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Ozonization of Solid Potassium *t*-Butoxide and Potassium *t*-Perbutoxide[1a]

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Solid potassium dioxide, potassium *t*-butoxide and potassium *t*-perbutoxide have been ozonized at −78° by a countercurrent method. In all cases potassium ozonide was formed as shown by the oxygen evolved and by paramagnetic spin measurements. In the case of potassium *t*-butoxide and potassium *t*-perbutoxide, di-*t*-butyl peroxide and acetone were found as the other products of ozonization, although in the second case evidence was obtained for the existence, at low temperatures, of di-*t*-butyl tetroxide. A tentative interpretation of the results has been given.

The ozonization of solid potassium hydroxide and other hydroxides[2-4] led to the isolation of the paramagnetic potassium ozonide and other ozonides of this class. More recently the paramagnetic ammonium ozonide[5] and tetramethylammonium ozonide[6] were detected in the ozonization products of liquid ammonia and of tetramethylammonium hydroxide, respectively. In no case, however, has any attempt been made to determine the fate of the hydroxyl or other groups attached to the metal or ammonium ions. The present communication will describe the countercurrent ozonization of solid potassium *t*-butoxide and potassium *t*-perbutoxide with the emphasis on the fate of the *t*-butoxy and *t*-perbutoxy radicals.

As a preliminary investigation to test our countercurrent method, we ozonized samples of potassium dioxide,[7] the structure of which has been well established.

Using the apparatus shown in Fig. 2, powdered potassium dioxide was ozonized at −78° to potassium ozonide. From the decomposition of the latter the net oxygen evolved corresponded to 9.1% conversion. Since potassium ozonide is known to decompose quantitatively to potassium dioxide,[2] the amount of the dioxide should remain the same at the end of the experiment. By analyzing[7] the total potassium dioxide remaining in the vessel and comparing it with the amount originally used, it was possible to calculate the percentage conversion to potassium ozonide. The results seem to indicate that at −78° ozone attacks potassium dioxide in such a way as to cause the ejection of an oxygen molecule leaving behind an electron together with the potassium atom attached to the ozone molecule. The mechanism of this reaction eq. 1 is not clear at present and may be clarified by the use of isotopic oxygen.

$$\mathrm{KOO\cdot} + \mathrm{O_3} \xrightarrow{-78^\circ} \mathrm{O_2} + \mathrm{KOOO\cdot} \xrightarrow{40^\circ} \mathrm{KOO\cdot} + {}^1/_2\mathrm{O_2} \quad (1)$$

When solid potassium *t*-butoxide was allowed to react with ozone at −78° under the same conditions as potassium dioxide, the over-all yield of potassium ozonide estimated from the net oxygen evolved, at the end of the experiment, was about 10%. The residue was then extracted at −78° with pure pentane and the latter removed in vacuum (60 mm.) at 0°. A vapor phase chromatogram of this residue showed the presence of acetone, *t*-butyl alcohol and di-*t*-butyl peroxide. Acetone was also identified by its 2,4-dinitrophenylhydrazone which had the correct m.p. A microfractionation of the residue afforded a pure sample of di-*t*-butyl peroxide which had an infrared spectrum identical with that of an authentic sample. Its purity was also confirmed by a vapor phase chromatogram. The yield of di-*t*-butyl peroxide was estimated to be about 60% of that of potassium ozonide or about 6%. Apparently some of the *t*-butoxy radicals must have decomposed to acetone and methyl radicals, thereby diminishing the yield of di-*t*-butyl peroxide. The fate of the methyl radicals was not determined because of experimental difficulties.

The existence of potassium ozonide in the original reaction mixture was demonstrated more precisely by measuring its paramagnetic spin resonance. Purification of the ozonide by liquid ammonia extraction[2] was not feasible since potassium *t*-butoxide was also soluble in this solvent. To avoid the presence of *t*-butoxy radicals or other organic radicals during the paramagnetic spin resonance measurements, the original reaction mixture was extracted several times at −78° with pure liquid propane and the extracts filtered through a special apparatus into a large flask. Evaporation of the propane left a residue which exhibited a vapor phase chromatogram identical with that obtained from the pentane extracts.

