bp 89–92° (32 mm). For degradative and nmr spectral purposes a middle cut, bp 90–91° (32 mm), was employed. This middle cut was quite pure except for a small 1–2% material that showed up on the tail of **13** when subjected to vpc analysis on a 10 m × $^1/_8$ in., 20% Carbowax 20M, 60–80W column at 140°. Similarly, there was a small blip in the baseline of the ^{19}F nmr of **13**. It was not unreasonable to assume that this small impurity corresponded to the cis ring fused isomer of **13** that may arise from dehalogenation of the 1–2% of **8** in the starting adduct mixture. Preparative vpc was employed for ir and mass spectral samples of **13** where purity was more critical and smaller samples were practical. The first part of 2–3-μl injections of the fraction, bp 90–91° (32 mm), coming through a 10 m × 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column at 155° gave **13** free of this minor impurity.

Running a somewhat small scale dehalogenation on the same adduct mixture for 60 hr caused the reaction to go to completion. The product distribution before distillation and separation into fractions was 1% **9** and 97–99% **13** depending upon whether 0–2% of material was hidden under the tail end of the **13** peak. On isolation **13** proved identical with that isolated above.

Ozonolysis of 13. Ozone was bubbled through a Dry Ice–2-propanol cooled solution of 0.9 g of freshly bulb-to-bulb distilled **13** in 10 ml of ethyl acetate until the solution turned blue. Excess ozone was blown out with nitrogen. The ethyl acetate solution was transferred to a rotary evaporator operating under high vacuum. When the temperature rose above 0°, the flask containing the residue was transferred to a Dry Ice–2-propanol bath. To the chilled residue, 20 ml of 88% formic acid and 7 ml of 30% hydrogen peroxide were added. The solution was stirred magnetically at room temperature for 3.5 days after which time the gradual oxygen evolution perceptibly slowed. The reaction mixture was refluxed for 1 hr after which it was treated with Norit and filtered. Addition of methylcyclohexane–ether and extended evaporation on a rotary evaporator produced an oil that eventually changed to a sticky solid. The solid was washed onto a vacuum filter with water. Repeated washings with ice–water followed by sucking dry overnight gave 0.48 g of sweet-smelling, greenish-yellow crystals. The crystals were dissolved in refluxing ether, treated with Norit, and filtered. Addition of methylcyclohexane and cooling produced 0.16 g of white crystals, mp 146–148° (lit.[22] 145–147°), corresponding to acid **11**.

Cycloaddition of *trans*-Cyclooctene to Butadiene. About 20 g of butadiene, 5 g of 60% *trans*-, 40% *cis*-cyclooctene, and a trace of hydroquinone were heated for 2 hr at 125° in a sealed tube under nitrogen. Fractional distillation of the product was carried out in a large flask on account of a tendency to foam strongly. There was obtained 2.7 ml bp 55–61° (43 mm), 0.5 ml bp 61–142° (43 mm), and 3.4 ml bp 142–143° (43 mm). For ^1H and mass spectral purposes the bp 142–143° (43 mm) fraction was distilled a second time giving 2 g (45%) of bicyclo[6.4.0]dodec-10-ene, bp 102–103° (10 mm). This material gave a single vpc peak on a 3 m × 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column at 162° with a 29-min retention time.

Mass spectrum: exact mass parent 164.156 (calcd 164.157); $P + 2/P = 0.13$ (calcd 0.13); peak at mass 110 (cyclooctene)$^+$; peak at mass 54 (butadiene)$^+$. Nmr: 2 vinyl protons, 18 alkyl protons.

A small scale control reaction was run in order to determine the extent of isomerization of *trans*- to *cis*-cyclooctene under the reaction conditions. About 50 μl of 98.6% pure *trans*-cyclooctene and 0.25 g of butadiene were heated under nitrogen for 2 hr at 125°. Vpc analysis at the end of this period gave the following uncorrected trace areas on TCEP: 4-vinylcyclohexene (8.3), *cis*-cyclooctene (1.0), *trans*-cyclooctene (1.1), and adduct (97.9). Vpc areas were left uncorrected on the basis of a sample of 114.8 mg of adduct (76.9 mol %) mixed with 23.2 mg of *cis*-cyclooctene (23.1 mol %) which showed relative vpc trace areas of 78.6 for adduct and 21.4 for *cis*-cyclooctene.

