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THE PEROXY DERIVATIVES OF ADAMANTANE

SYNTHESIS AND SOME REACTIONS OF t-BUTYL-1-ADAMANTANE PERCARBOXYLATE

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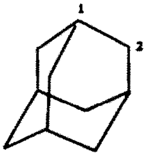
Abstract—The kinetics and thermal decomposition of t-butyl-1-adamantane percarboxylate has been studied in n-heptane, benzene, and carbon tetrachloride. The data obtained agree with the concerted perester decomposition mechanism yielding initially 1-adamantyl, t-butoxy radicals and carbon dioxide.

The 1-adamantyl radical easily abstracts chlorine from carbon tetrachloride yielding 1-chloroadamantane; it abstracts hydrogen from n-heptane yielding adamantane and adds to benzene, yielding 1-phenyl adamantane.

The perester obtained is an active initiator of methylmethacrylate polymerization, it is three times as active as the benzoyl peroxide.

THE possible existence of tertiary bridgehead free radicals unable to stabilize themselves by becoming planar because of their rigid structure was proved by the appearance of 1-apocamphyl[1] and 1-triptyl[2] radicals in the thermal decomposition of the respective diacyl peroxides, and also 1-adamantyl and other bridgehead radicals[3] in decarbonylation of the respective aldehydes. The unique rigid and strain-free cyclic system of adamantane (AdH, I)[4] is not liable to skeletal rearrangements or to double-bond formation due to its rigidity and low energy.[4] Therefore, the 1-adamantyl radical should be highly reactive and should not undergo disproportionation and recombination.



(AdH)

I

Concerning free-radical substitution in adamantane[5–7] yielding 1- and 2-substituted derivatives the higher reactivity of the 1-position to free-radical attack should be noted.

In an attempt to obtain 1-adamantoyl peroxide $(AdCO_2)$, a possible source of 1-Ad radicals, 1-adamantane carbonyl chloride and aqueous sodium peroxide yielded 1-adamantane carboxylic acid (23 mole%), the anhydride of this acid (30 mole%) and 1-adamantyl 1-adamantane carboxylate $AdCO_2$ Ad (II) (35 mole%). A symmetric peroxide $(AdCO_2)_2$ is unstable and yields the ester II after decomposition in solvent "cage".[8] The t-butyl-1-adamantane percarboxylate (TBAP) is stable and was obtained by acylation of t-butyl hydroperoxide.

Like many other peresters[9] TBAP liberates iodine actively but not quantitatively from an acidified solution of potassium iodide. Heated to 90–100° it decomposes with explosion. The purity of the peroxide was determined by elementary analysis and IR spectrum.

If the reagents used for the TBAP synthesis are not dry the perester is contaminated by the adamantane carboxylic acid anhydride. After prolonged standing at room temperature the perester contained traces of the ester II.

Both impurities show frequencies of a C═O bond 1817 and 1728 cm^{-1}, respectively in their IR spectra displaced relative to the peroxide C═O band frequency 1773 cm^{-}1.

Though the reaction of the TBAP with acidified potassium iodide does not proceed quantitatively, by application of the Silbert method,[11] equal quantities of active oxygen 4·15% (6·35% theor) were determined in the pure peroxide and its solutions. This procedure was used for the kinetic measurement of thermal decomposition of the peroxide in organic solvents.

A first order decomposition of the peroxide in benzene, carbon tetrachloride and n-heptane was found. The results are given in Table 1. The values of rate constants and activation energies of thermal decomposition for all the three solvents are quite close.

Table 1. The first-order decomposition of the TBAP in solvents

Temp	$k \cdot 10^5$, sec^{-1}		
	Benzene	Carbon tetrachloride	n-Heptane
60°	4·1	—	—
65°	7·2	3·7	3·6
70°	16·0	7·0	7·3
75°	—	13·4	—
E kcal/mole	32·5	31·0	32·3

TBAP is an active peroxide with a half-life in benzene at 60° of 300 min—i.e. nearly the same as that of t-butyl-trimethyl peracetate in chlorobenzene.[9, 10] The half-lives of t-butyl peroxybenzoate and benzoyl peroxide under similar conditions are 30,000 and 6,000 min, respectively.[10] The TBAP is an efficient initiator for methyl methacrylate mass polymerization, the kinetic data for benzoyl peroxide are given for comparison (Table 2).