The temperature of the reaction vessel then was allowed to rise to about −30° and samples of the orange-red solid residue, now free from any organic radicals, were withdrawn in capillary tubes, sealed in nitrogen at low temperatures, and the paramagnetic spin resonance measured at −196°. Curve A of Fig. 1 shows the paramagnetic spin resonance spectrum of the orange-red solid with a g-value of 2.00. This can be attributed to potassium ozonide which is known to possess an unpaired electron. At higher temperatures (30° to 40°) the orange-red solid decomposed into a yellow solid with evolution of oxygen, a typical reaction of potassium ozonide.[2] Moreover, the final yellow solid was decomposed with water and the oxygen

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[1] (a) A preliminary report of this work was published in *Chem. Ind.*, **1962**, 405–407 (1962). (b) Postdoctorate Research Associate.

[2] I. A. Kazarnovski, G. P. Nikolskii and T. A. Abletsova, *Doklady Akad. Nauk, U.S.S.R.*, **64**, 69 (1949); *C. A.*, **43**, 4169 (1949); G. P. Nikolskii, Z. A. Bagdazarian and I. A. Kazarnovski, *Doklady Akad. Nauk U.S.S.R.*, **77**, 69 (1951); *C. A.*, **45**, 5554 (1951).

[3] T. P. Whaley and J. Kleinberg, *J. Am. Chem. Soc.*, **73**, 79 (1951).

[4] A. D. McLachlan, J. C. R. Symons and M. G. Townsend, *J. Chem. Soc.*, 952 (1959).

[5] I. J. Solomon, K. Hattori, A. J. Kacmarek, G. M. Platz and M. J. Klein, *J. Am. Chem. Soc.*, **84**, 34 (1962).

[6] I. J. Solomon, A. J. Kacmarek, J. M. McDonough and K. Hattori, *ibid.*, **82**, 5640 (1960).

[7] C. A. Kraus and E. F. Parmenter, *ibid.*, **56**, 2384 (1934).

evolved measured. This was equivalent to the potassium dioxide formed from the decomposition of the ozonide.

Although there may be other interpretations of these results, we favor the one given by eq. 2.

$$2(CH_3)_3COK + 2O_3 \xrightarrow{-78^\circ}$$

$$\begin{array}{l} 2KOOO\cdot \\ \quad + \\ 2(CH_3)_3CO\cdot \end{array} \left\{ \begin{array}{l} \longrightarrow 2(CH_3)_2CO + 2CH_3 \\ \longrightarrow (CH_3)_3COOC(CH_3)_3 \end{array} \right. \qquad (2)$$

When solid potassium *t*-perbutoxide was ozonized under the same conditions as potassium *t*-butoxide and the vessel A (Fig. 2) connected to an Orsat apparatus, the rate of oxygen evolution between −30° and −10° was very rapid and could not be accounted for by the expansion of the gas between these two temperatures. Since potassium ozonide is stable at these temperatures, the oxygen evolved must have come from the spontaneous decomposition of some unstable intermediate. Our suspicion that di-*t*-butyl tetroxide might have formed at −78° and decomposed at higher temperatures to di-*t*-butyl peroxide and oxygen was confirmed when the original mixture was extracted several times at −78° with pure liquid propane and the extracts collected as before. When the combined extracts were allowed to evaporate at −40° to −35°, a crystalline solid residue remained which decomposed spontaneously at −30° to 18° to give a liquid and oxygen gas. A vapor phase chromatogram of the liquid showed the presence of di-*t*-butyl peroxide and acetone together with some undetermined quantity of *t*-butyl alcohol. On the basis of the net gas evolved, calculated at S.T.P., the over-all conversion of solid potassium *t*-perbutoxide to di-*t*-butyl peroxide, acetone and oxygen was 10.75 mole per cent. Since acetone was formed to the extent of 1.8 mole per cent., there should have been an equivalent amount of ethane in the gaseous mixture. Unfortunately, however, the gas mixture was not analyzed for this substance. Samples of the orange-red residue in vessel A were then taken in capillary tubes, sealed in nitrogen at low temperatures and the paramagnetic spin resonance measured at −196°. The spectrum is shown in curve B of Fig. 1 from which the *g*-value of 2.00 was obtained.

