(6) A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964).
(7) J. A. Deyrup and R. B. Greenwald, *J. Am. Chem. Soc.*, **87**, 4538 (1965), and references contained therein.
(8) For a variation, see D. Seyferth and W. Tronich, *J. Organomet. Chem.*, **21**, P-3 (1970); D. Seyferth, W. Tronich, and H. Shih, *J. Org. Chem.*, **39**, 158 (1974).
(9) H. E. Zaugg and R. W. Denet, *J. Org. Chem.*, **36**, 1937 (1971).
(10) F. W. Fowler, *Adv. Heterocycl. Chem.*, **13**, 45 (1971).
(11) N. G. Leonard and B. Zwanenburg, *J. Am. Chem. Soc.*, **89**, 4456 (1967).
(12) K. Bunge, R. Huisgen, R. Raab, and H. Stang, *Ber.*, **105**, 1279 (1972).
(13) A. M. von Leusen, B. E. Hoagenboom, and H. Siderius, *Tetrahedron Lett.*, 2369 (1972).
(14) S. H. Pines, *J. Org. Chem.*, **38**, 3854 (1973).
(15) A. Padwa, D. Dean, and J. Smolanoff, *Tetrahedron Lett.*, 4087 (1972).
(16) F. W. Fowler and A. Hassner, *J. Am. Chem. Soc.*, **90**, 2875 (1968).
(17) S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jpn.*, **40**, 2938 (1967).
(18) H. M. Kissman, D. S. Tarbell, and J. Williams, *J. Am. Chem. Soc.*, **75**, 2959 (1953).
(19) Solubility in alcohol: sodium azide (0.314 g/100 g); lithium azide (20.26 g/100 g).
(20) R. E. Brooks, J. O. Edwards, G. E. Levey, and F. Smyth, *Tetrahedron*, 1279 (1966).
(21) K. Ichimura and M. Ohta, *Tetrahedron Lett.*, 807 (1966); *Bull. Chem. Soc. Jpn.*, **40**, 1933 (1967).
(22) R. Nicoletti and M. L. Forcellese, *Tetrahedron Lett.*, 153 (1965).
(23) This steric preference has been previously observed in hydride and Grignard additions to azirines: ref 16.
(24) (a) H. W. Heine, *Angew. Chem., Int. Ed., Engl.*, **1**, 528 (1962); (b) *J. Am. Chem. Soc.*, **85**, 2743 (1963); (c) H. W. Heine, D. C. King, and L. A. Portland, *J. Org. Chem.*, **31**, 2662 (1966); (d) H. W. Heine and M. S. Kaplan, *ibid.*, **32**, 3069 (1967).
(25) (a) D. W. Kashelikar and P. E. Fanta, *J. Am. Chem. Soc.*, **82**, 4930 (1960); (b) P. E. Fanta and M. K. Kathan, *J. Heterocycl. Chem.*, **1**, 293 (1964); (c) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1965); **31**, 59 (1966); (d) I. J. Burnstein, P. E. Fanta, and B. S. Green, *ibid.*, **35**, 4085 (1970).
(26) (a) Y. Iwakura, A. Nabeya, and T. Nishiguchi, *J. Org. Chem.*, **32**, 2362 (1967); (b) T. Nishiguchi and Y. Iwakura, *ibid.*, **35**, 1591 (1970); (c) T. Nishicuchi, Tochio, A. Nabeya, and Y. Iwakura, *J. Am. Chem. Soc.*, **91**, 5835, 5841 (1969).
(27) (a) P. Scheiner, *J. Org. Chem.*, **32**, 2628 (1967); (b) T. A. Foglia, L. M. Gregory, and G. Maerkel, *ibid.*, **35**, 3779 (1970); (c) W. L. Nelson and B. E. Sherwood, *ibid.*, **39**, 66 (1974); (d) D. Haidukewych and A. I. Meyers, *Tetrahedron Lett.*, 3031 (1972).
(28) A. Hassner and A. B. Levy, *J. Am. Chem. Soc.*, **93**, 5469 (1971).
(29) (a) The assignment is based on the magnetic anisotropic effect of the 2-phenyl group. (b) S. J. Brois, *J. Org. Chem.*, **27**, 3532 (1962). We have observed resonances generally 0.3 ppm to lower field than that reported for compounds in this paper.
(30) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, Calif., 1964, Chapter 7.
(31) This is consistent with spectra of the 2-oxazolidones. S. L. Spassov, J. N. Stefanofsky, B. J. Kurtev, and G. Fodor, *Chem. Ber.*, **105**, 2462 (1972).
(32) (a) W. W. Heine, D. C. King, and L. A. Portland, *J. Org. Chem.*, **31**, 2662 (1966); (b) A. Hassner and S. S. Burke, *Tetrahedron*, in press.
(33) All melting points were recorded on a Fisher-Johns melting point block and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrometer; mass spectra were recorded on a Varian MAT CH-5 instrument. NMR spectra were obtained using Varian A-60A and EM 360 spectrometers with Me_4Si as internal standard. Microanalysis was performed by Atlantic Microlabs, Atlanta, Ga.
(34) J. H. Burckhalter and R. C. Fuson, *J. Am. Chem. Soc.*, **70**, 4184 (1948).
(35) M. Bachstez, *Chem. Ber.*, **47**, 3163 (1914).

Radical-Induced Decomposition of Peracetic Acid[1,2]

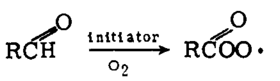
R. A. Kenley and T. G. Traylor*

Contribution from the Department of Chemistry, Revelle College, University of California, San Diego, La Jolla, California 92037.

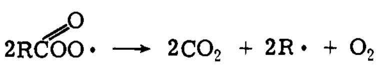
Received December 17, 1974

Abstract: The induced decomposition of peracetic acid in acetic acid can be initiated by sources of *tert*-butoxy radicals. This decomposition, studied in the presence of either pure $^{36}O_2$ or pure $^{32}O_2$, is shown to involve the formation of acetyl tetroxide in the same way as does the termination step in acetaldehyde autoxidation. These results confirm the mechanism of interaction of acetylperoxy radicals previously proposed.