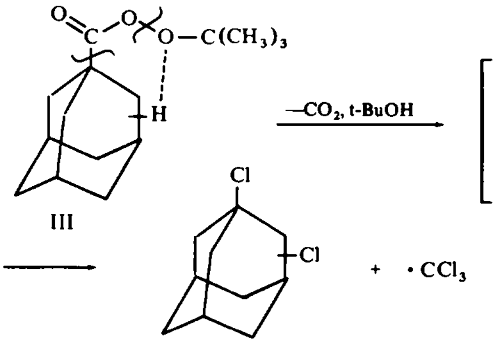
Table 2. The kinetic data of the TBAP initiated polymerization of methyl methacrylate

Initiator	Concentration$\cdot 10^3$, mole·liter^{-1}	Temp °C	Rp$\cdot 10^4$, mole·liter^{-1}	$k \cdot 10^4$, mole$^{\frac{1}{2}}$·liter$^{\frac{1}{2}}$·sec^{-1}	E $\frac{\text{kcal}}{\text{mole}}$
TBAP	4·10	40	0·64	1·06	
	4·10	50	2·09	3·45	18·8
	4·10	60	3·86	6·37	
	4·10	70	9·10	15·02	
	2·37	70	6·70	—	—
	1·12	70	4·42	—	—
Benzoyl peroxide	4·10	70	3·07	5·05	—

Table 2 shows that TBAP is three times as efficient an initiator as the benzoyl peroxide. The TBAP thermal decomposition products in benzene, n-heptane and carbon tetrachloride (Table 3) support the free-radical mechanism.

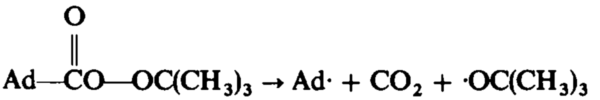
The main reaction product of the peroxide with carbon tetrachloride is not mono—but dichloroadamantane (8 and 60%, respectively), as well as carbon dioxide, t-butanol, hexachloroethane and chloroform.

Probably, dichloroadamantane is the peroxide decomposition product in the reaction cycle III where an intramolecular abstraction of hydrogen without a preliminary formation of the monochloroderivative takes place.



The formation of considerable quantities of trichloroadamantanes (26%) could be due to dichloroadamantane attack by trichloromethyl radicals yielding chloroform. Then thermal decomposition of the peroxide in the presence of 1-chloroadamantane would reduce the trichloroadamantane and increase the dichloroadamantane content of the decomposition products. In fact relative contents of mono-, di-, and trichloroadamantanes in reaction products remained unchanged in this experiment, (Table 3, column 4) the proportion of chloroform being considerably increased and that of hexachloroethane decreased.

Hence a concerted TBAP decomposition with the formation of 1-adamantyl, t-butoxy radicals and carbon dioxide in the primary step is the most probable reaction mechanism.



$$\mathrm{Ad{-}\overset{\overset{\displaystyle O}{\|}}{C}O{-}OC(CH_3)_3 \rightarrow Ad\cdot + CO_2 + \cdot OC(CH_3)_3}$$

Adamantyl radicals abstract chlorine from carbon tetrachloride yielding 1-chloroadamantane and trichloromethyl radicals; t-butoxy radicals abstract hydrogen either from the molecules of the original peroxide or from the chloroadamantane yielding t-butanol and respective radicals, which in turn abstract chlorine from the solvent. Trichloromethyl radicals partly abstract hydrogen from the adamantane cycle and partly recombine into hexachloroethane. This mechanism is further confirmed by (a) the high velocity of the TBAP thermal decomposition, (b) the order of the polymerization reaction of methyl methacrylate with TBAP which is close to 0·5 (calculated from Table 2), and (c) the reaction with benzene and n-heptane in which adamantane carboxylic acid is not produced.

