture immediately frozen and vacuum-sealed. On thawing, the reaction was monitored by ^1H NMR. A pale yellow precipitate formed within an hour and continued to form over the following week. After 9 days, the tube was opened under dry N_2, the bulk of the supernatant solution removed by syringe, and the sample dried *in vacuo*. The resulting sample was not weighed, as quantitative transfer was not possible. A small sample was ground with KBr in air and immediately analysed by FTIR: ν(cm^{-1}): 739(w), 883(w), 1156(w), 1302(w), 1436(m), 1522(m), 1624(m), 1700(w), 2362(w), 3258(br, vs), 3375(br, vs). For NMR analysis, a drop of D_2O was added to a small sample resulting in an immediate white suspension, to which MeCN-d_3 was added and analysed by NMR. Microanalysis of the precipitate was conducted by the Australian National University microanalysis laboratory.

For FTIR assays: aliquots of $TiCl_4/CH_2Cl_2$ stock solution were added directly to CH_2Cl_2 solutions of TPTP, EP and 3P (50 mM) in dry, sealed vials. The samples were injected into the liquid IR cell through septa and the spectrum taken immediately. For titanium-limited reactions, the sample was allowed to proceed in the vial at ambient temperature (~20°C) and aliquots were observed at 30 min intervals.

For $TiCl_4L_2$ reactions, EP and 3P were dried over molecular sieves for 4 h under N_2. In a dry vial, 10 mL of 0.41 M $TiCl_4$ (4.1 mmol) in CH_2Cl_2 was cooled to 0°C under N_2 with a magnetic stir bar. 0.87 mL (8.2 mmol) 3P or 0.96 mL (8.2 mmol) EP was added dropwise (strong exothermic reaction) to the stirred $TiCl_4$, resulting in a clear orange solution once the sample warmed to RT. The residual $CHCl_3$ solvent signal of a batch of dry $CDCl_3$ was quantified by integration against a solid aliquot of hexamethylbenzene. 50 µL of the $TiCl_4L_2$ CH_2Cl_2 solution was dissolved in 500 µL of the same stock of dry $CDCl_3$ and [L] determined by ^1H NMR integration. The sample was also subjected to the [Ti] determination method described above, with both methods corresponding to $[TiCl_4L_2] = 0.40\ M \pm 0.02\ M$.

24.5 mg TPTP (0.08 mmol) was weighed into a 2 mL dry volumetric flask and made up to the mark with the standardised

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$CDCl_3$. 500 μL of this 0.04 M solution was added to a 5 mm NMR tube, the required amount of 0.4 M $TiCl_4L_2$ solution added under a dry N_2 atmosphere and the mixture immediately frozen in liquid N_2. The tube was flame sealed under high vacuum. The sample was thawed and well shaken immediately prior to inserting into the NMR spectrometer for measurement.

$SbCl_3$ experiments

In initial experiments, 10 mM solutions of TPTP were added to solid $SbCl_3$ under dry conditions, and the mixture sampled directly by GCMS. It was found that this method resulted in very fast degradation within the injection liner of the GCMS. The following method was then employed to study the reaction.

TPTP (61.2 mg, 0.2 mmol) and $SbCl_3$ (45.6 mg, 0.2 mmol) were separately weighed into two dry 10 mL volumetric flasks and sealed, then diluted with dry CH_2Cl_2 to make 10 mM solutions. 1 mL of each sample was added to a dry ampoule with a manifold attached. Upon the addition of the solutions, the sample was frozen in liquid N_2, vacuum degassed and flame sealed under vacuum. 14 samples were prepared and stored in liquid N_2 (two reserved as t_0 controls). To commence the reaction, 12 samples were quickly thawed in warm water with agitation, then placed in a temperature controlled bath at 50 °C and the stopwatch started. At 5, 10 and 20 min, 4 samples were removed and immediately frozen in liquid N_2. One by one, the samples were thawed and the ampoule opened. A 500 μL aliquot was removed for Sb^{3+} determination, and the remaining sample quenched over $CaCO_3$ with a drop of water. The sample was syringe filtered, then 500 μL was placed in a 2 mL volumetric flask along with 20 μL of 0.2 M ethyl acetate in MeCN as an internal standard and made up to the mark with MeCN. Samples were analysed by GCMS.

In parallel, the reserved 500 μL reaction sample was used for spectrophotometric determination of Sb^{3+} using a method based on that of Christopher *et al.*[24] Samples of known [Sb^{3+}] in CH_2Cl_2 were used to confirm that adding CH_2Cl_2 reaction samples directly to the buffer did not affect the accuracy of the described method. The absorption at 560 nm was recorded and compared against standard calibration samples. The t_0 samples were excluded from the Sb^{3+} determination results due to a sampling error.

Conclusions

The reactions of $TiCl_4$ and $SbCl_3$ described in this paper present a new direction in the search for a rapid means of degrading cyclic peroxides like TATP. As mentioned in the introduction, TPTP has previously been shown to be an effective model for TATP and by inference our current findings are expected to be applicable to the degradation of TATP and DADP.

Even though the reactions herein require anhydrous conditions, which would limit field application in degradation and neutralisation of cyclic peroxides, this does not diminish their significance. The effectively instantaneous degradation of the cyclic peroxide in solution by a molar equivalent of $TiCl_4$ at room temperature proceeds by a novel mechanism that deserves further investigation. In particular, we are planning calorimetric experiments to help understand if the rearrangement reaction itself is exothermic, and thus safe to scale up to larger reactions or on solid samples.

A number of key characteristics of the reaction present useful advances in terms of peroxide degradation. Most importantly, the organic reaction products cannot re-form peroxides. The sequestering of peroxide oxygen atoms into the organic products is a significant step forward, giving products of low reactivity unlike the reported acidic degradation process. In addition, the modification of the Ti reagent as a pre-formed ketone adduct ($(TiCl_4{:}EP)_2$) also highlights a potential for improved performance.

The ability of these metal compounds to induce a degree of oxygen insertion as part of the breakdown of the cyclic peroxide provides the tantalising possibility of creating a reaction that could be truly catalytic. The observation that Ti_A continues to react with TPTP demonstrates that other titanium complexes may maintain their activity with cyclic peroxides, but be more suitable to cycle back to an active state.

Finally, the evidence of a highly active chlorinating species, which mediates facile chlorination side-reactions on carbonyl compounds at room temperature, could also make this newly identified reaction interesting for general chemical synthetic development. The isolation and/or further characterisation of reaction intermediates described in this exploratory work has the potential to yield useful synthetic methodologies.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [1]NMR spectra of catalysed degradation of TPTP reaction mixtures under varying conditions of temperature time and catalyst ratios. Included are FTIR spectra of reaction soltuions and solid by-products. See DOI: 10.1039/b000000x/.

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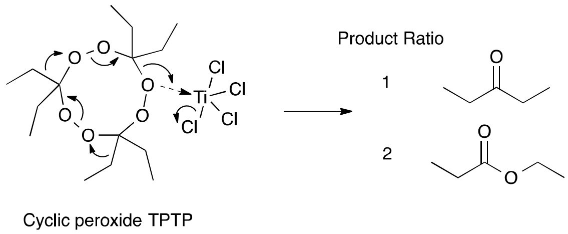
Rapid and safe degradation of a cyclic peroxide (TPTP) to relatively innocuous products.



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