The previous papers[3-5] reported studies of the interactions of acylperoxy radicals which are intermediates in aldehyde autoxidation.



$$\mathrm{RC(=O)H} \xrightarrow[\mathrm{O_2}]{\text{initiator}} \mathrm{RC(=O)OO\cdot} \tag{1}$$



$$\mathrm{2RC(=O)OO\cdot} \longrightarrow \mathrm{2CO_2} + \mathrm{2R\cdot} + \mathrm{O_2} \tag{2}$$

To further document reaction 2 and the fate of the resulting alkyl radicals we have sought an alternate source of acylperoxy (in this case acetylperoxy) radicals from induced peracid decomposition.

$$\mathrm{CH_3C(=O)OOH} + t\text{-}\mathrm{BuO\cdot} \longrightarrow \mathrm{CH_3C(=O)OO\cdot} + t\text{-}\mathrm{BuOH} \tag{3}$$

The analogous induced decomposition of *tert*-butyl hydroperoxide[6-8] had been used to study the interaction of *tert*-butylperoxy radicals as an alternative to the autoxidation of isobutane.[9] The reaction sequence is, in this case, very simple[6] ($(CH_3)_3COMMOC(CH_3)_3$ is the initiator where MM is $-N_2-$ or $-OC(O)C(O)O-$).

$$\mathrm{(CH_3)_3COMMOC(CH_3)_3} \longrightarrow \mathrm{2(CH_3)_3CO\cdot} + \mathrm{2M\ or\ MM} \tag{4}$$

$$\mathrm{(CH_3)_3COOH} + \mathrm{RO\cdot} \longrightarrow \mathrm{ROH} + \mathrm{(CH_3)_3COO\cdot} \tag{5}$$

$$\mathrm{2(CH_3)_3COO\cdot} \rightleftharpoons \mathrm{(CH_3)_3COOOOC(CH_3)_3} \longrightarrow [\mathrm{(CH_3)_3CO\cdot O_2\cdot OC(CH_3)_3}]_{\mathrm{cage}} \tag{6}$$

$$[\mathrm{(CH_3)_3CO\cdot O_2\cdot OC(CH_3)_3}]_{\mathrm{cage}} \xrightarrow[\text{and termination}]{\text{cage collapse}} \mathrm{(CH_3)_3COOC(CH_3)_3} \tag{7}$$

$$[\mathrm{(CH_3)_3CO\cdot O_2\cdot OC(CH_3)_3}]_{\mathrm{cage}} \xrightarrow[\text{and propagation}]{\text{diffusion}} \mathrm{2(CH_3)_3CO\cdot} + \mathrm{O_2} \tag{8}$$

This sequence is similar to that found in cumene autoxidation.[10,11]

Because reaction 2 leads to acylperoxy radicals which decarboxylate rapidly, we expect the induced decomposition of peracids to be more complex. But we should find the same oxygen and carbon dioxide evolution as that observed in acetaldehyde autoxidation if the proposed mechanisms are correct. In addition, ^{18}O labeling experiments afford some information not available from autoxidation studies, as we shall see.

But we and others[12] have previously attempted the induced decomposition without success. First, the OH bond is stronger in peracids than in hydroperoxides, and there is strong hydrogen bonding[13] in peracids which would further reduce the reactivity of the O–H bond. Second, there ap-

Table I. Yields of Acetone and *tert*-Butyl Alcohol from Induced Decompositions of Peracetic Acid, Initiated by DBH or DBPO

Solvent	Temp of decomposition, °C	[HOOAc],[a] *M*	Yield acetone[b]	Yield TBA[b]	% acetone[c]
Benzene	45	0	5.70	3.60	61.0
	45	0.257	4.19	8.60	32.8
	45	0.466	6.15	16.5	27.2
	45	0.888	6.18	16.6	27.2
	45	1.12	4.00	13.7	22.5
Acetic acid	52	0	39.4	2.90	94.3
	52	1.0	23.4	19.3	54.8
d	25	1.35	117	121	49.3
	52	3.0	19.6	25.7	43.5

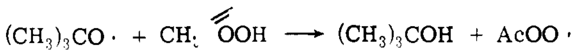
[a] Benzene solutions prepared by procedure B (see Experimental Section). [b] Yields of acetone and *tert*-butyl alcohol in units of $M \times 10^3$ for decompositions in benzene, yields in GLC peak area units corrected for GLC sensitivity for decomposition in acetic acid. [c] % acetone = (100)(yield acetone)/(yield acetone + yield *tert*-butyl alcohol). [d] This decomposition was initiated by DBPO, all others by DBH.

pear to be ionic[14] and/or trace metal catalyzed[15] peracid decompositions which might interfere.

We have overcome these difficulties by using relatively high peracetic acid concentrations and rather low temperatures, and have discovered a short chain decomposition of peracetic acid in both benzene and acetic acid.

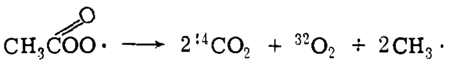
This discovery makes possible the separate examination of acetylperoxy and methylperoxy radicals by using doubly labeled molecular oxygen and unlabeled peracid (M = CO_2 or N)

$$(CH_3)_3COMMOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot + 2M \text{ or } M_2 \quad (4)$$



$$(CH_3)_3CO\cdot + CH_3C(=O)OOH \longrightarrow (CH_3)_3COH + AcOO\cdot$$

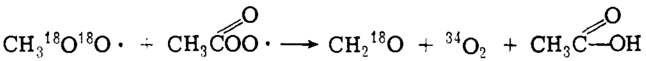
(3)



$$CH_3C(=O)OO\cdot \longrightarrow 2\,{}^{14}CO_2 + {}^{32}O_2 + 2CH_3\cdot$$

(9)

$$CH_3\cdot + {}^{18}O^{18}O \longrightarrow CH_3{}^{18}O^{18}O\cdot \quad (10)$$



$$CH_3{}^{18}O^{18}O\cdot + CH_3C(=O)OO\cdot \longrightarrow CH_2{}^{18}O + {}^{34}O_2 + CH_3C(=O){-}OH$$

(11)

$$CH_3{}^{18}O^{18}O\cdot + CH_3{}^{18}O^{18}O\cdot \longrightarrow {}^{36}O_2 + CH_2{}^{18}O + CH_3{}^{18}OH \quad (12)$$

We report here the demonstration of induced decomposition, the study of carbon dioxide evolution by GLC and by mass spectrometry, and oxygen exchange, using oxygen labeling experiments.

Experimental Section

Materials. Benzene, di-*tert*-butyl peroxyoxalate (DBPO), di-*tert*-butyl hyponitrite (DBH), labeled oxygen (98.907% $^{36}O_2$), and other reagents were the same as those used in the previous paper.[3-5] Glacial acetic acid (B.A. Reagent) was distilled before use.

Peracetic acid solutions were prepared by methods of Swern.[16] For anhydrous solutions in benzene, 7.1 g of 53.6% peracetic acid solution in water was added dropwise into a stirred slurry of 10 g of phosphorus pentoxide in 250 ml of benzene at 0°. This slurry was then filtered, titrated, and found to be 0.21 *M* in peracid.