TABLE 3. THE TBAP THERMAL DECOMPOSITION PRODUCTS IN SOLVENTS AT 75°; THE PEROXY ESTER 10 M MOLES, A SOLVENT 25 ML

Solvent / Products (mole/mole peroxide)	Benzene	n-Heptane	Carbon tetrachloride	Carbon tetrachloride + 1-chloroadamantane (5·8 m moles)
Carbon dioxide	0·77	0·82	0·93	0·90
t-Butyl alcohol	0·73	0·75	0·70	0·58
Adamantane	0·27	0·56	—	—
1-Phenyl adamantane	0·28	—	—	—
Diphenyl	0·03	—	—	—
1-Adamantyl 1-adamantane carboxylate	0·11	0·15	present	present
1-Chloroadamantane	—	—	0·08	The proportions are the same as without AdCl
Dichloroadamantane	—	—	0·60	
Trichloroadamantanes	—	—	0·26	
Hexachloroethane	—	—	0·80	0·42
Chloroform	—	—	0·42	0·83
Hydrogen chloride	—	—	0·025	0·028
Non-identified products (g/g peroxide)	resin 0·6	liquid 0·3	—	—
1-Adamantyl group accounted for (%)	77	86	94	94·5
Carbon dioxide accounted for (%)	88	97	93	93

The high reactivity of 1-Ad radicals is supported by (a) H-abstraction from n-heptane yielding adamantane (56%), (b) reaction with benzene yielding phenyl adamantane (28%), and (c) H-abstraction from the adduct of 1-Ad radical with benzene IV yielding adamantane (27%).

IV

The adamantane cycle itself is liable to a radical attack which is evidenced by the formation of large quantities of di- and trichloroadamantanes in the TBAP decomposition in carbon tetrachloride.

EXPERIMENTAL

Adamantane was obtained in 15–16% yield by isomerization of tetrahydrocicyclopentadiene catalysed by $AlCl_3$.[12]

Tetrahydrodicyclopentadiene was obtained by hydration of the technical grade dicyclopentadiene purified by alkaline treatment and catalysed by Rh–Ni[13] in accordance with a slightly modified procedure.[14] Purified dicyclopentadiene (270 ml), abs EtOH (700 ml), and the Ni (16 g) were placed into a rotatory autoclave and purged with H_2 at room temp and then heated at 90–100° and 10–15 atm for 10–12 hr. After cooling, the EtOH was distilled off. The tetrahydrodicyclopentadiene crystallized after cooling to room temp, yield 180–200 g (68–76%), m.p. 71–63°. It was used to give adamantane without further purification.

The 1-adamantane carboxylic acid was obtained from bromoadamantane in accordance with the procedure.[15]

1-Adamantyl carbonyl chloride. 1-Adamantane carboxylic acid (20 g) and distilled $SOCl_2$ (22 ml) were refluxed during 2 hr. After cooling the extra $SOCl_2$ was distilled off *in vacuo* at room temp. Traces of $SOCl_2$ were removed under high vacuum, 21·9 g (99·5%) of acid chloride was obtained, m.p. 53–54°. (Found: Cl, 17·75. Calc. for $C_{11}H_{15}ClO_2$: Cl, 17·88%).

The reaction of the 1-adamantyl carbonyl chloride with sodium peroxide

A fresh aqueous suspension of sodium peroxide (obtained from 2·4 g 30% H_2O_2 and 1·7 g NaOH) was added to a soln of 4·2 g freshly made acid chloride in 50 ml ether with agitation and cooling at 0°. After the mixture was left overnight at 0–+3° the ether layer showed no peroxide reaction with acidified KI. The reaction mixture was diluted with water and 0·91 g of the 1-adamantane carboxylic acid, m.p. 180°, neutr. equiv. 181, (m.p. 181°[15]) was isolated from the water layer after acidification. The ether layer was dried and evaporated in vacuo, 2·3 g of a solid neutral product was obtained. Its IR spectrum shows intensive bands of 1815, 1750 and 1728 cm^{-1}. 0·5 g of the product was boiled for 1 hr with 15% alcoholic NaOH eq without agitation. It was cooled and extracted by ether.