Finally, the simplest interpretation of our results is shown by eq. 3 and 4.

$$2(CH_3)_3COOK + 2O_3 \xrightarrow[10.75\%]{-78^\circ}$$

$$2KOOO\cdot + (CH_3)_3COOOOC(CH_3)_3 \qquad (3)$$

$$(CH_3)_3COOOOC(CH_3)_3 \xrightarrow[10.75\%]{-30^\circ \text{ to } 18^\circ}$$

$$\left.\begin{array}{l} O_2 \\ \quad + \\ 2(CH_3)_3CO \end{array} \begin{array}{l} \xrightarrow{83.2\%} (CH_3)_3COOC(CH_3)_3 \\ \xrightarrow[16.8\%]{} 2(CH_3)_2CO + CH_3CH_3 \end{array} \right\} \qquad (4)$$

These results seem to establish the possible existence, at low temperatures, of di-*t*-butyl tetroxide. Moreover, these results are in agreement with those of Blanchard[8] and Traylor and Bartlett[9] who postulated the formation of dicumyl tetroxide by the coupling of the percumyloxy radicals during the auto-oxidation of cumene.

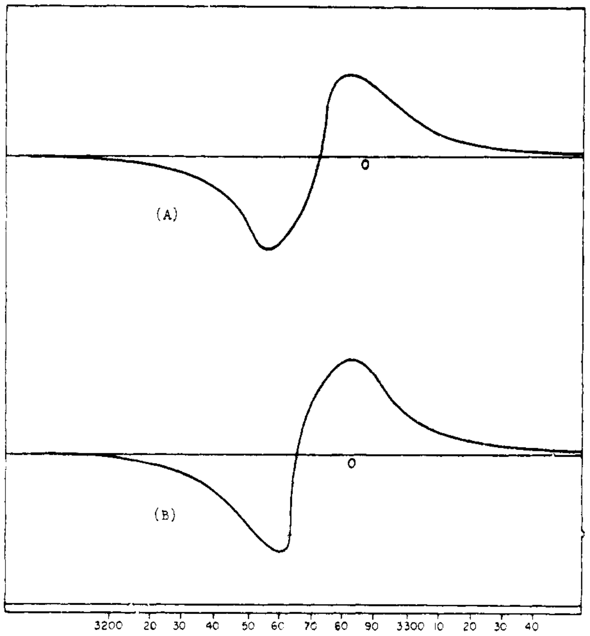

Fig. 1.—Paramagnetic spin resonance spectra of: (A), KO_3 from the ozonization of solid $(CH_3)_3COK$; (B), KO_3 from the ozonization of solid $(CH_3)_3COOK$. Each curve is a field derivative of absorption d*x*″/d*H vs.* field *H*. Frequency, 9.290 kmc.; gain, −46 dbmax.; phase, 4; mod. amp., 0.3 gauss; field interval, 140 gauss sweep.

Experimental

Potassium dioxide was prepared by the oxidation of metallic potassium with dry oxygen in liquid ammonia,[7] and analyzed by decomposing weighed samples with water and measuring the oxygen evolved using an Orsat apparatus. The yellowish KO_2 obtained was found to be 99.2% pure.

The ozonization apparatus is shown in Fig. 2 and consists of A, the reaction vessel, with a magnetic stirrer B. By means of ground-glass joints C and D a well-machined Teflon block E is attached to the reaction vessel and to the reservoir F which contains the finely powdered solid to be ozonized. The Teflon block is equipped with a well-machined Teflon plunger G with a slot H which receives the solid at I and delivers it at J. The plunger is so designed that it acts like a pump and a pinhole at K was essential to make its back-and-forth movement easier. The glass plunger at L was also essential since highly dry powders would not drop automatically and had to be forced downward.