Because this solution could not be concentrated without decomposition, more concentrated solutions were made by adding 90% peracetic (3.5 g) acid to 25 ml of stirred benzene, cooling to 5°, and removing the water layer. The benzene solution was then titrated for peracid by the iodide method.[13]

The 90% peracetic solution above was found by ceric ion titration to contain less than 0.2% hydrogen peroxide. Solutions in acetic acid were made by adding the proper amounts of this solution and titrating the resulting solutions for peracid.

Apparatus. Gas-liquid phase chromatographic analyses for acetone, *tert*-butyl alcohol, and carbon dioxide were performed as described in the second paper of this series.[4] The GLC kinetic experiments were also carried out in the apparatus described there.

Mass spectra were taken on an LKB Model 9000 GC-mass spectrometer.

The kinetic experiments involving mass spectra were carried out in the apparatus shown in Figure 1 which is similar to that reported previously.[11,17]

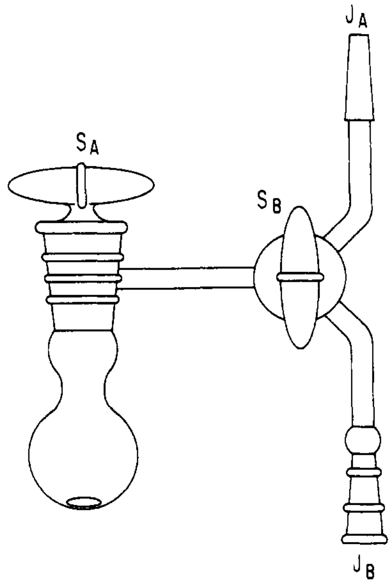


Figure 1. Reaction flask used in mass spectral determination of gas evolution and exchange during peracetic acid decomposition. This flask, similar to those previously described, has an internal volume of 43.24 ml and a sampling space between the stopcocks S_A and S_B of 1.03 ml.

Reactivity of Peracetic Acid. In order to show that *tert*-butoxy radicals from the initiators di-*tert*-butyl hyponitrite (DBH)[18] or di-*tert*-butyl peroxyoxalate (DBPO)[19] abstract the O-H hydrogen from peracid, these initiators were decomposed for 6-8 half-lives in benzene and acetic acid with and without added peracetic acid. The solutions were then analyzed by GLC for acetone and *tert*-butyl alcohol. The results are tabulated in Table I.

Initiated CO_2 Evolution. To show that the postulated reaction 3 leads to CO_2 evolution, solutions of peracetic acid in benzene or in acetic acid were kept at constant temperature for some period of time during which GLC analyses for CO_2 were made as previously described.[3] Then, initiator was added (see ref 2) and the analyses were continued. The amounts of evolved CO_2, calculated using the appropriate corrections for GLC sensitivity, etc., as previously described,[3,4] are plotted vs. time in Figures 2 and 3.

The CO_2 evolution from decomposition of 6.5×10^{-3} *M* DBPO in acetic acid at 25° in the absence of peracid was followed in the same way. The rate of CO_2 evolution was 1.77×10^{-7} *M* sec^{-1}. In a separate experiment 1% water (based on the solvent) was added in the middle of the run without effect on this rate.

Mass Spectral Rate Studies, CO_2 and O_2 Evolution. The technique is similar to those previously described.[4,11] Typically the initiator was weighed into the flask followed by the addition of the appropriate solution (19.78 ml) using a calibrated syringe[19] equipped with polyethylene needle. The flask was closed and the solution was frozen quickly in a Dry Ice-acetone bath, evacuated, and carried through four freeze-evacuate-thaw cycles. With the

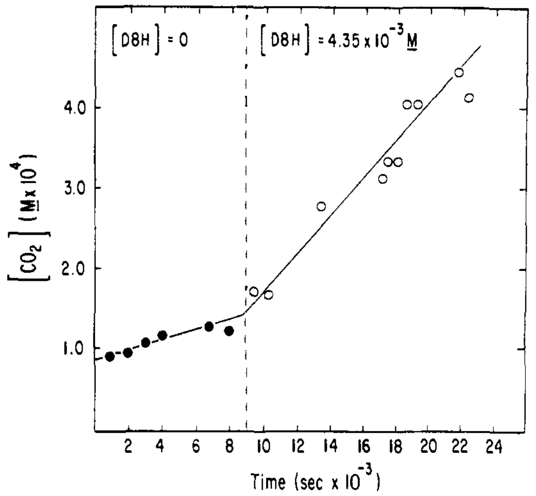


Figure 2. Concentrations of CO_2 evolved vs. time for 0.21 M peracetic acid in benzene solution at 45°: ●, no initiator added (slope = 0.472×10^{-7} M sec^{-1}); ○, with 4.35×10^{-3} M DBH added (slope = 2.08×10^{-7} M sec^{-1}) (analysis: GLC).

flask evacuated and cooled in liquid nitrogen, the argon standard was introduced in 1.03-ml aliquots as follows. The stopcock S_A was closed and 1 atm of argon was allowed into the 1.03 ml evacuated space between S_A and S_B. After closing S_B, this aliquot was admitted into and condensed in the flask by opening S_A. Repetition of this procedure allowed any number of 1.03-ml aliquots of argon (or other gases) to be admitted. Either normal or 99% labeled oxygen was then introduced from either J_A or J_B in a similar manner. The amounts introduced were determined by mass spectrometer comparisons with the known amounts of argon. The flask was then brought quickly to the desired temperature and stirred, and samples of 1.03 ml each of gas were removed for analyses as previously described.

To convert observed peak heights (H_i) to moles of gases we first determined the amount of argon initially added (N_{Ar}^{init}) by multiplying the number of moles of argon in 1.03 ml at 1 atm by the number of aliquots admitted. This, and all other amounts, was divided by the solution volume to express all amounts in moles/liter. Then, for any point, n, the amount of argon is N_{Ar}^{init} minus that removed by sampling. Therefore the argon peak height must be multiplied by the factor

$$F = \frac{\text{(volume of gas)}}{\text{(volume of gas)} - (n-1)1.03} \tag{13}$$

in order to relate the H_{Ar} to N_{Ar}^{init}, which is known. Similarly, an amount of gas i, given approximately by

$$\text{correction for gas } i = \frac{1.03}{\text{volume of gas}} \sum_{n=1}^{n} (N_i)_{n-1} \tag{14}$$

must be added to the observed value at point n. The amount of gas $(N_i')_n$ at point n then becomes

$$(N_i')_n = (\text{sens})_i \left(\frac{H_i'}{H_{40}}\right) \frac{N_{Ar}^{init}}{F} (\text{sol})_i + \frac{1.03}{\text{volume gas phase}} \sum_{n=1}^{n} (N_i)_{n-1} \tag{15}$$

The corrected peak heights (H_i') are obtained from the observed peak heights (H_i) by subtracting contributions from fragments or isotope accompanying higher molecular weight as follows:

$$H_{28}' = H_{28} - H_{28}^{\text{background}} - (0.062)H_{44} \tag{16}$$

$$H_{44}' = H_{44} - H_{44}^{\text{background}} \tag{17}$$

$$H_{36}' = H_{36} - (0.0038)H_{40} \tag{18}$$

The correcting factor $(\text{sol})_i$ is necessary for carbon dioxide because of its high solubility in acetic acid (α = 2.68 ml/ml solution at 45° and α = 4.29 ml/ml solution at 25°)[20] and in acetic acid containing 0.7 M peracetic acid (α = 3.50 ml/ml solution at 25°).