Acidification of the alkaline layer gave 0·24 g of the adamantane carboxylic acid. After the evaporation of the dry ether extract 0·23 g of 1-adamantyl 1-adamantane carboxylate, m.p. 240–243° was obtained. (Found: C, 80·36; H, 9·85; m.w. 310. Calc. for $C_{21}H_{30}O_2$; C, 80·20; H, 9·62%; m.w. 314·4). 0·47 g of the neutral product was boiled with agitation for 10 hr with 15% alcoholic NaOH aq. After acidification of alkaline layer 0·29 g of the adamantane carboxylic acid was obtained. After evaporation of the ether extracts and sublimation of the residue *in vacuo*, 0·12 g of the 1-oxiadamantane was obtained, m.p. 283° (sealed tube) (m.p. 282°[15]). It was identified by comparison of IR spectra with an authentic sample.

t-Butyl 1-adamantane percarboxylate. Freshly made 1-adamantyl carbonyl chloride (21·8 g), dry n-hexane (120 ml) and anhydr t-butyl hydroperoxide (15·7 g) were placed in a flask with a stirrer, dropping funnel and thermometer. The mixture was cooled to 0° and dry pyridine (13·2 ml) was added during 30 min. The stirring was continued for 3 hr and the mixture left overnight at 0–+3°. Then the mixture was diluted with ice water. The hexane layer was separated. The aqueous layer was extracted with hexane. The combined hexane extracts were washed with cold 5% HCl aq, 5% Na_2CO_3 aq and water, dried and chromatographed through a column of activated alumina. The hexane was distilled *in vacuo* at room temp to constant weight of the residue. The perester (24·8 g; 89%) was obtained as a viscous colourless oil, n_D^{20} 1·4900, d_4^{20} 1·0562. After standing 2 days at +3° the oil was crystallized, m.p. 26–26·5. (Found: C, 71·06; H, 9·72; m.w. 246. Calc. for $C_{15}H_{24}O_3$: C, 71·39; H, 9·58%; m.w. 252). The contents of the peroxide oxygen[11] was 4·15% (calc. 6·35%).

If the reagents used for the perester synthesis are not completely dry and the hexane soln is not chromatographed through alumina, the oily perester is contaminated with solid adamantane carboxylic acid anhydride. The latter can be separated on a porous glass filter and the residue washed with a little cold EtOH.

The anhydride has m.p. 148–150°. (Found: C, 73·20; H, 8·61; Sapon equiv. 175. Calc. for $C_{22}H_{30}O_4$: C, 73·80; H, 8·45%; Sapon. equiv. 171).

The perester thermal decomposition in solvents

A weighed amount of peroxide and some solvent were placed into a 2-necked flask with reflux and an inlet tube. The flask was cooled to 0–+5° and N_2 passed through. The supply of N_2 was stopped, and the flask placed in a bath at 75° for 10–15 hr. The CO_2 evolved was absorbed into 15% NaOH aq. After heating, N_2 was passed through the mixture until complete removal of CO_2. No other gaseous decomposition products (except traces of HCl in CCl_4 soln) were found. t-Butyl alcohol was found in the reaction mixture,[16] but tests for acetone and acidity were negative. 1-Adamantyl-1-adamantane carboxylate was determined quantitatively by saponification of aliquot sample with 15% alcoholic NaOH aq followed by acidification and definition of precipitated adamantane carboxylic acid by weighing it.

