

Improved Iodometric Method of Analysis for *tert*-Butyl Peresters

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► Iodometric methods reported in the literature for analysis of *tert*-butyl peresters are inconvenient, require long reaction times, and are of relatively low accuracy. Traces of iron salts in the acetic acid and sodium iodide accelerate iodine liberation from the reaction of peresters with iodide ion, thus permitting an improvement of the Wheeler method for analysis of *tert*-butyl peresters. The new procedure employs 0.002% ferric chloride hexahydrate in glacial acetic acid as solvent. Reaction times are reduced to 5 to 10 minutes and the method does not require extensive precautions for oxygen exclusion. The method gives precise and accurate results (standard deviation of determinations, $\pm 0.42\%$; average per cent deviation between calculated and found values, 0.29%). Both aliphatic and aromatic *tert*-butyl peresters can be analyzed. A redox-free radical mechanism is proposed to account for the stoichiometry and products of reaction.

AN ACCURATE procedure was required for the analysis of high-purity peroxides being synthesized in the laboratory, while a convenient, rapid procedure was also required to study their decomposition rates. The reaction of hydroperoxides, per acids, and diacyl peroxides with sodium or potassium iodide in acetic acid solution to liberate iodine is rapid and well established (14-16). However, it is time-consuming, inconvenient, and inaccurate for the analysis of *tert*-butyl peresters. Milas and Surgenor (9) found that 3 to 4 hours were required to determine the purity of some *tert*-butyl peresters. Blomquist and Ferris (3) reduced the reaction time to 2 hours by using 3% orthophosphoric acid in glacial acetic acid. In following the kinetics of thermal decomposition of *p*-substituted *tert*-butyl perbenzoates, Blomquist and Bernstein (2) used hydriodic acid in place of sodium iodide, with extensive preflushing of the reaction flask, and improved the accuracy and reduced the reaction time to 30 to 60 minutes. Their reported precision to $\pm 3\%$, however, is not satisfactory for pure peresters.

While attempting to improve the

Wheeler iodometric method (16) for analysis of *tert*-butyl peresters the present authors found that traces of iron salts in the acetic acid and sodium iodide markedly accelerate the rate of iodine liberation from the reaction of peresters with iodide ion. This catalytic activity of iron (approximately 10^{-3} mole per mole of perester) formed the basis for development of the present rapid, convenient, and accurate iodometric procedure.

REAGENTS

Acetic acid, Baker analytical reagent grade, redistilled in an all-glass fractionating column. The fraction boiling at 117°C . was used.

Chloroform, Baker analytical reagent grade, redistilled.

Ferric chloride hexahydrate (0.1% solution), 0.25 gram, dissolved in 250 ml. of acetic acid. Specified concentrations of ferric chloride in acetic acid were prepared by pipetting appropriate volumes of the 0.1% stock solution into volumetric flasks containing acetic acid.

Sodium iodide, analytical reagent and USP grades, used directly.

Sodium thiosulfate, standard solution, 0.1*N*.

Starch solution, prepared by dissolving 1 gram of soluble starch in 500 ml. of boiling distilled water.

COMPOUNDS STUDIED

tert-Butyl peresters of the saturated fatty acid series were prepared by reaction of the appropriate fatty acid chlorides with *tert*-butyl hydroperoxide (13).

tert-Butyl per-*p*-nitrobenzoate [melting point $77.0-77.5^\circ\text{C}$. (Fisher-Johns melting point apparatus, Fisher Scientific Co.); reported melting point 79°C . (2)] was prepared from *p*-nitrobenzoyl chloride (Eastman Kodak White Label grade) and *tert*-butyl hydroperoxide. The product was crystallized from ethyl ether to a constant active oxygen content and constant melting point.

tert-Butyl perbenzoate, di-*tert*-butyl diperphthalate, and *tert*-butyl permaleic acid were generously supplied by the Lucidol Corp., Division of Wallace and Tiernan Co. These peresters were used directly without further purification.

