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O^{18} TRACER EVIDENCE OF THE TERMINATION MECHANISM IN THE AUTOXIDATION OF CUMENE

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The chain terminating step in many autoxidations is known from the non-dependence of rate on oxygen pressure to be an interaction of two alkylperoxy radicals.[1 - 4] Reaction (1) is considered to occur with tertiary $RO_2\cdot$ radicals[5], but the indicated re-formation of an oxygen molecule could not be demonstrated directly.

$$2\ ROO\cdot \longrightarrow O_2 + ROOR \qquad (1)$$

Also it has been unknown whether the two oxygen atoms which form the free oxygen molecule originate from the same alkylperoxy radical[6] or from different ones[5,7].

With the availability of 99.4% oxygen-18 in the form of molecular oxygen[8], (called here O* O*) a direct experimental answer to this question is now possible. Cumene, autoxidized with a known mixture of

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[1] E. J. Bowen and E. L. Tietz, J. Chem. Soc. 1930, 234.

[2] H. L. J. Bäckström, Z. phys. Chem. B 25, 99 (1934).

[3] C. H. Bamford and M. J. S. Dewar, Proc. Roy. Soc. A 198 252 (1949).

[4] C. Walling, Free Radicals in Solution. John Wiley and Sons, New York, 1957, pp. 418-427, 442-447.

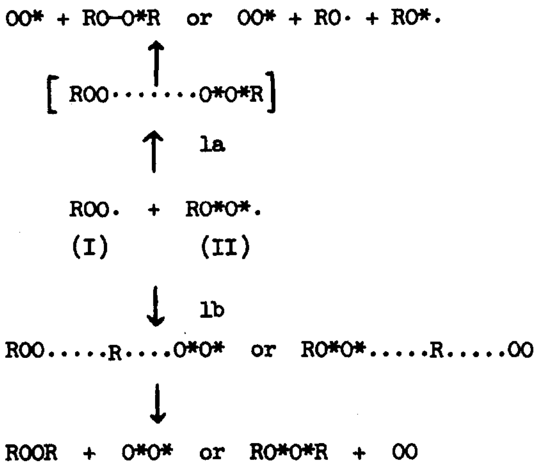
[5] G. A. Russell, J. Amer. Chem. Soc. 79, 3871 (1957).

[6] C. E. Boozer, B. W. Ponder, J. C. Trisler, and C. E. Wightman, ibid. 78, 1506 (1956).

[7] H. S. Blanchard, ibid. 81, 4548 (1959).

[8] Obtained from the Isotope Department, Weizmann Institute of Science, Rehovoth, Israel.

OO and O*O*, must form cumylperoxy radicals (I and II) each containing two identical oxygen atoms.



Reaction mode 1a, involving head-to-head reaction of I and II, must then produce the unsymmetrical oxygen -34 molecule, OO*, whereas any displacement mechanism such as 1b will produce only O_2^{32} (OO) and O_2^{36} (O*O*), without resulting equilibration with O_2^{34}.

Experimental conditions were chosen under which the organic products have already been investigated by Blanchard[7]. In a typical run, a reaction flask connected by a glass stopcock to an evacuable sampling lock was charged on the vacuum line with 41.3 ml of a solution of cumene (1.36 M) in chlorobenzene containing azobis-isobutyronitrile (AIBN) at a concentration of 0.0952 M. Into the 82-ml gas space ordinary oxygen, oxygen-36 (O*O*), and argon were introduced in the ratio of 25.40: 0.73: 4.36. The reaction was conducted in a thermostat at

59.85°C with vigorous magnetic stirring. Samples (0.66 ml) of gas were taken at time intervals as shown in Table 1, and the intensities of the peaks at masses 28, 32 34, 36, and 40 were recorded using a Consolidated Type 21-103C mass spectrometer. The analyses beyond the first were all evaluated relative to the argon which was taken as constant at 4.36×10^{-4} moles, based on the original composition at 25°. The amount of OO* (oxygen-34) initially present (0.113×10^{-4} moles) is close to that (0.112×10^{-4} moles) calculated from the natural abundance (0.204%) of O^{18} in ordinary oxygen, confirming the reported purity of the O*O*. From Table 1 it is evident that nitrogen is being evolved and that OO* (O_2^{34}) is appearing.