Other reaction products were identified and defined quantitatively by GLC, IR spectroscopy and on the basis of physical constants. "Tzvet-1" has been used for chromatographic analysis. The 2 meter column, diethylene glycol succinate (15%) on bricks INZ-600, as a stationary phase and a gas-carrier helium (4 l/hr) was used. After complete thermal decomposition of TBAP, the mixture was quantitatively analysed:

chloroform at 50°, adamantane at 90°, hexachloroethane at 120°, 1-chloroadamantane, 1-phenyl adamantane and diphenyl at 180°.

IR spectra were obtained with UR-10 apparatus for liquids as films between KBr plates, for solids as 1–3% pellets with KBr. The results are given in Table 3.

Identification and quantitative determination of thermal decomposition products of 2·52 g TBAP

(a) *In n-heptane.* The reaction products consisted of CO_2 (0·362 g), BuOH (0·56 g), adamantane (0·76 g) and ester II (0·47 g). Heptane was distilled *in vacuo* from the mixture to constant weight of the residue (2 g of semisolid mass). The IR spectrum shows absorption bands characteristic of adamantane and ester II. The crystals were filtered off, washed with heptane and dried. Adamantane was isolated by sublimation *in vacuo* (5 mm) at 80–100° and was identified by m.p., mol wt and IR spectrum. The residue left after sublimation was ester II. The latter was identified by the complete coincidence of IR spectra of the isolated substance and the authentic specimen.

(b) *In benzene.* The reaction products consisted of CO_2 (0·334 g), t-BuOH (0·54 g), adamantane (0·37 g), 1-phenyladamantane (0·60 g), diphenyl (0·05 g) and ester II (0·34 g). After the removal of solvent, 2·9 g of viscous semisolid product remained. The bands characteristic of 1-phenyladamanatane[15, 17] and ester II are present in IR spectrum. Adamantane was identified by retention time in the chromatographic column at 90° and 180°, 1-phenyl adamantane and diphenyl were identified at 180° by introducing authentic substances into the chromatographed sample.

(c) *In carbon tetrachloride.* The reaction products consisted of CO_2 (0·408 g), t-BuOH (0·52 g), $CHCl_3$ (0·50 g) and hexachloroethane (1·9 g). 4·6 g of semisolid residue remained after removal of the solvent. Hexachloroethane was isolated from the mixture by sublimation at atm press and temp 100°, identified by m.p., retention time on chromatographic column and elementary analysis. After removal of the hexachloroethane 2·3 g of chloroadamantanes mixed with a little of ester II and possibly some chlorinated derivatives of II were obtained. The chloroadamantanes (2 g) were separated by sublimation at a pressure of 3 mm and temp 100°. Repeated sublimation gave a product with m.p. 122–124° (sealed tube). (Found: C, 55·90; H, 6·56; Cl, 37·48; ml. wt. 210. Calc. for $C_{10}H_{14}Cl_2$: C, 58·53; H, 6·83; Cl, 34·64; mol. wt. 205; for $C_{10}H_{13}Cl_3$: C, 50·52; H, 5·47; Cl, 44·41%; mol. wt. 239·5).

The composition of mixture of mono-, di-, and trichloroadamantanes was calculated by the peak areas in the chromatogram, mono- −6·5%, di, −62%, tri- −31·5%.

The calculation based on results of elementary analysis gives approximately the same proportion of components. It was impossible to separate these compounds by fractional sublimation and recrystallization from solvents.

The kinetic measurements

The TBAP thermal decomposition kinetics was measured as follows: 2 ml portions of a 0·06 M soln of peroxide were poured into glass ampules. The ampules were connected to a vacuum system and the contents degassed by intermittent freezing at $-80 \div -180°$ and melting at room temp.

During freezing, the vacuum was applied at residual press 5×10^{-2} mm. The ampules were sealed and placed in a bath regulated to ±0·1°. The ampules taken out after certain periods of time, were cooled in a cooling mixture, unsealed and the peroxide was determined,[11] using 0·02 N $Na_2S_2O_3$. Methyl methacrylate polymerization kinetics with the TBAP as initiator were measured in bulk in mercury dilatometers.

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