PROCEDURE

Sufficient compound (0.1 to 0.2 gram)

was accurately weighed in an iodine flask to give a 10- to 15-ml. titration with 0.1*N* sodium thiosulfate. The sample was dissolved in 10 ml. of chloroform, and the flask was flushed with nitrogen for 20 seconds. Saturated sodium iodide solution (2 ml.) was added, followed by glacial acetic acid (15 ml.) containing the desired per cent of ferric chloride (0.002% ferric chloride is optimum). The flask was permitted to stand in the dark for a predetermined time (5 to 10 minutes was sufficient), 50 ml. of water was added, and the solution was titrated to a starch end point with 0.1*N* sodium thiosulfate. A blank determination was run on the reagents. Per cent active oxygen was calculated as follows:

$$\% \text{ active oxygen} = \frac{(A - B) \times \text{normality} \times 0.8}{W}$$

where

- A = volume of 0.1*N* sodium thiosulfate required by sample
 B = volume of 0.1*N* sodium thiosulfate required by blank
 W = weight of sample, grams

RESULTS AND DISCUSSION

Determination of Optimum Iron Concentration. Solutions of 0.0001, 0.001, 0.002, 0.005, and 0.01% ferric chloride hexahydrate in glacial acetic acid were prepared from the 0.1% stock solution. Samples of *tert*-butyl perpelargonate (calculated active oxygen content 6.947%) were weighed into iodine flasks and analyzed for active oxygen; the solutions were allowed to stand for predetermined times up to 180 minutes. Results are listed in Table I. In the absence of iron, reaction occurred to the extent of only 12% in 1 hour but was quantitative in 15 minutes with 0.001% ferric chloride hexahydrate. The optimum concentration of ferric chloride hexahydrate was 0.002%. Above this concentration, secondary catalytic decomposition effects were evident, as shown by a significant reduction in the active oxygen values.

Analysis of Pure *tert*-Butyl Peresters of Aliphatic Acids. The procedure employing 0.002% iron reagent was applied to a series of pure *tert*-butyl peresters of the saturated fatty

Table I. Effect of Iron Content and Time in Analysis of *tert*-Butyl Perpelargonate^a

Time, Min.	FeCl ₃ ·6H ₂ O in Acetic Acid, %						
	0	0.0001	0.001	0.002	0.005	0.01	0.1
	Active Oxygen, %						
< 1						6.81	6.65
1			3.19	..	6.72	..	6.72
5			6.83	6.95	6.75	6.77	6.74
10			6.83	6.91	6.78	6.77	
15	0.38	0.29	6.90	..	6.75	6.79	
30	0.40	0.56	6.94	6.78	
60	0.84	1.40	6.92				
120	1.24						
180	3.03						

^a Active oxygen calculated, 6.95%.

acid series. Reactions were conducted for 5, 10, and 15 minutes (Table II). Iodine was quantitatively liberated within 5 minutes, the active oxygen values remaining unaltered up to 15 minutes' reaction time. The precision (standard deviation of determinations) was to $\pm 0.42\%$; the accuracy (average per cent deviation between calculated and found values) was to 0.29%. The blank titrations were dependent on the iron concentrations. The maximum amount of iodine liberated by the reaction of 15 ml. of 0.002% iron reagent with sodium iodide was equivalent to 0.03 ml. of 0.1*N* sodium thiosulfate. Special purification of the reagents was unnecessary for routine analysis, as commercial reagents of high purity also gave identical results.

Analysis of Miscellaneous *tert*-Butyl Peresters. The method was tested on a pure aromatic derivative, *tert*-butyl per-*p*-nitrobenzoate, and on several commercial *tert*-butyl peresters—namely, *tert*-butyl perbenzoate, di-*tert*-butyl perphthalate, and *tert*-butyl permaleic acid (Table III). These derivatives are of interest because they have electron-withdrawing groups in positions which would be expected to decrease the rate of reaction (2).

Analysis of *tert*-butyl per-*p*-nitrobenzoate was quantitative in the 5- to 15-minute range by this method, compared with only 90% reaction in 1 hour by the Wheeler method. By the improved procedure, the negative nitro group in the para position significantly in-

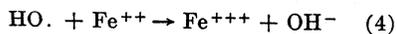
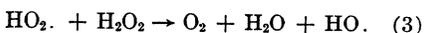
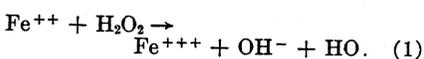
creased the rate of reaction, contrary to expectation.

Analysis of commercial peresters was also complete in 5 to 10 minutes by the improved procedure. These peresters ranged in purity from 95 to 97%.