In the beginning of the experiment the vessel A was slowly cooled to −78° by the bath M and powdered Dry ice N, while a stream of dry oxygen was flowing through the apparatus. Dry oxygen containing 6% ozone was then allowed to pass upward as shown, while finely powdered potassium dioxide (2.2 g.) was dropped downward into the vessel A in the course of 5 hours. As the solid powder moved downward, it turned orange-red immediately upon coming in contact with ozone. Since the reaction of solid powders is a surface reaction, the magnetic stirrer at the bottom of the vessel served to agitate the solid in order to increase the degree of ozonization. The trap 0 immersed in a Dry Ice–acetone mixture was necessary to catch traces of powder that were carried over by the oxygen–ozone stream and to permit quantitative measurements of the ozone at the exit tube before, during and after the reaction. At the end of the reaction, the dropping apparatus was quickly replaced with a ground-glass stopper and dry oxygen, free from ozone, was

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[8] H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

[9] T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, **No. 24**, 30 (1960).

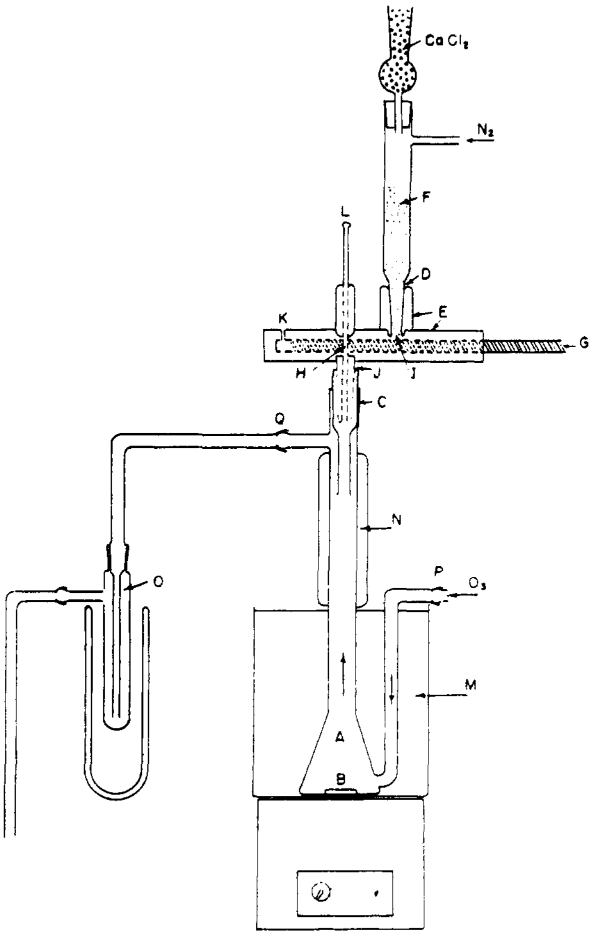

Fig. 2.—Ozonization apparatus.

passed through the vessel A with stirring for a half-hour. The vessel A was then allowed to come to room temperature with continued stirring, then heated for 48 hr. at 40° and the total oxygen evolved measured and reduced to S.T.P. The same operation was repeated without anything in vessel A. The gas due to expansion from −78° to 40° was measured and reduced to S.T.P. The difference between the two measurements gave the volume of oxygen due to the decomposition of the orange-red solid KO_3 to the yellowish solid KO_2. This was 31.5 ml. which corresponds to a conversion of 9.1%. Since KO_2 is stable at 40°, a sample of it was analyzed by decomposition with water and the oxygen evolved measured as before. The purity of the remaining KO_2 was identical (99.2%) with that of the original. These results seem to justify the reaction shown in eq. 1.