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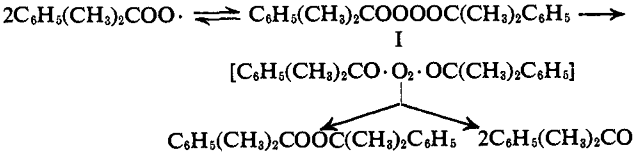
Bimolecular Self-Reaction of Peroxy Radicals. An Oxygen-18 Isotope Study

J. E. Bennett and J. A. Howard* [1]

Contribution from the Shell Research Limited, Thornton Research Centre, Chester, CH1 3SH, United Kingdom. *Received November 30, 1972*

Abstract: A technique using electron spin resonance spectroscopy has been developed to determine the isotopic distribution of the oxygen evolved from the decomposition of an equimolar mixture of the peroxy radicals $R^{16}O^{16}O\cdot$ and $R^{18}O^{18}O\cdot$ (where R was a primary, secondary, or tertiary alkyl, acetyl, or 2-pyridyl group) in an inert solvent. In each case the mixed isotope, $^{16}O^{18}O$, was observed in the oxygen that was evolved in the termination reaction. These results provide additional evidence that the rate controlling termination reaction for the liquid phase autoxidation of hydrocarbons with labile primary, secondary, and tertiary hydrogens involves a head-to-head reaction of two alkylperoxy radicals.

There is at the present time considerable interest in the kinetics and mechanisms of the bimolecular self-reactions of alkylperoxy radicals.[2] The self-reaction of tertiary alkylperoxy radicals is fairly well understood[3] and is believed to occur *via* a tetroxide intermediate, I. For example



$$2C_6H_5(CH_3)_2COO\cdot \rightleftharpoons \underset{\text{I}}{C_6H_5(CH_3)_2COOOOC(CH_3)_2C_6H_5} \longrightarrow [C_6H_5(CH_3)_2CO\cdot O_2\cdot OC(CH_3)_2C_6H_5] \longrightarrow C_6H_5(CH_3)_2COOC(CH_3)_2C_6H_5 + 2C_6H_5(CH_3)_2CO\cdot$$

The oxygen molecule formed in this reaction is produced by the elimination of the terminal oxygen atom from each radical. This has been confirmed by the detection of $^{34}O_2$ during the oxidation of cumene (ini-

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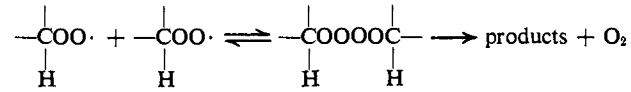
[2] (a) D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6555 (1971); (b) J. A. Howard and J. E. Bennett, *Can. J. Chem.*, **50**, 2374 (1972).

[3] J. A. Howard, *Advan. Free-Radical Chem.*, **4**, 42 (1972).

tiated by azobisisobutyronitrile) in the presence of a mixture of $^{32}O_2$ and $^{36}O_2$ (1–6%).[4] That is

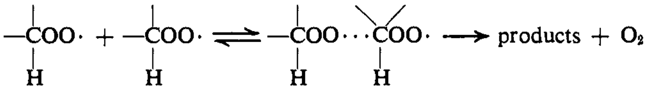
$$C_6H_5(CH_3)_2C^{16}O^{16}O\cdot + C_6H_5(CH_3)_2C^{18}O^{18}O\cdot \longrightarrow \text{products} + {}^{16}O^{18}O$$