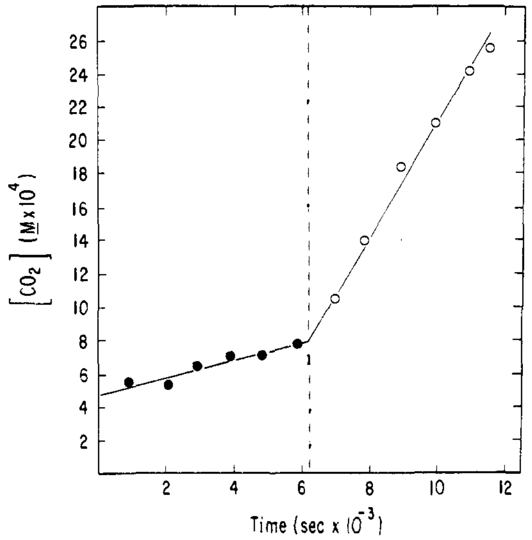


Figure 3. Concentrations of CO_2 evolved vs. time for 0.65 M peracetic acid in acetic acid at 25°C; ●, no initiator added (slope = 0.527×10^{-7} M sec^{-1}); ○, with 5.75×10^{-3} M DBPO added (slope = 3.37×10^{-7} M sec^{-1}). Slope calculated for CO_2 from DBPO decomposition = 1.61×10^{-7} M sec^{-1} (analysis: GLC).

$$(\text{sol})_i = \frac{\text{volume of gas phase} + \alpha_i \text{ (volume of solution)}}{\text{volume of gas phase}} \tag{19}$$

The term $(\text{sens})_i$ is the sensitivity of gas i to the mass spectrometer under the conditions used.

$$(\text{sens})_i = \left(\frac{\text{moles } i}{\text{moles Ar}}\right)\left(\frac{H_{Ar}}{H_i}\right) \tag{20}$$

The $(\text{sens})_i$, determined by taking the mass spectra of mixtures of gases i with argon, are listed in the tables.

The efficiencies of initiation were calculated from the cage effect data of Kiefer and Traylor[18] and the viscosities of solvents used (e = 0.83 in acetic acid at 25°).[21]

First, the decomposition of DBPO in acetic acid alone was followed. The data are tabulated in Table II and plotted in Figure 4.

The same mass spectra method was used to determine the oxygen and carbon dioxide concentrations as a function of time during the induced decomposition of peracetic acid under $^{32}O_2$ using DBPO and DBH. These data are plotted in Figures 5 and 6.

Labeling Experiment. Decomposition of a 0.70 M solution of peracetic acid in acetic acid, similar to that shown in Figure 5, was repeated using about 99% $^{36}O_2$ instead of $^{32}O_2$. The peak heights, H_i observed at various sampling times, are listed in Table III and calculated amounts of gases are listed in Table IV. The amounts of gases are plotted vs. time in Figure 7.

Discussion

Because peracids have strong (perhaps 6–7 kcal/mol) internal hydrogen bonds[13b] and have not previously displayed the kind of induced decomposition shown by alkyl hydroperoxides, we must first provide evidence that the reaction we are studying here is indeed begun by the abstraction step shown in reaction 3 rather than the several other possibilities which might also result in some CO_2 evolution. We could imagine the following processes (eq 21–25).

First, it is clear from Table I that *tert*-butoxy radicals get hydrogen somewhere when peracetic acid is present but mostly decompose to acetone (eq 22) in acetic acid. Table I shows the yield of acetone decreasing from 94% in pure acetic acid to 50% in 1 M peracetic acid. This result excludes reaction 21 because the reactivities of acetic and peracetic

Table II. Observed Peak Heights (H_i) and Calculated Concentrations (N_i') for Decomposition of 7.5 × 10^{-3} M DBPO in Acetic Acid at 25° under $^{32}O_2$[a,b]

		Observed peak heights				Calculated concentrations	
n	Time, sec	BG_{44}	H_{32}	H_{40}	H_{44}	N_{32}', M × 10^4	N_{44}', M × 10^4
1	1000	3.5	1762	1034	36.1	136[c]	6.14
2	2000	4.6	1641	987	48.9	133	8.45
3	3000	3.8	1641	991	57.1	132	9.70
4	5000	5.1	1629	841	67.1	130	12.7
5	6000	5.2	1368	881	86.2	129	15.0
6	7000	17.1	1611	967	115.4	127	15.8
7	8000	5.0	1558	395	79.0	128	26.5

[a] As determined by mass spectrometry. [b] Experimental parameters: $(\text{sens})_{O_2} = 1.28$, $(\text{sens})_{CO_2} = 0.685$, $\alpha_{CO_2} = 4.28$; volume solution = 19.78 ml, $N_{Ar}^{init} = 6.25 \times 10^{-3} M$. [c] $136 \times 10^{-4} M = 0.33$ atm of $^{32}O_2$ at 25°.

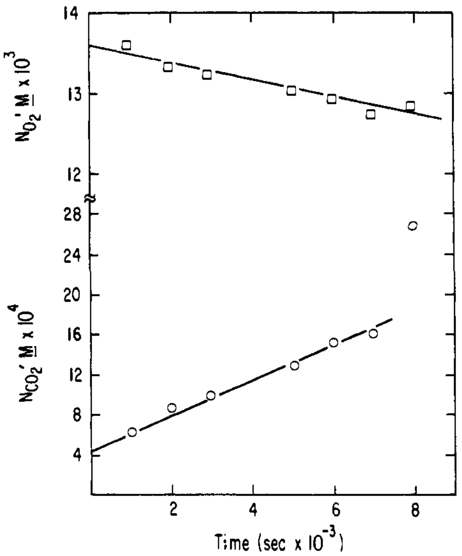


Figure 4. Concentrations of $^{44}CO_2$ (N_{CO_2}') and $^{32}O_2$ (N_{O_2}') vs. time for 7.3 × 10^{-3} M DBPO in acetic acid solution under $^{32}O_2$ at 25°: ○, $^{44}CO_2$ (slope = 1.73 × 10^{-7} M sec^{-1}); □, $^{32}O_2$ (slope = −1.37 × 10^{-7} M sec^{-1}); $2k_{DBPO}[DBPO] = 2.11 \times 10^{-7}$ M sec^{-1} (analysis: mass spectra).