Potassium *t*-Butoxide.—To 200 ml. of freshly distilled (over calcium hydride) *t*-butyl alcohol was added 10 g. of potassium metal and the mixture refluxed gently in an atmosphere of dry nitrogen until all of the potassium reacted. The excess *t*-butyl alcohol was then removed in a rotating evaporator at 50° under high vacuum. The white solid residue was powdered in dry nitrogen, washed several times with anhydrous petroleum ether and subjected again to a high vacuum at 50°. The final product was analyzed by titration with standard hydrochloric acid. An attempt to remove all the *t*-butyl alcohol at higher temperatures under high vacuum caused considerable decomposition.

Anal. Calcd. for $(CH_3)_3COK{\cdot}(CH_3)_3COH$: $(CH_3)_3COK$, 60.23. Found: $(CH_3)_3COK$, 60.18.

Ozonization of Solid Potassium *t*-Butoxide.—Finely powdered potassium *t*-butoxide (2.5 g. equivalent to 0.0134 mole of $(CH_3)_3COK$) was dropped in small portions at −78° in the course of 4 hr. with magnetic stirring while dry oxygen containing 6% ozone was allowed to pass through the apparatus (Fig. 2) countercurrently at the rate of 0.230 mmole of ozone per min. The solid assumed an orange-red color immediately upon coming in contact with ozone. At the end of the reaction, the dropping apparatus was quickly replaced by a ground-glass stopper, and dry oxygen, free from ozone, was passed through vessel A for a half-hour with continued stirring. The vessel A was then connected to an Orsat apparatus, the cooling bath removed and the vessel allowed to come to room temperature, then heated at 30° for 3 days with stirring continued. The total gas evolved was measured and converted to S.T.P. The same operation was repeated without any solid in vessel A and the gas due to expansion from −78° to 30° measured and converted to S.T.P. The difference between the two measurements gave the volume of oxygen due to the decomposition of the orange-red KO_3 to the yellowish solid KO_2. This was 15.00 ml. which corresponds to 10% conversion.

The yellowish solid residue was then extracted several times with pure pentane and the combined extracts concentrated to a small volume in vacuum (60 mm.) at 0°. A vapor phase chromatogram of the extract showed the presence of acetone, *t*-butyl alcohol and di-*t*-butyl peroxide. By comparing this chromatogram with the chromatogram of a known mixture, the total amount of di-*t*-butyl peroxide was estimated to be 58.7 mg. and that of acetone 31 mg. These quantities correspond to 60 and 40%, respectively, of the oxygen evolved. A microfraction in a capillary apparatus of the pentane concentrate afforded a pure sample of di-*t*-butyl peroxide, which had an infrared spectrum identical with that of an authentic sample. Moreover, its purity was confirmed by a vapor phase chromatogram. The acetone was further identified by the preparation of its 2,4-dinitrophenylhydrazone which had the correct m.p.

In another experiment, 4.6 g. of powdered potassium *t*-butoxide (2.76 g. calculated as 100% $(CH_3)_3COK$) was ozonized under the same conditions, but the final product was extracted several times at −78° with liquid propane and the extracts filtered at this temperature into a large flask maintained at −78°, using pure, dry nitrogen to force the clear liquid into the flask. After the filtration, the vessel A was connected to an Orsat apparatus and the net gas evolved from the decomposition of the orange-red solid in this vessel measured as before. This gas (27.8 ml. at S.T.P.) was equivalent to 10.1% conversion. When the propane solution was allowed to evaporate, a liquid remained which had, besides *t*-butyl alcohol, 112 mg. of di-*t*-butyl peroxide and 58 mg. of acetone. On the basis of the oxygen evolved from the decomposition of KO_3 and eq. 2, 62% of the *t*-butoxy radicals coupled to form di-*t*-butyl peroxide and 38% decomposed to form acetone and methyl radicals.