Similar isotopic labeling experiments have not been reported for the self-reactions of primary and secondary alkylperoxy radicals[5] and there is, therefore, no experimental evidence to support the assumption that these radicals react head-to-head rather than head-to-tail. That is



$$-\underset{H}{\overset{|}{\underset{|}{C}}}OO\cdot + -\underset{H}{\overset{|}{\underset{|}{C}}}OO\cdot \rightleftharpoons -\underset{H}{\overset{|}{\underset{|}{C}}}OOOO\underset{H}{\overset{|}{\underset{|}{C}}}- \longrightarrow \text{products} + O_2$$

rather than



$$-\underset{H}{\overset{|}{\underset{|}{C}}}OO\cdot + -\underset{H}{\overset{|}{\underset{|}{C}}}OO\cdot \rightleftharpoons -\underset{H}{\overset{|}{\underset{|}{C}}}OO\cdots\underset{H}{\overset{\diagdown\diagup}{\underset{|}{C}}}OO\cdot \longrightarrow \text{products} + O_2$$

In this communication, we report the novel use of electron spin resonance spectroscopy to study the isotopic distribution of the oxygen evolved from the self-reaction of peroxy radicals prepared from the appropriate radical and an equimolar mixture of $^{32}O_2$ and $^{36}O_2$. Using this method we have obtained *direct* evidence that the self-reactions of a variety of peroxy radicals involve a head-to-head reaction.

Experimental Section

An equimolar mixture of the labeled peroxy radicals, $R^{16}O^{16}O\cdot$ and $R^{18}O^{18}O\cdot$, was prepared in high purity (*i.e.*, with respect to other free radicals) at −196° in a rotating cryostat.[7] Briefly, the method involved the sequential deposition of an inert matrix, an organic halide, sodium atoms, and a mixture of $^{32}O_2$ and $^{36}O_2$ (50:50 by volume; mass spectrum *m/e* (rel intensity) 32 (25), 34 (1) 36 (22)) on the drum of the rotating cryostat. Perdeuteriobenzene or cyclopropane was used as the inert matrix and was present in a large excess. Specific peroxy radicals were prepared from the corresponding halide, RX, by the sequence of reactions

$$RX + Na \longrightarrow R\cdot + NaX$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

The deposit was transferred at −196° and under high vacuum to an esr sample tube. After examination at −196°, the sample was warmed *in situ* in the sample cavity of the esr spectrometer (Varian V-4500) to a temperature at which the peroxy radicals diffused in the matrix and underwent self-reaction.

It was originally intended to analyze the isotopic distribution of the oxygen evolved by mass spectrometry. However, it was found to be more convenient to perform this analysis by esr spectroscopy. This was because molecular oxygen is paramagnetic, and at low pressures (below *ca.* 2 Torr) its esr spectrum consists of very many sharp lines (over 100 have been observed) which arise because of coupling between the unpaired electrons and the rotational motion of the molecule. Because of this coupling, the esr spectra of $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$ are all different, and the relative amounts of each of the three molecules in a mixture can be determined from the relative intensities of their spectra. This method proved very successful for the present study, because the decay of the peroxy radicals and the oxygen evolution could be monitored simultaneously as the samples were warmed *in situ* in the spectrometer. The sensitivity of the method was high since an oxygen pressure of 0.1 Torr in a volume of 1.0 cc could easily be detected (equivalent to less than 10^{-9} mol of oxygen).

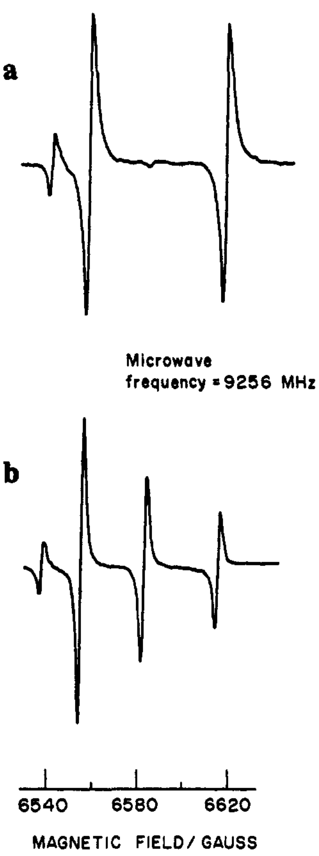


Figure 1. Part of the first derivative esr spectrum of (a) a 50:50 mixture of $^{32}O_2$ and $^{36}O_2$ (*ca.* 1 Torr) and (b) a 39:46:15 mixture of $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$. (The departure from the expected 25:50:25 mixture is caused by exchange with $^{32}O_2$ adsorbed on the walls of tube.)