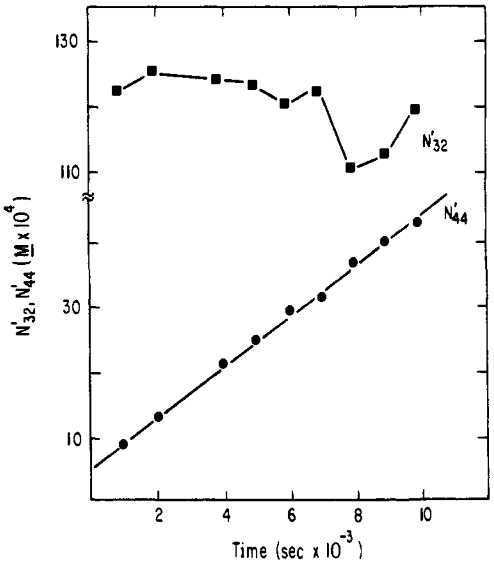
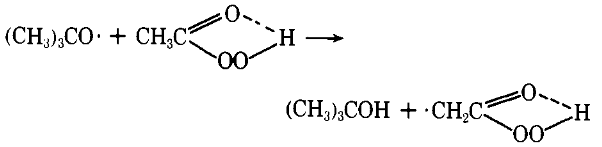
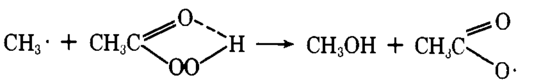
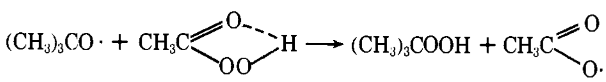


Figure 5. Concentrations of $^{44}CO_2$ (N_{44}') and $^{32}O_2$ (N_{32}') vs. time for 1.2 M peracetic acid in acetic acid solution under $^{32}O_2$ at 25° with 7.14 × 10^{-3} M DBPO as initiator: ●, $^{44}CO_2$ (slope = 3.76 × 10^{-7} M sec^{-1}); ■, $^{32}O_2$; R_i = 1.64 × 10^{-7} M sec^{-1}, $(d[CO_2]/dt)_{calcd}$ = 2.00 × 10^{-7} M sec^{-1}.


$$(CH_3)_3CO\cdot + CH_3C(=O\cdots H)OO \longrightarrow (CH_3)_3COH + \cdot CH_2C(=O\cdots H)OO \quad (21)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + (CH_3)_2CO \quad (22)$$


$$CH_3\cdot + CH_3C(=O\cdots H)OO \longrightarrow CH_3OH + CH_3C(=O)O\cdot \quad (23)$$


$$(CH_3)_3CO\cdot + CH_3C(=O\cdots H)OO \longrightarrow (CH_3)_3COOH + CH_3C(=O)O\cdot \quad (24)$$

$$(CH_3)_3CO\cdot + (CH_3)_3COOH \longrightarrow (CH_3)_3COH + (CH_3)_3COO\cdot \quad (25)$$

acids could not differ greatly toward this process. The reaction of methyl radicals with the peroxy oxygen according to reaction 23 can be excluded by referring to the decomposition of di-*tert*-butyl peroxyoxalate (DBPO) in acetic acid. Among peroxides, DBPO is perhaps the most sensitive toward induced decomposition by alkyl radicals in reactions analogous to reaction 23. Yet we (and others) observe that its induced decomposition is effectively inhibited by the presence of molecular oxygen which reacts rapidly with alkyl radicals. (In all our studies molecular oxygen was present.) Compare the CO_2 evolution rate observed in the decomposition of 6.5 × 10^{-3} M DBPO in acetic acid, 1.77

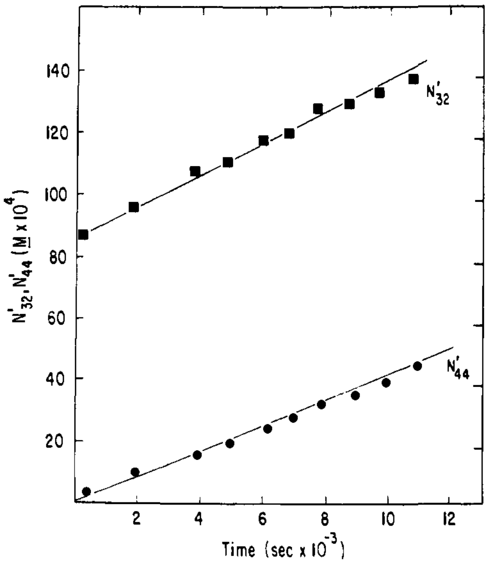


Figure 6. Concentrations of $^{44}CO_2$ (N_{44}') and $^{32}O_2$ (N_{32}') vs. time for 1.96 M peracetic acid in acetic acid under $^{32}O_2$ at 45° with 2.98 × 10^{-3} M DBH as initiator: ●, $^{44}CO_2$ (slope = 3.75 × 10^{-7} M sec^{-1}); ■, $^{32}O_2$ (slope = 4.45 × 10^{-7} M sec^{-1}); R_i = 1.42 × 10^{-7} M sec^{-1}.

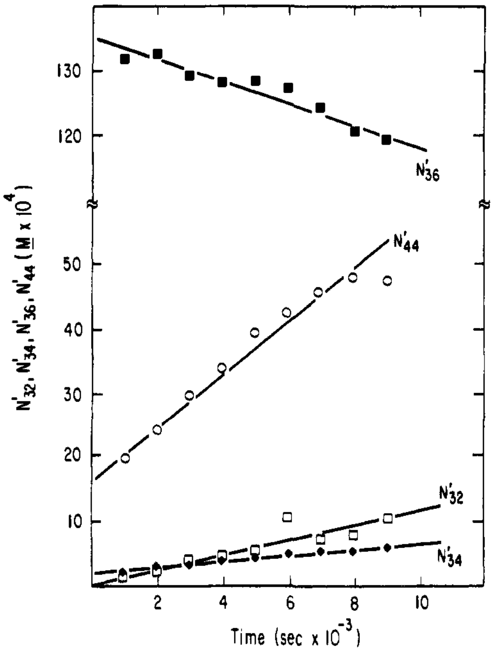


Figure 7. Concentrations (N_i') of $^{44}CO_2$, $^{32}O_2$, $^{34}O_2$, and $^{36}O_2$ vs. time for induced decomposition of 0.70 *M* peracetic acid in acetic acid solution under $^{36}O_2$ at 25° with 7.60 × 10^{-3} *M* DBPO as initiator: ■, $^{36}O_2$ (slope = −1.64 × 10^{-7} *M* sec^{-1}); ○, $^{44}CO_2$ (slope = 4.13 × 10^{-7} *M* sec^{-1}); □, $^{32}O_2$ (slope = 1.04 × 10^{-7} *M* sec^{-1}); ◆, $^{34}O_2$ (slope = 0.431 × 10^{-7} *M* sec^{-1}); $(d[CO_2]/dt) = k_{init}[DBPO] = 2.15 \times 10^{-7}$ *M* sec^{-1}, $R_i = 1.76 \times 10^{-7}$ *M* sec^{-1}.