The Wheeler method was examined using USP and analytical reagent sodium iodide. With the USP grade, iodine was liberated at an increased rate. This study shows that the rate at which perester liberates iodine by the Wheeler method depends upon the purity of the reagents. Blanks also increased with increased reaction time, producing a corresponding decrease in accuracy in the final results.

MECHANISM

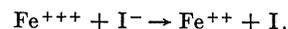
The Haber-Weiss (7) redox-free radical mechanism for the catalytic decomposition of hydrogen peroxide by iron salts explains the rapid decomposition of hydrogen peroxide and the formation of the products:



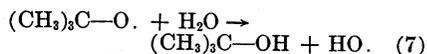
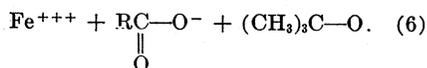
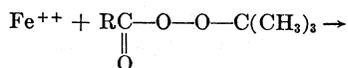
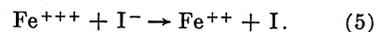
The initiation step (Equation 1) involves attack by ferrous ion on hydrogen peroxide to give ferric ion, hydroxyl radical, and hydroxyl ion. Equations 2 and 3 represent chain-transfer steps whereby hydroxyl radical and perhy-

droxyl radical are alternately formed to attack hydrogen peroxide. The fourth step is termination in which hydroxyl radical attacks ferrous ion to yield ferric ion and hydroxyl anion, termination obviously being favored by an increase in acidity. The Haber-Weiss scheme was also amplified to account for the kinetic influence of ferric ion in acid media on the decomposition of hydrogen peroxide.

When *tert*-butyl peresters are inserted in the Haber-Weiss scheme in lieu of hydrogen peroxide, the mechanism suggested that iron can be used in catalytic amounts if ferrous ion is regenerated from ferric ion as illustrated by the ferric ion-iodide ion reaction:



The Haber-Weiss scheme must then be modified to account for the stoichiometric formation of iodine. The chain-transfer steps, in which reactive free radical species (such as hydroxyl radical) could attack perester, must terminate without initiating or continuing any reaction chains. The reaction is believed to proceed mainly through these five steps:



The first reaction is that between ferric ion and iodide ion (Equation 5) to yield ferrous ion and iodine radical. The second step (Equation 6), which normally would represent the Haber-Weiss initiation stage, regenerates ferric ion, an acid anion, and *tert*-butoxy radical. The ferric-ferrous cycle then proceeds alternately through these two steps, accounting for one half of the liberated iodine. The remaining one half of the iodine is produced by participation of the *tert*-butoxy radical. This radical (Equation 7) abstracts hydrogen from any reactive hydrogen-donating species present, such as water and acetic acid, to produce the active hydroxyl radical either directly or indirectly. The hydroxyl radical attacks iodide ion to produce hydroxyl anion and iodine radical. The iodine radical prefers combination to participation in a chain reaction for perester decomposition. Consequently, steps 8 and 9 are termination steps favored

Table II. Analysis of Pure Aliphatic *tert*-Butyl Peresters with 0.002% Ferric Chloride Hexahydrate

<i>tert</i> -Butyl Perester	Active Oxygen, %				
	Found				
	5 min.	10 min.	15 min.	Av.	Calcd.
Pelargonate	6.953	6.909		6.931	6.947
Caprate	6.623	6.568	6.543	6.578	6.548
Laurate	5.837	5.886	5.875	5.867	5.873
	5.885	5.852			
Myristate	5.369	5.321	5.337	5.342	5.322

Table III. Comparison of Methods for Analysis of Miscellaneous *tert*-Butyl Peresters

Compound	Wheeler Method										Calc. i.	
	Analytical Reagent Sodium Iodide			USP Sodium Iodide			Improved Method, 0.002% FeCl ₃ ·6H ₂ O in Acetic Acid					
	15 min.	30 min.	60 min.	15 min.	30 min.	60 min.	5 min.	10 min.	15 min.	30 min.		60 min.
<i>tert</i> -Butyl <i>p</i> -pernitrobenzoate	...	4.32	5.98	6.62	6.66	6.63	6.688
<i>tert</i> -Butyl permaleic acid ^a	4.16	7.04	8.68	8.24	8.28	8.20	8.18	...	8.556
<i>tert</i> -Butyl perbenzoate ^a	0.66	1.43	3.00	2.59	5.06	8.41	7.88	7.88	...	7.81	7.73	8.238
Di- <i>tert</i> -butyl perphthalate ^a	0.50	0.98	2.07	4.89	7.97	10.30	10.00	10.00	9.97	10.00	...	10.31

^a Commercial preparation.

by acid media. The quantitative formation of iodine is proof that perester decomposition by *tert*-butoxy and hydroxyl free radicals does not occur.