A convenient part of the O_2 spectrum for isotopic analysis occurred between 6500 and 6650 G. In this region an equimolar mixture of $^{32}O_2$ and $^{36}O_2$ gave two well-spaced lines arising from the ($K = 1$, $J = 2$, $M = 0 \rightarrow 1$) transition[8] (Figure 1a). A line from $^{34}O_2$ occurred approximately midway between these lines (Figure 1b) and is tentatively attributed to the ($K = 2$, $J = 1$, $M = -1 \rightarrow 0$) transition.[9] Because different transitions are involved, the relative intensities of the three lines are not directly related to the relative concentrations of the three isotopic species. A calibration was obtained by using a sample which had been scrambled by a brief exposure to an electric discharge and which was checked by mass spectroscopic analysis.

Results and Discussion

Table I summarizes the isotopic distribution of molecular oxygen evolved during the self-reaction of several peroxy radicals of quite different structure. For each peroxy radical examined $^{34}O_2$ was observed in the oxygen evolved. For complete statistical scrambling, a ratio of 1:2:1 (25:50:25) would be expected for the amounts of $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$, respectively. The lower yields of $^{34}O_2$ relative to the unscrambled molecules was most probably a result of the release during annealing of $^{34}O_2$ and $^{36}O_2$, which had been trapped in the matrix during preparation and had not reacted to form peroxy radicals.

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(4) (a) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **85**, 2407 (1963); (b) T. G. Traylor, *ibid.*, **85**, 2411 (1963).

(5) Kiefer and Traylor[6] have stated that the self-reaction of secondary alkylperoxy radicals results in the production of scrambled oxygen. However, no experimental evidence has been offered to support this statement.

(6) H. Kiefer and T. G. Traylor, Abstract of paper presented to the International Symposium on the Chemistry of Organic Peroxides, Berlin-Adlershof, Sept 1967.

(7) J. E. Bennett, B. Mile, B. Ward, and A. Thomas, *Advan. Phys. Org. Chem.*, **8**, 1 (1970).

(8) M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, **97**, 951 (1955).

(9) K. D. Bowers, R. A. Kamper, and C. D. Lustig, *Proc. Roy. Soc., Ser. A*, **251**, 565 (1959).

Table I. Isotopic Distribution of Molecular Oxygen Evolved during the Self-Reactions of Some Peroxy Radicals

Peroxy radical	Relative yields of oxygen, %[a] $^{32}O_2$	$^{34}O_2$	$^{36}O_2$
2-Propyl	43	14	43
1-Butyl	47	6	47
2-Butyl	29	42	29
tert-Butyl	44	12	44
Cyclopentyl	29	42	29
Acetyl	29	42	29
2-Pyridyl	37	26	37

[a] Yields of $^{32}O_2$ and $^{36}O_2$ corrected to allow for departures from 1:1 ratio in original oxygen mixture.

For *tert*-butylperoxy radicals (which gave a particularly low ratio of scrambled to unscrambled oxygen) it was possible to prepare a mixture of $t\text{-Bu}^{16}O^{16}O\cdot$ and $t\text{-Bu}^{18}O^{18}O\cdot$ in the liquid phase by photolysis of a mixture of di-*tert*-butyl peroxide and isobutane in the presence of $^{32}O_2$ and $^{36}O_2$. This radical was quite stable below −100° and the solution could be thoroughly degassed between −196 and −100° without the loss of a significant fraction of the radicals. Thus the unreacted oxygen could be removed completely from the system. When this sample was warmed to a temperature at which the radicals underwent self-reaction, the oxygen evolved was scrambled statistically (25:50:25). This result would appear to confirm our suspicion that the low yields of $^{34}O_2$ observed for some of the radicals (Table I) were caused by unreacted oxygen trapped in the matrix.