TABLE 1

Gas Composition During the Autoxidation of 1.36 M Cumene in Chlorobenzene Containing 0.0952 M AIBN at 59.85° (Run 1)

Time (sec)	Quantity of Gas in Moles x 10^4					
	N_2^{28}	O_2^{32} (x)	O_2^{34} (y)	O_2^{36} (z)	w= x+y+z	O^{18} Atom %
0	0.422	25.29	0.113	0.731	26.13	3.02
495	0.497	24.65	0.119	0.669	25.44	2.86
1200	0.639	23.64	0.133	0.666	24.44	2.99
2280	1.333	20.94	0.152	0.580	21.67	3.02
3750	1.95	18.09	0.173	0.485	18.75	3.05
5640	2.80	14.40	0.180	0.366	14.95	3.07
9240	4.23	7.99	0.158	0.176	8.424	3.07
13560	6.05	1.18	0.03	0.02		
16920	7.36	.14				
34560	13.8	.09				

We found no equilibration among the species OO, O*O*, and OO* on long standing, or during photooxidation of rubrene, or from thermal decomposition of rubrene peroxide or in presence of decomposing unlabeled t-butylhydroperoxide. Therefore, the appearance of O_2^{34} (OO*) is best accounted for as indicating the formation of oxygen molecules by path 1a in the course of chain termination. This interpretation is supported by the kinetic analysis of the results.

Under the experimental conditions nitrogen is evolved at a constant rate R_i and total oxygen is absorbed at a constant rate b. (From R_i we estimate a first-order rate constant of 1.20×10^{-5} sec $^{-1}$ for AIBN decomposition, to be compared with Russell's value[5] of 1.15×10^{-5}). Assuming the generally accepted[4] mechanism for cumene autoxidation, plus path 1a for chain termination, we can derive Equations 2 and 3 which are convenient for determining the rates C_w and G_w of consumption and generation, respectively, of oxygen during the experiment.

$$\ln \frac{f_y - (M_y)_o}{f_y - M_y} = \frac{G_w}{b} \ln \frac{w_o}{w} \qquad (2)$$

$$\ln \frac{z_o}{z} = \frac{C_w}{b} \ln \frac{w_o}{w} \qquad (3)$$

Here f_y is the probability that a terminating collision of two RO_2 radicals will be between a labeled and an unlabeled radical. This probability is taken as equal to $2\alpha(1-\alpha)$, where α is the atom-fraction of O^{18} in the total oxygen, and isotope effects are neglected. Total oxygen is $w = x+y+z$ (see Table 1) and M_y is the mole-fraction of O_2^{34} (OO*) in the oxygen.

Equations 2 and 3 afford independent determinations of G_w and C_w

from the measurements of masses 34 and 36 as functions of total oxygen. Since $b = C_w - G_w$, these results can be checked against each other. Figures 1 and 2 show the plots of Equation 2 and 3 for the run described and Table 2 lists the quantities entering into these equations and derived from them.

If AIBN produces free radicals with an efficiency e, and if β oxygen molecules are re-formed for each pair of kinetic chains which terminates, then $G_w = e\beta R_i$. The values of $e\beta$ from the "y" and "z" slopes are 13% apart, and agree approximately