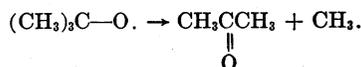
The scheme for Equations 6 and 7 is supported by product analysis. Lauric acid, the identity of which was proved by acid number, melting point, and mixed melting point, was isolated quantitatively by ether extraction of the *tert*-butyl perlaurate-ferrous iodide ion reaction after reduction of the iodine by sodium thiosulfate. *tert*-Butoxy radical is known to give two products, *tert*-butyl alcohol by hydrogen abstraction, and acetone (plus methyl radical) by decomposition (5, 12, 17). The presence of both *tert*-butyl alcohol and acetone was demonstrated in a separate series of qualitative isolation experiments.

tert-Butyl perpelargonate (2 grams) was dissolved in acetic acid (100 ml.). Saturated sodium iodide solution (20 ml.) was added, followed by addition of 0.10% ferric chloride hexahydrate in acetic acid (2 ml.). The mixture was allowed to stand for 15 minutes, water (100 ml.) was added, and the iodine was reduced by dropwise addition of concentrated sodium thiosulfate. The solution was then neutralized by slow addition of cold 50% sodium hydroxide while the reaction mixture was cooled in an ice bath. The neutralized solution was extracted with five 25-ml. volumes of petroleum ether which was free of acetone, alcohol, and olefin.

The presence of *tert*-butyl alcohol in the petroleum ether extract was confirmed by use of Denigès reagent, which was prepared by dissolving mercuric oxide (5 grams) in sulfuric acid (20 grams) and water (100 ml.) (8, 11). The petroleum ether extract (10 ml.), described in the preceding paragraph, was added to a mixture of Denigès reagent (5 ml.) and water (5 ml.). The flask was loosely stoppered, and the mixture was heated on a steam bath with careful shaking to extract the alcohol from the ether layer. A heavy yellow precipitate formed within 2 minutes confirming the presence of substantial amounts of *tert*-butyl alcohol.

Rothea's reaction was used for detection of acetone (4). The test was performed by adding 10 ml. of the petroleum ether extract of the reduced neutralized perester to a mixture consisting of water (1 to 2 ml.), 5% sodium nitroprusside (5 drops), ammonium acetate (2 to 4 grams), and ammonium hydroxide (1 to 2 ml.). The mixture was shaken and the presence of acetone was indicated by a violet-red coloration.

A positive test was also obtained on the original aqueous reaction mixture prior to hydrocarbon extraction. The low intensity of color, when compared to prepared standards, indicated acetone to be present in only trace amounts. The test is sensitive to 0.005% acetone. Formation of acetone can be accounted for by decomposition of *tert*-butoxy radical in a reaction which also maintains stoichiometry:



The modified method was tried as an alternative to current methods of analysis for peroxides that are difficult to analyze, such as di-*tert*-butyl peroxide and ascaridole (or oil of chenopodium). The former, known to be unreactive with ferrous ion and with alkali iodides in acetic acid (6), and the latter, which requires an empirical factor to account for the nonstoichiometric liberation of iodine (1, 10, 14), could not be analyzed successfully by the modified method.

SUMMARY

The Wheeler method for the iodometric analysis of peroxides has been modified by the use of 0.002% ferric chloride hexahydrate in glacial acetic acid as solvent, thus making the procedure applicable to the analysis of both aliphatic and aromatic *tert*-butyl peresters. The improved method shortens reaction times to 5 to 10 minutes as compared to other methods and does not require extensive pre-

cautions for oxygen exclusion. The method gives precise and accurate results (standard deviation of determinations, ±0.42%; average per cent deviation between calculated and found values, 0.29%). A five-step redox-free radical mechanism is proposed to account for the stoichiometry and products of reaction.

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