Table III. Observed Peak Heights (H_i) for Various Gases from the Induced Decomposition of 0.70 *M* Peracetic Acid in Acetic Acid Solution under $^{36}O_2$ at 25°, Initiated by 7.60 × 10^{-3} *M* DBPO[a]

Time, sec	BG_{32}	BG_{44}	H_{32}	H_{34}	H_{36}	H_{40}	H_{44}	H_{46}
1000	2.5	8.1	18.1	32.6	1869	1669	132	2.31
2000	3.1	7.8	34.0	40.5	1841	1638	162	2.11
3000	2.7	7.8	48.7	46.2	1750	1602	203	1.79
4000	2.4	9.7	57.2	49.1	1588	1478	221	2.17
5000	2.8	9.0	65.8	50.0	1428	1315	242	2.12
6000	2.2	6.3	153	57.0	1418	1319	273	2.02
7000	3.0	2.7	87.1	59.7	1289	1230	289	1.97
8000	2.7	2.6	97.2	62.3	1232	1210	315	1.85
9000	7.3	4.0	126	70.9	1057	1045	282	1.66

[a] As determined by mass spectrometry.

× 10^{-7} *M* sec^{-1}, with that calculated from the published first-order decomposition rate at 25° which is 1.82 × 10^{-7} *M* sec^{-1}.

Reaction 24 can be excluded on the same grounds. Neither peroxy nor oxy radicals induce the decompositions of peresters, DBPO, etc. In addition, reactions 24 and 25, although plausible, would not give the ^{18}O labeling results reported here.

We conclude that any CO_2 evolved which is in excess of that from DBPO must come from reaction 3 or from some decomposition not initiated by DBPO (or DBH). Plots of CO_2 concentrations vs. time shown in Figures 2 and 3 indicate that the rate of CO_2 evolution is indeed greatly increased by the addition of the initiators DBH or DBPO. Even though peracid solutions in benzene or acetic acid decompose slowly at 25° without initiator, this decomposition increases by a factor of 3.5 in the presence of 5.75 × 10^{-3} *M* DBPO (see Figure 3) after correcting for the CO_2 evolution from DBPO.

Table IV. Calculated Concentrations (N_i') of Various Gases from the Induced Decomposition of 0.70 *M* Peracetic Acid in Acetic Acid Solution at 25°, Initiated by 7.60 × 10^{-3} *M* DBPO[a, b]

		N_i', *M* × 10^4					
n	Time, sec	*F*	N_{32}'	N_{34}'	N_{36}'	N_{44}'	N_{46}'
1	1000	1.0	1.11	2.29	131.4[c]	19.6	0.341
2	2000	1.045	2.18	2.89	132.5	23.7	0.302
3	3000	1.095	3.24	3.34	129	29.2	0.253
4	4000	1.149	4.10	3.79	128	33.5	0.320
5	5000	1.210	5.14	4.25	128	39.1	0.332
6	6000	1.277	10.4	4.72	127	41.9	0.302
7	7000	1.353	6.90	5.15	124	45.2	0.299
8	8000	1.437	7.63	5.34	120	47.6	0.282
9	9000	1.533	10.28	5.80	119	46.9	0.268

[a] Experimental parameters: $(sens)_{O_2} = 1.39$, $(sens)_{CO_2} = 0.749$, $\alpha = 3.50$, $N_{Ar}^{init} = 8.30 \times 10^{-3}$ *M*. [b] See text for definitions. [c] 131 × 10^{-4} *M* = 0.31 atm $^{36}O_2$ at 25°.

Mass Spectral Method. As a test of the method the evolution of carbon dioxide and consumption of oxygen during the decomposition of DBPO in acetic acid were followed by the mass spectral method described previously. The results, plotted in Figure 4, agree with previous decompositions in benzene, although the observed rate of CO_2 evolution is somewhat lower than that calculated from the amount of DBPO added (1.7 × 10^{-7} *M* sec^{-1} compared with 2.11 × 10^{-7} *M* sec^{-1}). However, the method clearly gives approximate rate data even for small amounts of CO_2 evolution. The observed consumption of oxygen is to be expected from oxidation of the 94% yield of methyl radicals produced in this decomposition.[2] When this decomposition was repeated in the presence of 1.2 *M* peracetic acid the results of Figure 5 were obtained. The oxygen uptake, although showing some scatter, seems to be very slight. This will be seen (below) to result from oxygen evolution. But CO_2 evolution is at least twice that which could come from the initiator.

In a similar decomposition, induced by DBH at 45°, oxygen is evolved (Figure 6) and, since no carbon dioxide comes from DBH (*t*-BuONNO-*t*-Bu), the observed carbon dioxide evolution must be that from peracid decomposition. Because Figure 2 showed that DBH increased the rate of CO_2 evolution greatly we conclude that this constitutes another proof of radical-induced peracetic acid decomposition.

Having concluded that induced peracid decomposition is occurring, we can draw some conclusions concerning the mechanism of interaction of acetylperoxy radicals from Table III in which decomposition under an atmosphere of almost pure $^{36}O_2$ is recorded.

First, because no $^{46}CO_2$ or $^{48}CO_2$ is observed, there is no oxidation of methyl radicals to carbon dioxide in this system. Any such oxidation would have come from $^{36}O_2$.

The concentrations of the gases $^{32}O_2$, $^{34}O_2$, $^{36}O_2$, and $^{44}CO_2$, calculated as if all the gases were in solution, are shown in Table IV and plotted as a function of time in Figure 7. In this as in the other figures strictly zero-order kinetics are observed as expected from the large concentration of peracid and the small fraction of initiator which is decomposed.

The slopes of these plots are converted to zero-order rate constants and listed along with calculated initiator generated carbon dioxide evolution rate and other derived quantities in Table V.