In a third experiment, samples of the orange-red solid in the vessel A, after propane extractions, were taken in capillary tubes which were sealed in nitrogen at low temperatures and the paramagnetic spin resonance measured at −196°. Spectrum A of Fig. 1 shows the results of the measurements which give a *g*-value of 2.00.

Potassium *t*-Perbutoxide.—Potassium *t*-perbutoxide was prepared previously, but it was always obtained with one mole of *t*-butyl alcohol of crystallization.[10] An attempt was therefore made to prepare potassium *t*-perbutoxide free from *t*-butyl alcohol. *t*-Butyl hydroperoxide was prepared from the commercial product (Lucidol Division of Wallace and Tiernan, Inc.) by extracting a petroleum ether solution of the commercial *t*-butyl hydroperoxide with cold aqueous sodium hydroxide solution. The hydroperoxide was regenerated by adding at 0° potassium acid sulfate at *p*H not higher than 4.5. The hydroperoxide was then extracted with ether, the latter dried over anhydrous magnesium sulfate, filtered, and the ether removed in a rotating evaporator under reduced pressure. The final product had a purity of 96.7%.[10]

To 200 ml. of anhydrous *t*-butyl alcohol was added 5 g. of potassium metal in an atmosphere of pure nitrogen. When the potassium had completely gone into solution, 12.6 g. (5% excess) of 96.7% *t*-butyl hydroperoxide was added, and 1 hr. was allowed for the exchange to take place. The excess alcohol was then removed in a rotating evaporator at 50° under high vacuum. The solid potassium *t*-perbutoxide was then powdered in an atmosphere of nitrogen, washed several times with anhydrous petroleum ether and again subjected to a high vacuum at 50°. Active oxygen determinations showed the final product to be 98.0% as potassium *t*-per-

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[10] N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).

butoxide. A vapor phase chromatogram taken of a hydrolyzate of this salt showed the presence of *t*-butyl hydroperoxide and small amounts of *t*-butyl alcohol, but no trace of di-*t*-butyl peroxide.

Ozonization of Solid Potassium *t*-Perbutoxide.—Finely powdered potassium *t*-perbutoxide (1.9 g.) was ozonized at −78° in the course of 3 hr. following the same procedure used with the first experiment on potassium *t*-butoxide. As in the previous experiments, the white solid assumed an orange-red color immediately upon coming in contact with the ozone. On the basis of the net oxygen evolved, at the end of the experiment, the over-all conversion was 39%. Moreover, the rate of oxygen evolution between −30° and −10° was very rapid as compared with that of the experiments with either potassium dioxide or potassium *t*-butoxide. It was, therefore, suspected that, in this case, an unstable intermediate must have been formed at −78° and decomposed spontaneously above −30°.

In another experiment, potassium *t*-perbutoxide (3.36 g. equivalent to 0.0257 mole of 100% $(CH_3)_3COOK$) was dropped into the vessel A (Fig. 2) in small portions at −78°, with magnetic stirring, in the course of 4 hr. while dry oxygen containing 6% ozone was allowed to pass through the apparatus countercurrently at the rate of about 0.230 mmole per min. At the end of the experiment the orange-red solid was extracted several times at −78° with liquid propane and the extracts filtered as before using the same technique which already has been described. The propane of the combined filtrates was then allowed to evaporate slowly until the temperature of the flask reached −30° which is 12° above the b.p. of propane. The flask was connected quickly to an Orsat apparatus and the white crystalline residue which remained began to disintegrate, with gas evolution, as the temperature of the flask was allowed to rise. The cooling bath was then removed and the temperature of the flask allowed to rise to 18°, at the temperature of which all the solid had changed into a liquid and the gas evolution stopped. The same operation was repeated with the flask empty to measure the gas due to expansion between −30° and +18°. Both volumes were converted to S.T.P. and the difference between the two gave the gas evolved (36.00 ml.) from the disintegration of the solid residue. A vapor phase chromatogram of the liquid showed the presence of 168 mg. of di-*t*-butyl peroxide and 26.9 mg. of acetone. The amount of *t*-butyl alcohol which was also present was not estimated since the original potassium *t*-perbutoxide contained *t*-butyl alcohol of crystallization.