TABLE 2

Kinetic Analysis of Data of Table 1

$\alpha = .0302$

$f_y = .0588$

$b = 1.98 \times 10^{-7}$ moles/sec

"y slope" $= \frac{G_w}{b} = .275$

"z slope" $= \frac{C_w}{b} = 1.244$

C_w from "z slope" $= 2.46 \times 10^{-7}$

$G_w = C_w - b = .48 \times 10^{-7}$

G_w from "y slope" $= .54 \times 10^{-7}$

$e\beta = \frac{G_w}{R_i}$

from "y slope" = 1.30

from "z slope" = 1.15

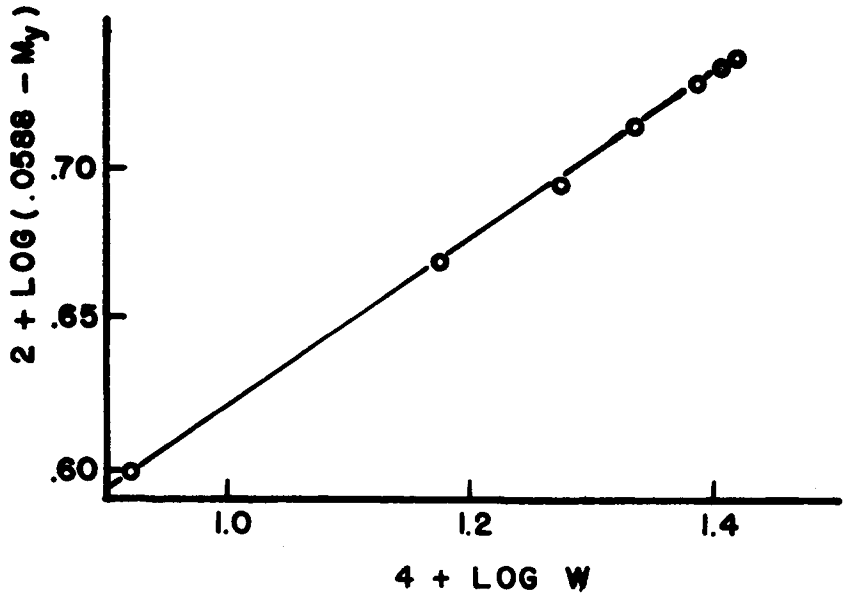


Figure 1. Plot of Equation 2 for O_2^{34} data.

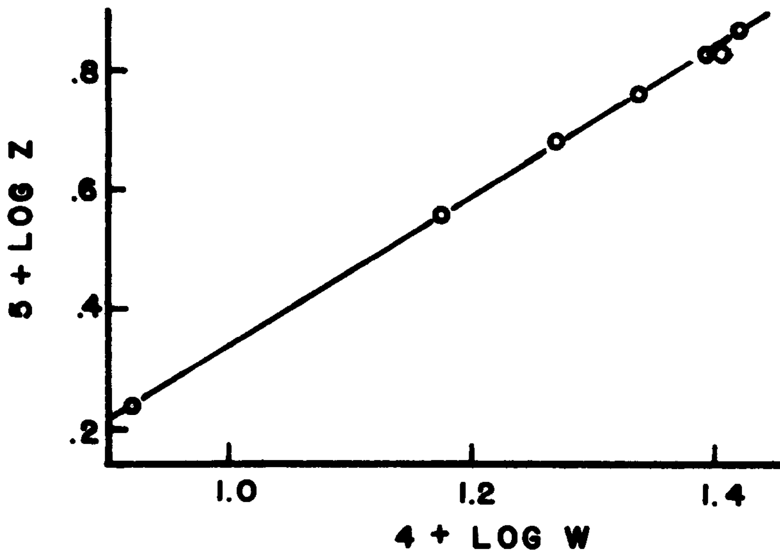


Figure 2. Plot of Equation 3 for O_2^{36} data.

(1.15 and 1.30 vs. 1.11) with the value estimated by Blanchard[7] from determination of the non-hydroperoxide products. Thus there is enough OO* produced in our experiments to account for <u>all</u> chain termination as proceeding by reaction path 1a, and likewise for that extra oxygen evolution, deduced by Blanchard, which is accompanied by the formation of cumyloxy radicals and acetophenone molecules rather than by chain-terminating R_2O_2 formation. The facts are well accommodated by the sequence

$$2\,RO_2 \longrightarrow ROOOOR \qquad (4)$$

$$ROOOOR \longrightarrow O_2 + [2RO\cdot] \qquad (5)$$

$$[2RO\cdot] \longrightarrow ROOR \qquad (6a)$$

$$[2RO\cdot] \longrightarrow CH_3COC_6H_5 + CH_3\cdot \qquad (6b)$$

If we adopt a value of 0.60 for e, as Blanchard does, then our two values of β are 1.92 and 2.17. If the species $[2RO.]$ of Equations 5 and 6 is a radical pair in a solvent cage, then its efficiency of escape is 48-54%, a normal value. Actually, the circumstances of Reaction 5 are enough like those of the original breakdown of AIBN so that the fate of the radical pair produced might be determined in an entirely similar way by the cage effect.

Details of the experiments over a range of conditions, kinetic derivations, and application of the method to other cases, will be described in a forthcoming publication.

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