The chain length of this decomposition can be obtained from Table V in terms of CO_2 or O_2 evolution. For CO_2 evolution the chain length (L^{CO_2}) is given by

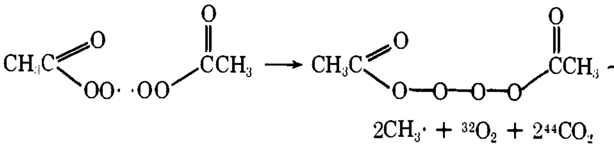
Table V. Rate Data[a] for the Decomposition of 0.70 *M* Peracetic Acid in Acetic Acid Solution under $^{36}O_2$ at 25°, 7.60 × 10^{-3} *M* DBPO as Initiator

	dX/dt, *M* sec^{-1}
R_i/e (CO_2 from initiator)	2.15×10^{-7}
R_i (Generated radicals)	1.76×10^{-7}
PTR[b]	0.880×10^{-7}
$^{44}CO_2$	4.13×10^{-7}
$^{46}CO_2$	0
$^{32}O_2$	1.04×10^{-7}
$^{34}O_2$	0.431×10^{-7}
$^{36}O_2$	-1.64×10^{-7}
$d[^{44}CO_2]/dt - (R_i/e)$($CO_2$ from peracid)	1.98×10^{-7}
$(d[^{44}CO_2]/dt - (R_i/e))/^{32}O_2$	1.90
$(d[^{44}CO_2]/dt - (R_i/e))$/PTR	2.25
$d[^{32}O_2]/dt$/PTR	1.18
$d[^{34}O_2]/dt$/PTR	0.489

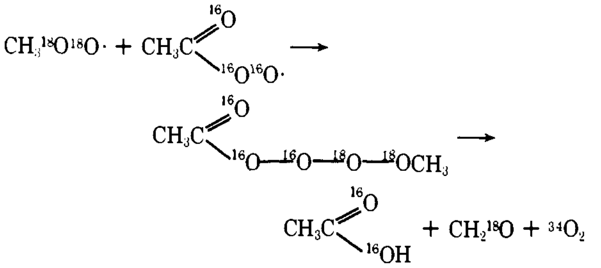
[a] Data of Figure 6 and Figure 7. [b] PTR = pair of terminating radicals. d(PTR)/dt = $R_i/2$.

$$L^{CO_2} = \frac{(d[^{44}CO_2]/dt - R_i/e)}{R_i} = \frac{1.98}{1.76} = 1.13 \quad (26)$$

This compares with 1.18 $^{32}O_2$ molecules evolved per pair of terminating radicals. While both calculations give a very short chain length, they are consistent with reaction 9.


(9)

The evolution of $^{34}O_2$ in the presence of essentially pure $^{36}O_2$ can arise only from cross reaction between methylperoxy radicals and acetylperoxy radicals as in eq 11


(11)

The number of such interactions per termination which, assuming eq 11 terminates, is the fraction of termination by this pathway, is given by

$$\text{fraction proceeding by eq 11} = \frac{2d[^{34}O_2]/dt}{R_i} = 0.49$$

This means that half the termination must be occurring in some other way. The logical mechanism is methylperoxy radical termination (reactions 12 and 27)

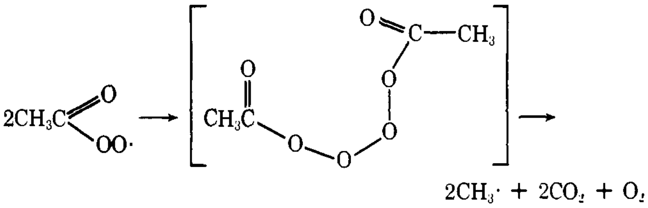
$$CH_3{}^{18}O^{18}O\cdot + \cdot O^{18}O^{18}CH_3 \longrightarrow CH_2{}^{18}O + {}^{36}O_2 + CH_3{}^{18}OH \quad (27)$$

Although we do not detect this reaction here, because $^{36}O_2$ is consumed, we have documented such a process for aldehyde autoxidation[2] and for oxidation of methyl radicals derived from DBPO or from acetyl peroxide. In acetaldehyde autoxidation a 30% yield of methanol (based upon termination) was observed. Also, the oxidation of methyl radicals (as in Table II) has been shown to evolve about one oxygen molecule per termination step (pair).

The inclusion of reaction 26 requires that the consumption of $^{36}O_2$ be corrected by the rate of reaction 27 which we conclude to be about equal to that of reaction 9, or 0.43 × 10^{-7} *M* sec. The consumption of $^{36}O_2$ is then (0.43 + 1.61) × 10^{-7} *M* sec^{-1} = 2 × 10^{-7} *M* sec^{-1}. This is satisfyingly close to the rate of CO_2 evolution, 1.98 × 10^{-7} *M* sec^{-1}, as it should be. By reaction 9 every evolved CO_2 is accompanied by an evolved methyl radical which in turn consumes one $^{36}O_2$ molecule through reaction 10.

Conclusions

The results of our studies of acetaldehyde autoxidation and induced peracetic acid decomposition are consistent with nonterminating interactions of acetylperoxy radicals to produce methyl radicals without cage collapses.



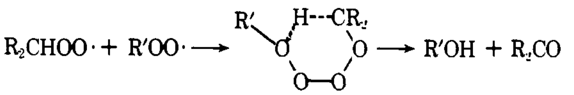
We find no evidence for a cyclic decomposition of the tetroxide to acetylperoxide either here or in the previous papers.[22]

The actual termination involves methylperoxy radicals just as did cumene autoxidation. Furthermore, these methylperoxy radicals terminate by interactions with acetylperoxy radicals or with themselves, the extent depending upon conditions. This leads to the conclusion that most autoxidations ultimately must probably terminate by the Russell[24] mechanism or some variation thereof, provided that secondary or primary radicals are available through fragmentation. We can now write for the general case:

$$2R_2CHXOO\cdot \longrightarrow [R_2CHXOOOOXCHR_2] \quad (28)$$

$$\xrightarrow{\text{(plus sometimes cage collapse)}} R_2CH\cdot + 2XO + O_2 \quad (29)$$

$$R_2CH\cdot + O_2 \longrightarrow R_2CHOO\cdot \quad (30)$$


(31)

The termination step for autoxidation of primary, secondary, or teriary hydrocarbons, ethers, or aldehydes is reaction 31 or an alternative acyclic mechanism giving the same products.[24-26]

Acknowledgment. We are grateful to the Air Force Office of Scientific Research for support of this research.