On the basis of these figures and eq. 3 and 4, the over-all conversion to the di-*t*-butyl tetroxide was calculated to be 10.75%. Since the tetroxide is assumed to decompose into oxygen and *t*-butoxy radicals, and the latter either couple to form di-*t*-butyl peroxide or decompose to give acetone and ethane, one could easily calculate the volume of oxygen produced. This comes out as 30.95 ml. But the volume actually obtained was 36.00 ml., so that the difference, 5.05 ml., must be due to ethane. Unfortunately, the presence or quantity of ethane was not determined. However, when calculated from the amount of acetone obtained, it comes out as 5.2 ml. which is close to the estimated volume.

In another experiment, samples of the orange-red solid in vessel A, after the propane filtrations, were taken in capillary tubes which were sealed in nitrogen at low temperatures and the paramagnetic spin resonance measured at −196°. Spectrum B of Fig. 1 shows the results of the measurements which give a *g*-value of 2.00.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. VIII. Di-*tert*-butyl Monoperoxyoxalate

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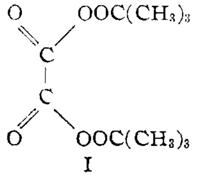
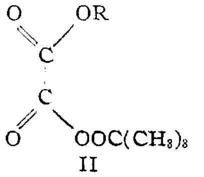
Di-*tert*-butyl monoperoxyoxalate (II, R = *tert*-butyl) decomposes in the temperature range 25–55° in benzene solution about three times as fast as di-*tert*-butyl diperoxyoxalate (I). In contrast to the latter ester, which in cumene solution yields 2 moles of carbon dioxide and 1.98 moles of free *tert*-butoxy radicals per mole of perester, the new compound affords 1.5 moles of carbon dioxide, 0.98 mole of scavengeable free radicals and 0.37–0.44 mole of di-*tert*-butyl carbonate. Most of the latter is shown to be formed by a cage effect; for in the presence of the efficient scavenger galvinoxyl[6] 0.348 mole of it is still formed from 1 mole of perester, while the carbon dioxide yield is cut to 1.01 moles. It follows that (1) the O–O and central C–C bond break in concert in the decomposition of di-*tert*-butyl monoperoxyoxalate; and (2) the carbo-*tert*-butoxy radical, $COOC(CH_3)_3$, is unstable but scavengeable, in contrast to the unscavengeable carbo-*tert*-butylperoxy radical $COOOC(CH_3)_3$. The present evidence is ambiguous as to whether the rapid decomposition of di-*tert*-butyl diperoxyoxalate (I) involves the concerted fission of three bonds or only two, but reasons are given for continuing to consider the former alternative.

Introduction

In previous work it has been found that the double perester, di-*tert*-butyl diperoxyoxalate (I), is an efficient initiator of chain reactions at temperatures as low as 25°, and shows no cage effect amounting to more than 1%.[1,2] This rapid decomposition could be approached, but not equaled, by esters of mono-*tert*-butylperoxyoxalic acid such as the ethyl (II, R = C_2H_5) or *p*-methoxybenzyl ester[3] (II, R = p-$CH_3OC_6H_4CH_2$).


I


II

The dependence of the decomposition rate of the substituted benzyl[3] and benzhydryl[4] esters of the type II upon the polar character of the substituents suggested the investigation of di-*tert*-butyl monoperoxyoxalate (II, R = *tert*-butyl) where electron release by the R group might be higher than in the previously examined cases.

Di-*tert*-butyl monoperoxyoxalate was prepared without difficulty by the reaction of *tert*-butylperoxyoxalyl chloride with *tert*-butyl alcohol in pentane solution in the presence of pyridine at −8 to −2°. It was isolated without warming, by

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(1) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

(2) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(3) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

(4) P. D. Bartlett and N. L. Bauld, to be published.