The detection of $^{34}O_2$ from the self-reaction of primary, secondary, and tertiary alkylperoxy radicals in this work provides further evidence that the transition state for this reaction involves a head-to-head interaction between two radicals. The results also show that a similar interaction occurs for the acetylperoxy and 2-pyridylperoxy radicals, and thus it probably occurs for organic peroxy radicals in general.

Acknowledgment. We thank Messrs. C. P. Rimmer and R. Summers for assistance with the experimental work.

Controlled Interaction between Nucleic Acid Bases. Intramolecular Stacking Interactions between Two Adenine Rings[1-3]

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Contribution from the Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801.

Received November 6, 1972

Abstract: In order to determine the stacking interactions between two parallel adenine rings oriented at different axis angles toward each other, we have synthesized a series of six different trimethylenebisadenine isomers. The per cent hypochromism, *H*, for the long wavelength ultraviolet absorption band for each of these compounds has been determined by comparison of the ultraviolet spectrum of the trimethylenebisadenine in aqueous solution with the composite spectrum of the two "half" molecules, the appropriate propyladenines. The *H* values obtained thereby for the trimethylenebisadenines are the following: 9,9′ isomer, 15%; N^6,$N^{6\prime}$, 16%; 8.8′, 21%; N^6, 9′, 16%; 8,9′, 19%; 7,9′, 16%. The per cent hypochromism follows a dependence upon the folded conformations available to the individual trimethylenebisadenines and offers the possibility of assessing the degree and orientation of overlap permitted or excluded for different ranges of *H* values.

In 1954 we described the use of the trimethylene bridge, $-(CH_2)_3-$, as a synthetic spacer in the construction of compounds for the detection of intramolecular interaction between electron-donating and electron-accepting groups.[4] Later, we used the trimethylene bridge as a synthetic spacer to simulate intramolecular interactions between nucleic acid bases, as in $B\text{-}(CH_2)_3\text{-}B$, and between the component heterocyclic rings of certain coenzymes in aqueous solution.[5,6]

We considered that this chain length was particularly advantageous in permitting nearly plane-parallel stacking of the rings, a feature that was verified in aqueous solution by ultraviolet hypochromism,[6] in an ethylene glycol–water glass at low temperature by the emission spectral characteristics,[6] and in the crystal, for the case of 1,1′-trimethylenebisthymine, by the X-ray structure analysis.[7-11]

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(1) This work was supported by Research Grant No. USPHS-GM-05829 from the National Institutes of Health, U. S. Public Health Service.

(2) The present paper is no. XII in the series on Synthetic Spectroscopic Models Related to Coenzymes and Base Pairs.

(3) For the preceding paper (XI) in this series, see N. J. Leonard, R. S. McCredie, M. W. Logue, and R. L. Cundall, *J. Amer. Chem. Soc.*, **95**, 2320 (1973); see references therein.

(4) N. J. Leonard, R. C. Fox, M. Ōki, and S. Chiavarelli, *ibid.*, **76**, 630 (1954).

(5) N. J. Leonard, T. G. Scott, and P. C. Huang, *ibid.*, **89**, 7137 (1967).

(6) D. T. Browne, J. Eisinger, and N. J. Leonard, *ibid.*, **90**, 7302 (1968).

(7) J. K. Frank and I. C. Paul, *ibid.*, **95**, 2324 (1973).

(8) For similar stacking of rings in another trimethylene-bridged compound, 8,8′-trimethylenebistheophylline, as determined by X-ray structure analysis, see L. S. Rosen and A. Hybl, *Acta Crystallogr., Sect. B*, **27**, 952 (1971).

(9) The geometry for the case of two slightly deformed benzene rings held nearly plane parallel by two trimethylene bridges is described in the X-ray structure of [3,3]paracyclophane; see P. K. Gantzel and K. N. Trueblood, *ibid.*, **18**, 958 (1965); also D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954); D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959); D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951).

(10) The X-ray structure of janusene provides a case in which two benzene rings are held slightly tilted away from the plane-parallel arrangement, at interatomic distances 3.1–4.0 Å: see S. J. Cristol and