References and Notes

(1) Supported by the Air Force Office of Scientific Research, Grant AFOSR-69-1639.
(2) Abstracted from the Thesis of R. A. Kenley, University of California, San Diego, Calif., 1973.
(3) N. A. Clinton, R. A. Kenley, and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 3746 (1975).
(4) N. A. Clinton, R. A. Kenley, and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 3752 (1975).
(5) N. A. Clinton, R. A. Kenley, and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 3757 (1975).
(6) R. Hiatt, J. R. Clipsham, and T. Visser, *Can J. Chem.*, **42**, 2754 (1964).
(7) R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).
(8) T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, **87**, 3698 (1965).
(9) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Adv. Chem. Ser.*, **No. 76**, 40 (1968).
(10) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).
(11) A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965).
(12) G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **47**, 3017 (1969).
(13) D. Swern, "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970: (a) pp 313–474;(b) pp 475–516.

(14) E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **65**, 2263 (1963).
(15) (a) M. J. Kagan and G. D. Lubarsky, *J. Phys. Chem.*, **39**, 837 (1935); (b) E. Koubek and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **25**, 1401 (1963).
(16) Reference 13, pp 350 and 368.
(17) T. G. Traylor, *J. Am. Chem. Soc.*, **86**, 244 (1964).
(18) H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, **49**, 6163 (1966).
(19) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).
(20) E. W. Washburn, "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology", Vol. 3, McGraw-Hill, New York, N.Y., 1928, p 207.
(21) Reference 20, p 265.
(22) The labeling experiments of McDowell and Sifniades,[23] which, although suggested tetroxide formation, also indicated a cyclic mechanism, have been explained by an alternative possibility.[5] They were most likely observing methyl radical and formyl radical oxidation rather than acetaldehyde autoxidation.
(23) C. A. McDowell and S. Sifniades, *Can. J. Chem.*, **41**, 300 (1963).
(24) (a) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956); (b) J. A. Howard and J. E. Bennett, *Can. J. Chem.*, **50**, 2374 (1972).
(25) D. Lindsay, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **51**, 870 (1973).
(26) J. E. Bennett and R. Summers, *Can. J. Chem.*, **52**, 1377 (1974).

Thermolysis of Nenitzescu's Hydrocarbon. Kinetic Studies with a Micro-Scale Stirred-Flow Reactor

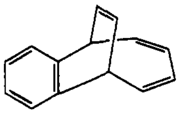
E. Vedejs* and E. S. C. Wu

Contribution from the Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706. *Received December 14, 1974*

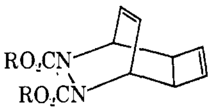
Abstract: Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**2**) and its *anti*-7,8-benzo derivative **1** equilibrate thermally with the syn-fused tricyclo[6.2.0.0^{2,7}]deca-3,5,9-triene (**8**) and the benzo derivative **13**, respectively. Hydrocarbon **8** cannot undergo disrotatory electrocyclic ring opening to bicyclo[6.2.0]deca-2,4,6,9-tetraene (**10**) because of unfavorable transannular interactions in the transition state. Instead, rate-determining homolytic bond fission occurs to give a freely rotating diradical **9** which can reclose to anti-fused tricyclo[6.2.0.0^{2,7}]deca-3,5,9-triene (**16**). Subsequent electrocyclic ring opening to bicyclo[6.2.0]deca-2,4,6,9-tetraene (**10**) occurs rapidly without interference by transannular steric interactions. Subsequent rearrangement of **10** to *trans*-9,10-dihydronaphthalene explains ultimate formation of 1,2-dihydronaphthalene as the major product. Minor cyclobutene opening to a 1,3-diene in the starting material or the Cope product **8** results in formation of *cis*-9,10-dihydronaphthalene. Labeling studies in the benzo analogs are consistent with the formation of diradical intermediates *after* initial Cope rearrangement. Kinetic studies by the stirred-flow method gave E_a = 46.4 kcal/mol with log A = 15.5 for the formation of 1,2-dihydronaphthalene, and E_a = 40.4 kcal/mol with log A = 12.2 for the appearance of *cis*-9,10-dihydronaphthalene. A technique for performing stirred-flow experiments on milligram scale is described, and its validity is demonstrated by comparison with literature activation parameters for pyrolysis of bicyclo[4.2.2]deca-2,4,7,9-tetraene.

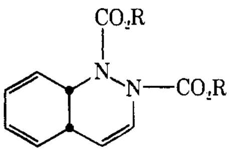
Introduction and Background

The first examples of $(CH)_{10}$ skeletal interconversion were published by Nenitzescu and coworkers.[1] Their paper described the thermal rearrangement of **1a** to 1,4-dimethoxyphenanthrene, and of **2a** into a mixture of esters having the naphthalene skeleton.[2] Several years later, the parent hydrocarbon **2** was prepared.[3] Pyrolysis of **2** was studied by three groups[4-6] and gave varying amounts of 1,2-dihydronaphthalene, *cis*-9,10-dihydronaphthalene, *cis*-1-phenylbutadiene, naphthalene, and minor side products (Table I),[6] depending on reaction conditions.

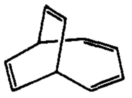


4



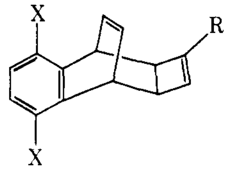


5

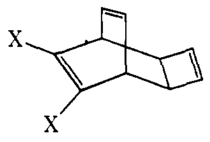


6

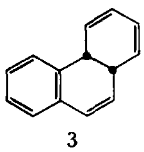
By 1970 other analogous transformations were known including conversion of **1** into 4b,8a-dihydrophenanthrene (**3**)[7,8] and rearrangement of the cyclooctatetraene–diethyl azodicarboxylate adduct into **5**.[9] Mechanisms were suggested involving initial cyclobutene opening to give bicyclo[4.2.2]deca-2,4,7,9-tetraene intermediates,[7,9] but experiments in our laboratory showed that cyclobutene ring opening is at best a minor side reaction in two cases.[6] Thus, pyrolysis of **2** in a flow system gives 1,2-dihydronaphthalene (84%), while **6** gives *cis*-9,10-dihydronaphthalene (86%) under identical conditions (Table I). Furthermore, 7,8-benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (**4**) is too unreactive to be an important intermediate between **1** and **3**.



1. X = R = H
1a. X = OCH$_3$; R = H
1b. X = H; R = CH$_3$



2, X = H
2a, X = CO$_2$CH$_3$



3

A clue to the correct mechanism appeared in 1969. Masamune et al. demonstrated the retro-Diels–Alder cleavage of basketene (**7**) to **8** followed by a Cope rearrangement to give **2**.[10] Labeling experiments revealed an equilibrium between **2** and **8** at 180° and ruled out a freely rotating diradical **9** as an intermediate at this temperature. Subsequently, the synthesis of **8** was completed in our laboratory and the facile Cope rearrangement to **2** was confirmed (E_a = 23.5 kcal/mol, log A = 11.5).[11]

In view of the evidence relating **2** and **8**, we proposed that